The Design, Synthesis and Characterization of New Building Blocks for the Preparation of Molecule-Based Magnetic Materials

by

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Abstract

Two new families of building blocks have been prepared and fully characterized and their coordination chemistry exploited for the preparation of molecule-based magnetic materials. The first class of compounds were prepared by exploiting the chemistry of 3,3'-diamino-2,2'-bipyridine together with 2-pyridine carbonyl chloride or 2-pyridine aldehyde. Two new ligands, 2,2'-bipyridine-3,3'-[2-pyridinecarboxamide] (L1, 2.3) and N'-bis(2-pyridylmethyl) [2,2′bipyridine]-3,3'-diimine (L2, 2.7), were prepared and characterized. For ligand L1, two copper(II) coordination compounds were isolated with stoichiometries [Cu2(L1)(hfac)2] (2.4) and [Cu(L1)Cl2] (2.5). The molecular structures of both complexes were determined by X-ray crystallography. In both complexes the ligand is in the dianionic form and coordinates the divalent Cu(II) ions via one amido and two pyridine nitrogen donor atoms. In (2.4), the coordination geometry around both CuII ions is best described as distorted trigonal bipyramidal where the remaining two coordination sites are satisfied by hfac counterions. In (2.5), both Cu(II) ions adopt a (4+1) distorted square pyramidal geometry. One copper forms a longer apical bond to an adjacent carbonyl oxygen atom, whereas the second copper is chelated to a neighboring Cu-Cl chloride ion to afford chloride bridged linear [Cu2(L1)Cl2]2 tetramers that run along the c-axis of the unit cell. The magnetic susceptibility data for (2.4) reveal the occurrence of weak antiferromagnetic interactions between the copper(II) ions. In contrast, variable temperature magnetic susceptibility measurements for (2.5) reveal more complex magnetic properties with the presence of ferromagnetic exchange between the central dimeric pair of copper atoms and weak antiferromagnetic exchange between the outer pairs of copper atoms. The Schiff-base bis-imine ligand (L2, 2.7) was found to be highly reactive; single crystals grown from dry methanol afforded compound (2.14) for which two methanol molecules had
added across the imine double bond. The susceptibility of this ligand to nucleophilic attack at its imine functionality assisted via chelation to Lewis acidic metal ions adds an interesting dimension to its coordination chemistry. In this respect, a Co(II) quaterpyridine-type complex was prepared via a one-pot transformation of ligand L2 in the presence of a Lewis acidic metal salt. The rearranged complex was characterized by X-ray crystallography and a reaction mechanism for its formation has been proposed. Three additional rearranged complexes (2.13), (2.17) and (2.19) were also isolated when ligand (L2, 2.7) was reacted with transition metal ions. The molecular structures of all three complexes have been determined by X-ray crystallography.

The second class of compounds that are reported in this thesis, are the two diacetyl pyridine derivatives, 4-pyridyl-2,6-diacetylpyridine (5.5) and 2,2'-6,6'-tetraacetyl-4,4'-bipyridine (5.15). Both of these compounds have been designed as intermediates for the metal templated assembly of a Schiff-base N3O2 macrocycle. From compound (5.15), a covalently tethered dimeric Mn(II) macrocyclic compound of general formula \{[Mn(N3O2)]Cl·H2O\}_2Cl·10.5H2O (5.16) was prepared and characterized. The X-ray analysis of (5.16) reveals that the two manganese ions assume a pentagonal-bipyramidal geometry with the macrocycle occupying the pentagonal plane and the axial positions being filled by a halide ion and a H2O molecule. Magnetic susceptibility data reveal the occurrence of antiferromagnetic interactions between covalently tethered Mn(II)-Mn(II) dimeric units. Following this methodology a Co(II) analogue (5.17) has also been prepared which is isostructural with (5.16).
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List of Compounds

(L₁, 2.3)  
(L₂, 2.7)  
(2.14)  
(2.16)  

(2.4)  
(2.5)  
(2.13)  

(2.17)  
(2.19)  
(5.5)  
(5.15)  

(5.16)  
(5.17)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-D</td>
<td>one-dimensional</td>
</tr>
<tr>
<td>2-D</td>
<td>two-dimensional</td>
</tr>
<tr>
<td>3-D</td>
<td>three-dimensional</td>
</tr>
<tr>
<td>amu</td>
<td>atomic mass unit, or Dalton (Da)</td>
</tr>
<tr>
<td>br</td>
<td>broad (IR and NMR peak descriptor)</td>
</tr>
<tr>
<td>calc</td>
<td>calculated</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>CI</td>
<td>chemical ionization</td>
</tr>
<tr>
<td>°C</td>
<td>degree Celsius</td>
</tr>
<tr>
<td>CDCl₃</td>
<td>deuterated chloroform</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>acetonitrile</td>
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<tr>
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<td>cyanide</td>
</tr>
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<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>d</td>
<td>doublet (NMR)</td>
</tr>
<tr>
<td>dec</td>
<td>decompose</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
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<td>EI</td>
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</tr>
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</tr>
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<tr>
<td>FAB</td>
<td>Fast Atom Bombardment</td>
</tr>
<tr>
<td>h</td>
<td>hour(s)</td>
</tr>
<tr>
<td>H</td>
<td>spin Hamiltonian</td>
</tr>
<tr>
<td>hfac</td>
<td>1,1,1,5,5,5-hexafluoroacetylacetonate</td>
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</table>
$J$ coupling constant (NMR), magnetic exchange parameter

KBr potassium bromide

m multiplet (NMR)

Me methyl

MeOH methanol

MgSO$_4$ magnesium sulfate

min minute

mmol millimole

m.p. melting point

m$_s$ electron spin state

MS mass spectrometry

m/z mass/charge ratio

NaCl sodium chloride

NaOH sodium hydroxide

Na$_2$SO$_4$ sodium sulfate

NMR nuclear magnetic resonance

ORTEP Oak Ridge Thermal Ellipsoid Plot Program

ppm parts per million

py pyridine

$R$ agreement factor

s singlet (NMR)

S spin multiplicity

SQUID superconducting quantum interference device

$\mathbf{t}$ triplet (NMR peak descriptor)

T temperature

$T_c$ critical temperature

TLC thin layer chromatography

triflate trifluoromethanesulfonate

UV ultraviolet

$\lambda$ wavelength
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi )</td>
<td>magnetic susceptibility</td>
</tr>
<tr>
<td>( \chi_m )</td>
<td>molar magnetic susceptibility</td>
</tr>
<tr>
<td>( \chi T )</td>
<td>product of the molar magnetic susceptibility with temperature</td>
</tr>
<tr>
<td>( \theta )</td>
<td>Weiss constant</td>
</tr>
<tr>
<td>( \mu )</td>
<td>magnetic moment</td>
</tr>
<tr>
<td>( \beta )</td>
<td>Bohr magneton</td>
</tr>
<tr>
<td>( g )</td>
<td>g-factor, proportionality constant</td>
</tr>
</tbody>
</table>
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Preface

One of the major challenges at the forefront of materials and supramolecular chemistry is to develop new synthetic routes to suitably functionalized organic ligands and to control/predict their assembly together with appropriate metal ions in the solid state for the preparation of materials with useful physical properties. In this respect, one has to overcome the unpredictable nature of weaker, non-covalent intermolecular interactions (e.g. $\pi-\pi$ stacking, H-bonding) in the solid state, as well as to comprehend fully the coordination chemistry, i.e. the binding preferences for each new organic ligand prepared. Numerous synthetic strategies for the preparation of coordination compounds have been widely surveyed in chemical literatures.\(^1\) One approach, first concerned with the preparation of discrete molecular structures from multidentate ligands coordinated with transition metal ions and then their assembly in the solid state, is a strategy commonly employed for the preparation of 1-, 2- and 3-D architectures with interesting and potentially exploitable magnetic properties.\(^2\) Following this methodology, the objectives of my masters research were to develop new synthetic routes to two new classes of organic ligands, namely 3,3'-disubstituted-2,2'-bpyridine ligands and suitably functionalized 4,4'-bpyridine ligands that serve as key precursors for the preparation of coordination compounds with interesting magnetic properties. As a consequence, my thesis is divided into two parts: Part 1 concerns the synthesis of 3,3'-disubstituted-2,2'-bpyridine derivatives together with the structural and magnetic characterization of their coordination complexes; Part 2 presents synthetic routes to organic precursors for the preparation of \(\text{N}_3\text{O}_2\) macrocycles. The long-term goals of both projects are the design and characterization of novel building blocks for the preparation and study of molecule-based magnetic materials.
Chapter 1 – An introduction to bipyridine chemistry

1.1 2,2'-Bipyridine Chemistry

Bipyridines are aromatic bidentate heterocycles which can form coordination complexes with a range of transition metal ions. This class of compounds consists of six possible isomers: 2,2' (1.1), 2,3' (1.2), 2,4' (1.3), 3,3' (1.4), 3,4' (1.5) and 4,4'(1.6), Figure 1.1. Bipyridine ligands chelate metals via both $\sigma$-donating nitrogen atoms and $\pi$-accepting molecular orbitals.

![Figure 1.1. The six bipyridine regioisomers.](image)

In general, the most usually used bidentate ligand would be the first structure, 2,2'-bipyridine, where the two pyridine rings are linked in the 2 position. 2,2'-bipyridine was first prepared more than 110 years ago by Fritz Blau using a dry-distilled copper salt of picolinic acid as the catalyst.\[^3\] Since then, several types of synthetic strategies have been developed for the preparation of bipyridine derivatives. Most of these strategies involve metal catalyzed coupling reactions for C-C bond formation, e.g. Ullmann, Stille-, Suzuki and Negishi-type cross-couplings in order to achieve high yields and incorporate straightforward work-up procedures.\[^4\] Recently, a comprehensive review has been published in the literature that evaluates the various synthetic strategies for the preparation of 2,2'-bipyridines and their substituted derivatives.\[^4\]

Since the establishment of the field of supramolecular chemistry in the early 1980's,
2,2'-bipyridine has become one of the most widely used bidentate ligands for the construction of coordination compounds possessing interesting physical properties. The potential applications of 2,2'-bipyridines and their substituted derivatives in the fields of supramolecular, macromolecular, nano-science and even drug design have attracted lots of interest due to the variety of oxidation states of the chelating metal ions, as well as the different chelating modes adopted by the ligands. Interestingly, the coordination chemistry of 4-，5- and 6-substituted 2,2'-bipyridine derivatives has been fully exploited in the past, leaving 3,3'-disubstituted-2,2'-bipyridine as the exception with significantly fewer reported investigations. This is mainly due to the common misunderstanding that large substituents in the 3,3'-positions would increase the van der Waals repulsion and thus prevents the adoption of a cis-coplanar conformation of the two pyridine rings, preventing chelation through the lone pairs on the pyridine nitrogen atoms. Despite of this, a few 3,3'-disubstituted-2,2'-bipyridine derivatives have been studied containing small functional groups such as methyl, carboxylic acid, hydroxyl and amino in the 3,3'-positions, Figure 1.2.\textsuperscript{[5, 6]}

\textbf{Figure 1.2.} Selected 3,3'-disubstituted-2,2'-bipyridine derivatives.\textsuperscript{[5, 6]}

3,3'-diamino-2,2'-bipyridine (1.10) has been prepared and its coordination chemistry towards a range of transition metal ions investigated by Pilkington \textit{et al.}\textsuperscript{[5]} As expected, coordination to the metal ion preferentially takes through the lone pair electrons of the two pyridine nitrogen atoms. Interestingly, upon protonation of these two heterocyclic nitrogen atoms, coordination
takes place through the two amino nitrogen atoms to afford a less favorable seven membered chelate ring. In this respect, Pilkington et al. have demonstrated that it is possible to use pH as a method of controlling the coordinating ability of this ligand.

The binding mode of 2,2'-bipyridine-3,3'-dicarboxylate (1.9) towards Cu(II) is slightly more complex as the two pyridine nitrogen atoms and three oxygen atoms, two from a second 2,2'-bipyridine-3,3'-dicarboxylate and one from a H₂O, are chelated to the first Cu(II), leaving the carboxylate substituents free to chelate to a second Cu(II) metal ion. In this way a multi-nuclear 1-D coordination polymer (1.11) has been assembled, Figure 1.3.⁶

![Figure 1.3](image)

**Figure 1.3.** Cu(II) 3,3'-dicarboxylate-2,2'-bipyridine dihydrate.⁶

In order to gain a good insight into the coordination chemistry of 2,2'-bipyridines, the application and study of 3,3'-disubstituted-2,2'-bipyridine compounds have been divided into the following categories: i) coordination compounds; ii) supramolecular compounds; iii) catalysts; iv) macrocyclic chemistry and v) molecule-based electronic materials.

### 1.2 Coordination compounds

The primary driving force for exploiting 3,3'-disubstituted-2,2'-bipyridine derivatives as ligands for the preparation of new functional materials lies in their ability to coordinate a wide range of transition metal and lanthanide ions. Among such complexes, manganese compounds have attracted lots of attention. The $d^5$ Mn(II) ion is a useful transition metal ion for the assembly...
of multinuclear clusters that display a number of unpaired electrons, and thus a large ground state spin. In this respect, manganese ions and 2,2'-bipyridine ligands have been exploited for the preparation of magnetic materials, typically clusters bearing a large number of unpaired electrons commonly known as single molecule magnets (SMMs).\[7\]

Manganese compounds have also found biological applications as enzyme models since certain complexes can mimic the biologically active centres of manganese-based enzymes. The most frequently encountered coordination complexes of 2,2'-bipyridine make use of the bidentate chelating ability through the heterocyclic pyridine nitrogen atoms. In one particular case however, the manganese centres were found to chelate through oxygens of the carboxylate functionalities instead of through the bipyridine nitrogen atoms, Figure 1.4.\[8\]

![Figure 1.4](image_url)

Figure 1.4. The complex \([\text{Mn}_3(\text{CH}_3\text{CO}_2)(\text{bpc})_2(\text{py})_4(\text{H}_2\text{O})_2]\cdot 0.5\text{H}_2\text{O} \text{ (1.12)}, \text{ where bpc} = 3,3'-\text{carboxylate}-2,2'-\text{bipyridine}.\[8\]

Pt(II) bipyridine coordination compounds have also been studied in recent years due to their potential biological applications. The discovery of cisplatin \(\text{cis-PtCl}_2(\text{NH}_3)_2\), Figure 1.5, as an effective anti-cancer drug has lead to the widespread investigation of new closely related compounds.\[9\] This work is largely driven by the cumulative drug resistance and toxic side-effects of cisplatin itself. Analogues of cisplatin have been prepared and tested in the search
for compounds possessing lower cytotoxicities. For example, 3,3'-disubstituted-2,2'-bipyridine ligands, \( \textit{cis-PtCl}_2(3,3'\text{-dicarboxyl-2,2'}\text{-bipyridine}) \) (1.14) and \( \textit{cis-PtCl}_2(3,3'\text{-bis(hydroxylmethyl)-2,2'}\text{-bipyridine}) \) (1.15) (Figure 1.5) have been prepared and their biological activities were exploited intensively so as to achieve anti-tumor drugs with low toxic side-effects and satisfactory solubilities.\(^\text{[10]}\)

![Chemical structures](image)

**Figure 1.5.** \( \textit{cis-PtCl}_2(\text{NH}_3)_2 \)\(^{[9]}\), \( \textit{cis-PtCl}_2(3,3'\text{-dicarboxyl-2,2'}\text{-bipyridine}) \) and \( \textit{cis-PtCl}_2(3,3'\text{-bis(hydroxylmethyl)-2,2'}\text{-bipyridine}) \)\(^{[10]}\)

Because of its cytotoxicity, photochemical probes for studying the binding of cisplatin analogues to DNA are extremely useful tools for targeting the design of anti-tumor cisplatin related drugs. In this respect, the mixed-metal Ru/Pt complex, \([(\text{bpy})_2\text{Ru(dpb)PtCl}_2]\text{Cl}_2 \) (dpb = 2,3-bis(2-pyridyl)benzoquinoxaline) that combines a \([(\text{bpy})_2\text{Ru}]^{2+} \) luminescent probe (bpy = 2,2'-bipyridine) together with the \( \textit{cis-Pt(II)Cl}_2 \) moiety has been prepared and studied.\(^\text{[11]}\) Results of these studies show that the compound is capable of binding to DNA in a concentration and time-dependent fashion and its binding behaviour is similar to that of cisplatin. The Ru(II) probe also indicated that the DNA conformation was greatly changed on binding to the mixed-metal complex. Some other similar polypyridyl Ru(II) complexes containing \( \textit{cis-Pt(II)Cl}_2 \) units have also been reported.\(^\text{[12]}\)

Considerable attention has been focused on ruthenium(II) heterocyclic compounds due to their stabilities and interesting physical properties. The coordination chemistry of \([\text{Ru(bpy)}_2]^{2+}\) complexes has afforded interesting results from the perspective of photochemical substitution
reactions.\textsuperscript{[13]} One example would be the photochemical substitution reaction involving the Ru\textsuperscript{2+} coordination compound [Ru(phen)\textsubscript{2}(dmbp)]\textsuperscript{2+}, dmbp = 3,3’-dimethyl-2,2’-bipyridine, Figure 1.6. A photochemically induced ligand substitution can occur when this coordination compound is exposed to light, in which the dmbp ligand was replaced by two acetonitrile ligands, as shown in Equation 1.1.

\[
[Ru(phen)\textsubscript{2}(dmbp)]^{2+} + 2 \text{CH}_3\text{CN} \xrightarrow{hv, \text{heat}} [Ru(phen)\textsubscript{2}(\text{CH}_3\text{CN})\textsubscript{2}]^{2+} + \text{dmbp}
\]

\textbf{Equation 1.1.} Photoinduced ligands exchange for [Ru(phen)\textsubscript{2}(dmbp)]\textsuperscript{2+}, dmbp = 3,3’-dimethyl-2,2’-bipyridine.\textsuperscript{[13]}

The significance here is that a multi-component system can be set into activity by sending light to the system so that the substitution of one of the components can be induced while the rest of the components remain inactive. The active ligand in the above example is 3,3’-dimethyl-2,2’-bipyridine, which was found to be photolabile when combined with the ruthenium phenanthroline compound, Figure 1.6. Substitution of this compound occurs with two acetonitrile ligands and then in turn, the acetonitrile ligands can be substituted by a bipyridine derivative in a thermal reaction, Equation 1.1.

In addition to these studies, the coordination chemistry of ruthenium(II) bipyridine compounds for applications as polypyridyl sensitizers has also been undertaken. Bipyridine derivatives were used in an attempt to make future sustainable energy systems, taking advantage of the physical properties of their Ru(II) coordination compounds, namely that they possess band
gap semi-conducting properties sensitive to visible light. In this respect, coordination compounds of this type could find applications in reactions that convert light into energy. For example, the 3,3'-dicarboxy-2,2'-bipyridine derivative, Ru(bpc)$_2$(NCS)$_2$ (Figure 1.7) has been attached to the surface of a nano-crystalline TiO$_2$ film, which initiates an electron charge transfer process involving interfacial charge separation and recombination.\cite{14}

![Figure 1.7. Molecular structure of [Ru(bpc)$_2$(NCS)$_2$] (1.17).\cite{14}](image)

Considerable efforts have been invested into the preparation and study of [Ru(II)(bpy)$_2$]$^{2+}$ compounds, not only for their interesting photophysical chemistry, but also as demonstrated earlier for their bio-reactive roles.\cite{15,16,17} In this respect, Zayat et al. have prepared a series of ruthenium complexes [Ru(II)(bpy)$_2$L$_2$]$^{2+}$ ($L$=butylamine, $\gamma$-aminobutyric acid, tyramine, tryptamine and serotonin), Figure 1.8, that are capable of transferring one molecule containing an amine group.\cite{15} Upon irradiation with visible light ($\lambda = 450$ nm), one of the molecules coordinated to the Ru(II) ion through the nitrogen atoms of its amine groups was released and this was characterized by $^1$H-NMR. As a result, the [Ru(II)(bpy)$_2$]$^{2+}$ functions as a protecting group, enabling the delivery of a bioactive substance from a coordination compound, thus expanding the field of drug delivery into coordination chemistry.
1.3 Supramolecular compounds

2,2'-bipyridine compounds are found to have interesting electrical and magnetic properties when combined with appropriate transition metal ions for the development of useful materials. One aspect that must be considered when choosing a suitable ligand is effective interactions between neighbouring metal centres. This means that the ligand cannot be too large, as close proximity between the metal centres is important for the desired magnetic and electronic properties. In this respect, 3,3'-disubstituted-2,2'-bipyridines are ideal bidentate ligands for the self-assembly of coordination polymers. Despite the fact that the subsequent strain derived from the steric effect of the 3,3'-substituents can be unfavorable for polymer formation, research has shown that this can be overcome through careful choice of substituents. Figure 1.9 shows the repeating unit of a 1-D coordination polymer assembled from a 3,3'-dicarboxylate-2,2'-bipyridine anion together with a Ni(II) metal ion.[18]

![Figure 1.8. Structure of [Ru(II)(bpy)_2(tyramine)_2]^{2+} (1.18).](image)

![Figure 1.9. Repeating unit of a 1-D Ni(II) 3,3'-dicarboxylate-2,2'-bipyridine coordination polymer (1.19).](image)

The 3,3'-dicarboxylate-2,2'-bipyridine ligand has also afforded 1-D coordination polymers
incorporating Co(II) and Cu(II) metal ions. In both cases, the structures of the polymers are similar with the Ni(II) polymer, that the heterocyclic bipyridine nitrogen atoms, two carboxylate oxygens from a neighbouring ligand together with two water molecules complete the octahedral coordination sphere around the metal ion.\cite{19}

Ligands capable of bridging two or more metal centres have been prepared to introduce efficient magnetic exchange within the polymeric structure. For example, ligands allowing further intermolecular bridging capabilities have been explored, such as the dianion of 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone, Figure 1.10a.\cite{19} In this case, the molecules assemble in zigzag-like chains (Figure 1.10b) and the interactions between the metal centres are antiferromagnetic.

![Figure 1.10. (a) Cu(II) (bpc) 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone (1.20); (b) Selected stereoview of the 'zigzag' chain along the c-axis.\cite{19}](image)

3,3'-diamino-2,2'-bpyridines have been used for the preparation of supramolecular architectures with highly uniform structures. One example is the stepwise acylation of
3,3'-diamino-2,2'-bipyridine to afford the dendrimer (1.21), Figure 1.11.

\[ \text{(1.21)} \]

Figure 1.11. Molecular structure of the 2,2-bipyridine dendrimer (1.21), its $C_3$ symmetry and a cartoon representation of its helical supramolecular stacking.\[20\]

In this case, a compact and highly symmetric structure is obtained from the self-assembly process driven by intramolecular $\pi-\pi$ stacking and hydrogen bonding between C=O and N-H groups. In addition, efficient chiral control has also been achieved to allow the self-assembly process to undergo a significant amplification of chirality. As reported, the mixture of chiral and achiral molecules can be separated within one hour into two phases, resulting in large helical stacks of right or left handedness from chiral molecules, affording helical fibers, Figure 1.11.\[20,21\]

Several studies have focused on exploiting inter-/intra- molecular interactions in 2,2'-bipyridine coordination compounds. The logistics behind such a study stem from the desire to exert greater control over the overall solid state structure and thus to control the physical properties. The objectives are focused on exploitation of non-covalent interactions, such as $\pi-\pi$ interactions, H-bonding, dipole-dipole interactions, all of which can affect the assembly process.
of the molecules.\cite{22}

1.4 Catalysts

The development of chiral molecules that can function as highly efficient catalysts is a promising application for 2,2'-bipyridine derivatives. It was discovered that axially chiral 2,2'-bipyridines-N,N'-dioxides (1.22, Scheme 1.1) can function as efficient catalysts for the asymmetric allylation of allyl(trichloro)silanes with aldehydes.\cite{23} 2,2'-bipyridines-N,N'-dioxides (1.22) can be isolated easily without any separations of enantiomers because that the last step of the synthesis for 2,2'-bipyridines-N,N'-dioxides (1.22) occurred at low temperatures to afford only one enantiomer. In this case, 2,2'-bipyridines-N,N'-dioxides act as chiral Lewis bases in the alkylation reaction, in which only a small amount of the catalyst is required (0.01-0.1 mol% compared with the usual amount of 5-10 mol% for those previously developed catalyst), providing 2,2'-bipyridines-N,N'-dioxides to be highly effective catalysts.\cite{23} The catalytic behaviour can also be tuned by modifying the 6,6'-substituents with electron donor/acceptors. A wide range of analogues with methyl, phenyl and tert-butyl groups substituted at 6,6' positions have been reported to-date, despite the fact that no alkylation took place for the 6,6'-tert-butyl-2,2'-bipyridines-N,N'-dioxide.\cite{24}

\[ R = \text{phenyl, methyl} \]

Scheme 1.1. The asymmetric alkylation of allyl(trichloro)silanes catalysed by 2,2'-bipyridine-N,N'-dioxide.\cite{23}

The phenyl derivative (1.22) has been proven to be an extremely efficient catalyst for this reaction affording an enantioselectivity of 98%. This is probably due to the \( \pi-\pi \) stacking
interactions between the phenyl group and the aromatic ring in the aryl aldehyde. The catalytic behavior of 6,6'-diphenyl-2,2'-bipyridines-N,N'-dioxide for the alkylation of other aldehydes was also excellent, proving this to be a powerful methodology for achieving satisfactory enantioselectivities from chiral biaryl skeletons.

The arene hydrogenation catalysed by transition metal complex catalysts is of great interest due to their high reactivities. Angelici et al. found that the catalytic behavior of transition metal complex catalysts can be improved by combing with a silica-supported metal heterogeneous catalyst to give the tethered complex on supported metal (TCSM) catalyst. The hydrogenation of arenes using rhodium 3,3'-disubstituted-2,2'-bipyridyl complexes (1.23) as catalysts have been found to be successful for the reduction of arenes containing electron withdrawing groups. In these catalysts, the rhodium(I) ion is coordinated to two cyclooctadiene double bonds and the nitrogen of the pyridine rings with amide groups in the 3,3'-positions, Figure 1.12. This complex was then tethered on a silica-supported palladium heterogeneous catalyst Pd-SiO₂, and the resulting catalytic species, Rh(NN)/Pd-SiO₂, provides high catalytic activity compared with other catalysts.

![Figure 1.12. Molecular structure of a Rh(I) 3,3'-disubstituted-2,2'-bipyridine catalyst (1.23).](image)

Recently, it was discovered that Mo(VI) complexes can also be used as catalysts for the epoxidation of cyclic olefins. Several tetrahedral dioxomolybdenum(VI) complexes in the form of MoO₂(OR)₂ (R= Me, Et, n-Pr, Ph, t-Bu, i-Pr, CH₂t-Bu) and MoO₂(OSiR₃)₂ (R= t-Bu, Ph)
have been reported.[26] Such compounds are generally stable and highly reactive for liquid phase olefin epoxidation catalysis reactions. Most complexes prepared and studied are comprised of tetrahedrally coordinated Mo(VI) metal centres. In 2006, Bruno and co-workers reported the catalytic behaviour of a MoO$_2$(OSiPh$_3$)$_2$(bpy) complex where the Mo(VI) metal centre is octahedrally coordinated, Figure 1.13.[26] Epoxidation of cis-cyclooctene at 55 °C using $t$-BuOOH as the oxidant together with this catalyst afforded 1,2-epoxycyclooctane as the only product, proving that the octahedrally coordinated MoO$_2$(OSiPh$_3$)$_2$(bpy) is an efficient catalyst with high selectivity for this class of reactions.

![Figure 1.13. Molecular structure of the MoO$_2$(OSiPh$_3$)$_2$(bpy) catalyst (1.24).][26]

1.5 **Macrocyclic Compounds**

The design and synthesis of new macrocyclic ligands as precursors to useful materials continues to be an expanding area with exploration of the ring size and a variety of combinations of donor ligands. In this respect, multi-site molecular receptors capable of binding sequentially two or more metal cations in close proximity is a promising strategy due to that the allosteric behaviour can result in efficient propagation of binding information to neighbouring metal centres. The second ligand must be polydentate so as to achieve chelation to different metal centres, thus making 2,2'-bipyridine an excellent candidate. One example comes from the research of Beer *et al.*, where a complex of two identical benzo-15-crown-6 subunits is incorporated onto a 2,2'-bipyridine framework via derivatization at the 3,3' positions, Figure
The complex is then coordinated to Ru(II) or Pt(II) metal ions via the heterocyclic nitrogen atoms of the bipyridine groups. Na\(^+\) cations were added and it was found that the chelation of transition metals at the allostERIC bipyridyl sites forced the bipyridyl group towards coplanarity. The resulting complex displays a sandwich-type architecture with a Na\(^+\) cation in the middle, Figure 1.14.[27]

![Figure 1.14](image)

**Figure 1.14.** Multi-site molecular receptor benzo-15-crown-6 chelated to a Ru(II) ion (1.26).[27]

One alternative route for the assembly of a macrocyclic unit between the 3 and 3' positions of the bipyridine ring involves reaction of 3,3'-disubstituted-2,2'-bipyridine with suitable polyethylene glycol-type compounds, Scheme 1.2. Among these complexes, the transition metal binds to the bipyridine nitrogen atoms while the alkali metals are encapsulated within the macrocyclic cavity bound to the crown ether oxygen atoms, which is the same as discussed before.

![Scheme 1.2](image)

**Scheme 1.2.** Crown ether macrocycle formation (1.27).[28]

### 1.6 Molecule-based electronic materials

The miniaturization of silicon based semiconductor technology is getting to its utmost due to the physical constraint. Molecular electronics, in another way, provides an alternative strategy
for assembling electronic materials that could potentially rival traditional silicon circuitry. Nowadays, the demand of achieving smaller, lighter and faster molecular circuits has become more and more urgent, pushing this field into fast development. Recent work has been primarily concerned with the synthesis, characterization and optimization of functionalized oligomers, for which, the 5,5'-disubstituted-3,3'-dinitro-2,2'-bipyridines derived from Ullmann coupling of 2-chloro-3-nitropyridine have displayed satisfactory results, Figure 1.15.[29]

![Chemical structure image]

Figure 1.15. 5,5'-disubstituted-3,3'-dinitro-2,2'-bipyridine derivatives, (1.28) and (1.29).

Molecular electronic devices can be structurally optimized so as to improve the efficiency, such as lower impedance, larger on:off ratio and longer electronic hold times.[29] The energy transportation needs to be amplified across the molecular device so as to achieve maximum efficiency. Further electrochemical exploration have also been carried out on polymeric 2,2'-bipyridine derivatives with substituents such as -N=N-, -O- and -NH-CO-NH-. These functional groups have been introduced to increase the electron withdrawing nature of the polymers and thus, in turn, influence the electrochemical response of the polymer.[30] The development of materials with interesting magnetic properties is also one of the potential applications when the diverse coordinating abilities of 2,2'-bipyridine derivatives are exploited together with appropriate paramagnetic centres.[31]

Bipyridine derivatives can also be coordinated to transition metals for the preparation of
luminescent systems, such as PtX₂(bpy), where X=dithiolate and bis(acetylide).[32] Considerable efforts have been invested in the realization of molecular-based illumination systems to understand key system components and intermediate steps such as the excited state dynamics and quenching of the chromophores. The PtX₂(bpy) have been chosen as the chromophore for the construction of a molecular photochemical device. The PtX₂(bpy) is connected to both an electron donor and an electron acceptor by ligand bridges through which electrons can be transferred. The advantage of such a system lies in the directionality of the charge transfer excited state, which makes it interesting to incorporate such systems into molecular photochemical devices for photoinduced charge separation and light-driven energy-storage reactions.

To summarize, 2,2'-bipyridine derivatives have displayed a range of coordination modes with different metal ions that have lent them to various applications in chemistry. The coordination chemistry for 3,3'-disubstituted-2,2'-bipyridine derivatives, on the other hand, remains much less developed. As a result, the objective of my research, was to design, synthesize and exploit the coordination chemistry of two new multi-dentate ligands prepared from a 3,3'-disubstituted-2,2'-bipyridine.

1.7 Carboxamide ligands

As previously discussed, there has been great interest in supramolecular transition metal coordination chemistry since self-assembly through coordinate bond formation has proven to be a powerful tool for constructing rings, polymers, and networks.[33] The carboxamide group present in the primary structure of proteins is an important building block for coordination chemists. Pyridine carboxamides are a promising class of multidentate ligands containing this
linkage that are available from condensation reactions between pyridyl-bearing amine or carboxylic acid precursors. Upon deprotonation of the carboxamide nitrogen atom, this centre and the pyridyl ring(s) of the anion chelate to metal ions. During recent years pyridine carboxamide ligands have found useful applications in asymmetric catalysis,\textsuperscript{[34]} molecular receptors,\textsuperscript{[35]} dendrimer synthesis\textsuperscript{[36]} and the preparation of platinum(II) complexes with antitumor properties.\textsuperscript{[37]} The behaviour of pyridine carboxamides towards biologically relevant \textit{d}-block metals has been widely investigated.\textsuperscript{[38]} Copper complexes have been particularly fruitful since pyridine dicarboxamide ligands support a range of coordination numbers, geometries and nuclearities for copper(II).\textsuperscript{[39]} Although studied for their biological\textsuperscript{[40]} and catalytic applications,\textsuperscript{[41]} these ligands have not yet been widely exploited as precursors to molecule-based magnetic materials. Furthermore, carboxamide ligands containing the 2,2'-bipyridine moiety are much more rare and have not realized their full potential as versatile ligands in the field of coordination chemistry.
Chapter 2 – Bipyridine ligands: results & discussion

2.1 A novel dinuclear tridentate bipyridine carboxamide ligand and its complexation to copper (II): synthesis, structure and magnetism.

A synthetic strategy for the preparation of 3,3'-diamino-2,2'-bipyridine together with an overview of its coordination chemistry was reported in 2002 by Pilkington et al.\textsuperscript{[42]} The objective of my research project was to exploit the amine functionality of this compound for the preparation of new ligands. In this respect, a novel multi-dentate bipyridine dicarboxamide ligand (compound 2.3, L\textsubscript{1}) has been prepared by reaction of 3,3'-diamino-2,2'-bipyridine (2.2) together with 2-pyridine carbonyl chloride (2.1).\textsuperscript{[43]} An overview of the synthesis of this ligand is presented in Scheme 2.1. An excess of dry triethylamine was added to deprotonate the HCl salt of 2-pyridine carbonyl chloride and the resulting triethylamine hydrochloride salt was removed by washing the ligand with water on work-up.

![Chemical structure](image)

**Reagents and Conditions:** (i) dry Et\textsubscript{3}N, Cl\textsubscript{2}CH\textsubscript{2}Cl\textsubscript{2}, 0 °C for 2 h, 80 °C for 3 h. (ii) NaHCO\textsubscript{3}, water, acetone.

**Scheme 2.1.** Synthetic route for the preparation of the bipyridine carboxamide ligand (compound 2.3, L\textsubscript{1}).\textsuperscript{[5]}

The molecular structure of the ligand was confirmed by \textsuperscript{1}H- and \textsuperscript{13}C- NMR, EI-MS and IR spectroscopy as well as C,H,N elemental analysis.
The 600 MHz $^1$H-NMR spectrum of the carboxamide ligand ($L_1$) is shown in Figure 2.1 and it provides good support for the successful preparation of this compound. The characteristic amide NH peak is observed as a singlet at 14.70 ppm in CDCl$_3$. The aromatic pyridine and bipyridine protons are carefully assigned based on H-H COSY and C-H correlation NMR experiments. The first doublet at 9.36 ppm is attributed to the 4-H protons of the bipyridine ring. The next two doublets at 8.75 and 8.62 ppm are assigned to the 6-H and 6'-H protons of the bipyridine and pyridine rings respectively. The following doublet at 8.26 ppm and the triplet at 7.90 ppm are assigned to the protons at the C$_3'$ and C$_4'$ positions of the pyridine rings. The final multiplet worth four protons at 7.48 ppm is due to the protons on both the C$_5'$ and C$_5$ postions of the pyridine and
bipyridine rings respectively. All peaks integrate with the correct ratios for the appropriate number of protons.

The 600 MHz $^{13}$C-NMR spectrum of ligand (L$_1$) is shown in Figure 2.2. It displays a characteristic peak at 164.01 ppm in CDCl$_3$ which is characteristic of the amide carbonyl. This is shifted with respect to the carbonyl peak of the starting material, 2-pyridinealdehyde, which appears at 193.86 ppm and thus provides the first evidence for the successful synthesis of this ligand. Peaks at 150.65 ppm, 148.52 ppm, 143.22 ppm, 141.48 ppm and 137.37 ppm are assigned to 2'-C, 6'-C, 2-C, 6-C and 4'-C, respectively. The next peaks at 136.01 ppm and 129.95 ppm are assigned to the bipyridine carbons at the 3 and 4 positions. The following peaks at 125.37 ppm and 124.83 ppm are assigned to carbons at the 5' and 5 positions, respectively. The final peak at 122.23 ppm is due to the 3'-C carbon of the pyridine ring. The IR spectrum of
the ligand has an intense amide C=O str at 1676 cm\(^{-1}\). The spectrum also displays a band at 3449 cm\(^{-1}\) assigned as the NH str and a band at 2929 cm\(^{-1}\) which is consistent with aromatic C-H stretches.

The high resolution EI mass spectrum of this ligand is consistent with its molecular structure, showing a parent ion peak at \(m/z = 396.1332\) amu that is in close agreement with the predicted value of 396.1335 amu for C\(_{22}\)H\(_{16}\)N\(_6\)O\(_2\). Finally the elemental analysis is in complete agreement with the calculated molecular structure of this ligand: the calculated and expected C,H,N values are all within the acceptable ± 0.4% limit.

Once the ligand had been prepared and fully characterized, the next objective was to investigate its coordination chemistry together with suitable paramagnetic transition metal ions. In this respect the first metal investigated was Cu(II). The synthesis of two dinuclear Cu(II) coordination complexes containing the dinucleating dianion (L\(_1\)) is shown in Scheme 2.2. Methanolic solutions of the ligand together with two equivalents of Cu(hfac)\(_2\) or CuCl\(_2\) in the presence of air produced green microcrystalline materials of [Cu\(_2\)(L\(_1\))(hfac)\(_2\)] (2.4) and [Cu\(_2\)(L\(_1\))Cl\(_2\)] (2.5) respectively. In both cases no base was required to deprotonate the ligand. Amide hydrogen atoms often become labile when the ligands undergo complexation since hydrogen bonding of the acidic amide H atoms to electron rich metal centres facilitates deprotonation.\(^{[44]}\) Both complexes were recrystallized from acetonitrile to afford single crystals of the acetonitrile solvates.
Reagents and Conditions: (i) Et$_3$N, CICH$_2$CH$_2$Cl, 0 °C, and then 80 °C for 3 h; (ii) 2 eq. Cu(hfac)$_2$, MeOH; (iii) 2 eq. CuCl$_2$, MeOH.

Scheme 2.2. Preparation of the amide ligand $L_1$ and coordination complexes (2.4) and (2.5).

The molecular structures of both compounds were determined by Prof. M Pilkington at Brock University by single crystal X-ray diffraction. Complex (2.4) crystallizes in the triclinic space group P-1 with two independent molecules per unit cell. An ORTEP$^{[45]}$ view of the molecular structure of one of the independent molecules along with the atom numbering scheme is shown in Figure 2.3. The ligand chelates in a dinuclear fashion to two Cu(II) metal ions through the deprotonated amide N and two pyridine N atoms leaving the carbonyl oxygen atom unchelated. Two additional oxygen atoms from the hexafluoroacetylacetonate (hfac) counter ions complete the pentacoordinate geometry around both copper(II) centres. The coordination geometry for
copper(II) ions is best described as intermediate between trigonal bipyramid (C₃ᵥ) and square-based pyramid (C₄ᵥ).

Figure 2.3. (a) ORTEP view of the structure of one independent molecule of \([\text{Cu}_2(\text{L})_{(\text{hfac})}_2] \cdot 3\text{CH}_3\text{CN} \cdot \text{H}_2\text{O} \) (2.4) (thermal ellipsoids are plotted at 50% probability); (b) packing diagram – projection down the a-axis, solvent is omitted for clarity.

Tables 2.1 and 2.2 summarize the selected bond angles and bond lengths for complex (2.4), respectively.
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Table 2.1. Selected bond angles [°] for [CuII2({L1(}hfac{)}2]:3CH3CN·H2O (2.4).
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Table 2.2. Selected bond lengths [Å] for \([\text{Cu}_{2}^{II}(\text{L}_{1})(\text{hfac})_{2}] \cdot 3\text{CH}_{3}\text{CN} \cdot \text{H}_{2}\text{O}(2.4)\).

In order to chelate in this manner, the two pyridine rings of the 2,2'-bipyridine are substantially twisted. The dihedral angle between the best planes of the two bipyridine rings is 38.7° for molecule (2.4). The molecules pack in a head to head arrangement, Figure 2.3(b). Intramolecular Cu(II)···Cu(II) distances are in the range 5.868 – 5.958 Å, whereas intermolecular Cu(II)···Cu(II) distances are slightly shorter, in the range 5.348 – 5.487 Å. The packing is such that the carbonyl oxygen atoms of the first independent molecule form short intermolecular contacts to neighbouring Cu(II) ions (O(12)···Cu(4) 3.408 Å, O(1)···Cu(2) 3.382 Å), whereas those contacts involving the carbonyl functionality of the second molecule are longer (O(9)···Cu(4) 4.010 Å, O(7)···Cu(3) 4.010 Å). All four independent carbonyl oxygen atoms form H-bonds to neighbouring pyridyl H-atoms that lie in the range 2.407 – 2.803 Å.

Complex (2.5) crystallizes in the monoclinic space group P2₁/n with four molecules per unit cell. A perspective view of the coordination complex along with the atom-numbering scheme is
shown in Figure 2.4. The ligand once again chelates in a tridentate manner to two Cu(II) metal ions through the deprotonated amide N and two pyridine nitrogen atoms, leaving the carbonyl oxygen atom unchelated. The pyridine rings of the 2,2'-bipyridine are twisted by an angle of 44.20° with respect to their best planes. Table 2.3 summarizes selected bond lengths and bond angles for complex (2.5).

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*Cl(2) 1-x, 2-y, 2-z

Table 2.3. Selected bond lengths [Å] and bond angles [°] for complex (2.5).
Figure 2.4. (a) An ORTEP view of the molecular structure of [Cu₂(L₁)Cl₂]-CH₃CN (2.5) showing the labelling scheme (thermal ellipsoids are plotted at 50% probability);

(b) Simplified view of the chloride bridged [Cu₂(L₁)₂Cl₂]-CH₃CN (2.5) showing the (4+1) coordination around the Cu(2) metal ion.

The two end Cu(1) ions have a CuN₃ClO ligand environment and are (4+1) pentacoordinated with a geometry that is intermediate between a trigonal bipyramid (C₃ᵥ) and a square-based pyramid (C₄ᵥ). The coordination geometry of the Cu(1) atom can be better described as a distorted base pyramid, where the basal coordination sites are occupied by an amide and three pyridine N atoms of the tridentate ligand, with bond distances in the range of 1.919(3) – 2.023(3) Å, together with a chloride ion at a distance of 2.2194(9) Å. The apical site is occupied by a neighbouring
carbonyl oxygen atom at a longer distance of C=O--Cu(II) 2.868(2) Å. The Cu(1) ion is raised from the mean basal plane toward the apical oxygen ion by 0.1911 Å. The geometry around the Cu(2) ion is also square pyramidal. Three N atoms from the tridentate ligand together with a chloride ion form the square plane, in this respect the bond lengths range from 1.942(3)-1.997(2) Å with the chloride ion at a distance of 2.2585(9) Å. The apical site is occupied by a chloride ion from another molecule at a longer distance of 2.7994(9) Å. The Cu(2) ion is raised from the mean basal plane toward the apical Cl ion by 0.1871 Å. Couples of these binuclear species are arranged to form linear [Cu₂(L₁)₂Cl₂]₂ moieties through chloride bridges formed between Cu(2) and a chloride ion of the adjacent binuclear species, Figure 2.4(b). The four copper atoms are coplanar, the Cu(1a)-Cu(2a)-Cu(2b)-Cu(1b) torsion angle being 180°. The shortest Cu···Cu separation between different tetranuclear units is 6.830 Å. The Cu···Cu distances within these units are 3.64 Å (interdimer) and 5.83 Å (intradimer). In this respect the compound can be considered to be a linear tetramer since the four copper ions of the dimeric unit are completely coplanar with each other. The packing diagram for (2.5) is shown in Figure 2.5. Intermolecular H-bonding interactions are in the range of 2.17 to 2.75 Å. H-bonding interactions from pyridyl H atoms to the chloride ion of a neighbouring molecule are 2.75 Å and are shown by dashed lines in Figure 2.5.
**Figure 2.5.** Packing diagram for complex (2.5), projection down the $a$-axis, short intermolecular contacts are shown via dashed lines.

**Figure 2.6.** Variation of the molar susceptibility (black circles) and fit (solid line) for complex 2.4. Inset $1/\chi$ vs $T$ and fit to the Curie-Weiss model.

**Magnetic Properties.** The magnetic data for all of the complexes presented in my thesis were collected by Dr. A. Alberola on the Quantum Design SQUID magnetometer at Brock University.
Figure 2.6 shows the magnetic behaviour of complex (2.4) in the form of $\chi_M vs T$ with $1/\chi$ in the inset. The susceptibility of the sample increases monotonically as the temperature lowers all the way down to 5 K where it shows a maximum and then drops. At high temperatures the susceptibility follows a typical Curie-Weiss behaviour, from which the Curie constant $C$ could be determined. The presence of two Cu(II) per molecule is confirmed by a Curie constant of 0.75 emu·K/mol (expected 0.76 emu·K/mol for two $S = 1/2$ and $g = 2.10$) and a value for the Weiss constant of $\theta = -6.29$ K (Figure 2.6). In order to evaluate the exchange interaction between neighbouring Cu(II) atoms, the variable-temperature susceptibility data were analyzed by Dr. Alberola to give a best fit, which is shown as the solid line in Figure 2.6. These data are consistant with the two spins on the copper metal ions being coupled antiferromagnetically.

![Graph](image)

**Figure 2.7.** $\chi T$ vs $T$ (black circles) and fit for complex (2.5) (solid line).

The results of magnetic susceptibility measurements for [Cu(L₄)Cl₂]₂ (2.5) are given in Figure 2.7 in the form of a $\chi T$ versus $T$ plot. Upon lowering the temperature from room temperature to about 50 K, $\chi T$ remains practically constant at a value of 1.43 emu·K mol⁻¹.
which is slightly lower than that calculated for four uncorrelated $S = 1/2$ spins (1.50 emu·K mol$^{-1}$ with $g = 2$). Between 60 K and 5 K, $\chi T$ decreases sharply to reach a value of 1.16 emu·K mol$^{-1}$, which is slightly larger than what is expected for two ferromagnetically coupled spins revealing the presence of competing ferro- and antiferromagnetic interactions.

A schematic view of the bridging framework in the tetramer is presented in Figure 2.8.

![Figure 2.8. Simplified view of the bridging framework of compound (2.5).](image)

The best fit of the magnetic data done by Dr. Alberola is shown by the solid line in Figure 2.7. The magnetic data have been modelled and the findings are consistent with intradimer ferromagnetic coupling between the Cu(II)-Cu(II) metal centres through the chloro bridging ligands ($J_2 = 32.9$ K) and a weaker interdimer antiferromagnetic coupling ($J_1 = -10.1$ K), which is similar in sign and magnitude to the value of $J = -9.86$ K observed in complex (2.4). The superexchange pathway involving the Cu(2) metal centres takes place mainly through a $\pi^*$ type interaction between the Cu $d_{x^2-y^2}$ and the apical p Cl orbitals. For an ideal geometry with a square core, the former overlap integral would be zero so that there would be no magnetic coupling between the Cu metal centres. Due to small structural deviations from the ideal squared Cu$_2$Cl$_2$ core, this complex presents $J_2$ value, which is consistent with its molecular structure. Examples
of pseudo-linear copper tetramers that have been magnetically characterized are scarce in the chemical literature.\textsuperscript{50, 52} A detailed search of the literature revealed only one other dinuclear copper(II) complex assembled from a bis-multidentate ligand.\textsuperscript{46} In this case, two binuclear moieties are held together through Cu-O (phenolate) interactions between neighbouring units to form a pseudo-linear [Cu(L)\textsubscript{2}]\textsubscript{2} tetramer, where L is a salen type ligand. Magnetic investigations reveal that the magnetic structure of the compound is fundamentally dominated by the nearest antiferromagnetic interactions.\textsuperscript{46}

2.2 The Preparation and Coordination Chemistry of a Highly Reactive 3,3-Disubstituted-2,2'-Bipyridine Ligand (L\textsubscript{2}).

In general, imine ligands possess lower reactivity due to the lower electrophilicity of the C=N bond than that of the C=O bond. However, their reactivity can be enhanced greatly by applying an appropriate activator acting as a suitable electron withdrawing group.\textsuperscript{47} In this respect, the subsequent electrophilicity of the C=N bond can be increased greatly that nucleophilic addition across the C=N bond is possible. This is an important property since it means that nucleophilic addition can happen when the C=N bond has already been coordinated to metal ions, resulting in different coordination compounds in solution. Furthermore, reactive imines can be easily hydrolyzed so care is taken to avoid exposure to moisture. The sensitivity and high reactivity make the coordination chemistry of imine compounds challenging.

The usual approach to coordination chemistry involves the study of how ligands of known structures combine with metal ions to form mononuclear, oligomeric or supramolecular structures, and is used in the search for materials with novel properties. Given the reactivity of the imine functionality, we decided to adopt an alternative in which a chemically reactive ligand
and a metal ion are combined, and the product formed depends on both the chemical reactions of the ligand and the coordinating power of the added metal ion. The objectives of this research project were therefore to prepare the highly reactive bis-imine ligand (compound 2.7, \( L_2 \)) by reacting 3,3'-amino-2,2'-bipyridine (2.2) with pyridine-2-carbaldehyde (2.6). The susceptibility of this ligand to nucleophilic attack at the imine functionality adds an extra dimension to reactions of its solutions with metal ions, especially since this attack can be intramolecular from a pyridine N atom.

The bis-imine (2.7) was prepared by reaction of the 3,3'-diamino-2,2'-bipyridine (2.2) with two equivalents of pyridine-2-carbaldehyde (2.6) in toluene in the presence of activated 4 Å molecular sieves, Scheme 2.3.\(^{[48]}\) The ligand is stable if kept in an inert environment box at room temperature and has been fully characterized by \(^1H\)-, \(^{13}C\)- NMR, HMS-EI and IR spectroscopy as well as by C,H,N elemental analysis.

\[
\text{Scheme 2.3. Synthetic route for the preparation of the bis-imine ligand (2.7, } L_2).^{[48]} \]

\[
\text{Scheme 2.3. Synthetic route for the preparation of the bis-imine ligand (2.7, } L_2).^{[48]} \]
Figure 2.9. 600 MHz $^1$H-NMR spectrum of ligand (2.7) in CDCl$_3$.

The fully assigned $^1$H-NMR spectrum of the ligand (2.7) is shown in Figure 2.9 and provides strong support for the successful synthesis of this compound. The characteristic imine CH=N proton is observed as a singlet downfield at 8.34 ppm. The aromatic bipyridine and pyridine CH protons were carefully assigned with the aid of 2-D, $^1$H-$^1$H COSY and C-H correlation spectra. The two downfield doublets at 8.71 ppm and 8.51 ppm were assigned to the protons in the 6-positions of the bipyridine and pyridine rings respectively. The next doublet at 7.79 ppm and the triplet at 7.69 ppm are assigned to C$_3$ and C$_4$ protons on the pyridine ring. The next doublet at 7.48 ppm is due to the proton at the C$_4$ position on the bipyridine. The two doublets of doublets at 7.43 ppm and 7.29 ppm are assigned to the protons at the C$_5$ and C$_5'$ positions, respectively. All of these peaks have the correct integral values.
The fully interpreted $^{13}$C-NMR spectrum of ligand (2.7) is shown in Figure 2.10. It displays the characteristic imine C=N peak at 162.30 ppm in CDCl$_3$ which provides the first evidential proof that a reaction has taken place. The imine proton is shifted upfield when compared with the carbonyl peak of the pyridine-2-carbaldehyde (2.6) starting material which is observed at 193.86 ppm. Peaks at 154.12 ppm, 151.47 ppm, 149.43 ppm, 147.54 ppm and 146.05 ppm are assigned to C$_2$, C$_6$, C$_6'$, C$_3$ and C$_2$, respectively. The peaks at 136.65 ppm and 125.71 ppm are due to the carbons at 4 and 4' positions. The following peaks at 125.26 ppm and 124.14 ppm are assigned to carbons at 5 and 5' positions, respectively. The last peak observed upfield at 121.55 ppm is assigned to C$_3'$ of the pyridine ring. The IR spectrum of (2.7) displays an intense C=N str at 1630 cm$^{-1}$ characteristic for the imine functionality. The IR also displays a distinct
band at 3053 cm\(^{-1}\), which is characteristic of aromatic C-H str. The high resolution (EI) mass spectrum of (2.7) is consistent with its molecular structure, showing a parent ion peak at \(m/z = 364.1435\), which is in good agreement with the calculated value of 364.1436 for C\(_{22}\)H\(_{16}\)N\(_6\). Furthermore, the C,H,N elemental analysis for compound (2.7) was found to agree well with the theoretical results, the discrepancy for C, H and N were only -0.53%, 0.00% and 0.36% respectively, providing additional evidence to support the successful synthesis of compound (2.7). With six \(sp^2\) N atoms, there are several possibilities for coordinating metal ions, e.g. via the bipyridine and/or via the iminopyridine groupings. It is known that 3,3’-disubstituted 2,2’-bipyridines can coordinate by their ring N atoms, even when the substituents make no attractive interaction, e.g. methyl.\(^{[5]}\) There is also the possibility of the bipyridine group adopting a trans conformation which opens other opportunities for metal ion coordination. However, here we observed an interesting transformation. Reaction of compound (2.7) with an excess of cobalt(II) perchlorate in wet acetonitrile at room temperature led to the isolation of single crystals of the metal complex (2.13) of the rearranged tetradentate ligand (2.8), which contains four contiguous heterocycles - three pyridines and one pyrido(2,3-d)pyrimidine in which a pyrimidine N atom is the coordinating centre and chelates in a similar manner as a quaterpyridine, Figure 2.11.

![Figure 2.11](image)

**Figure 2.11.** The molecular structures of the bis-imine ligand (2.7), the rearranged ligand (2.8), an intermediate compound in the rearrangement (2.9) and the Co complex (2.13).
X-ray crystallography of (2.13) reveals that (2.8) coordinates to the cobalt ion in a planar tetradentate fashion with one acetonitrile and one water molecule occupying the axial coordination sites, Figure 2.12. Selected bond lengths and bond angles for complex (2.13) are shown in Table 2.4. The four Co-N distances lie in the range 2.107(7) – 2.160(7) Å, and the N-Co-N angles lie in the range 74.2(3)-76.5(3)°. The tetradentate ligand is close to perfect planarity, the maximum angle between any of the four ring systems is 5.7(4)°.

Figure 2.12. The ORTEP representation of the Co(II)[bis-imine] complex (2.13) showing the tetradentate binding site of the quaterpyridine-type ligand. Thermal ellipsoids are drawn at the 50% probabilty level.
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</tr>
</tbody>
</table>

**Table 2.4.** Selected bond lengths [Å] and bond angles [°] for complex (2.13).

The formation of this ligand from the bis-imine (2.7) can be rationalised by the mechanism shown in Scheme 2.4. Intramolecular attack of a bipyridine N atom on the imine belonging to the second ring creates a pyridinium cation fused to a dihydropyrimidine (2.10). Coordination of the imine functionality to the Lewis acidic Co(II) metal centre most likely facilitates activation of the imine towards nucleophilic attack by the lone pair on the pyridine nitrogen. The pyridinium ring is then opened by water to give aldehyde (2.11) containing a tetrahydropyrimidine. The latter opens to form an amine and an imine, and the former drives the formation of a new pyridine ring in (2.12). Finally, the Lewis catalyzed nucleophilic addition of the imine to the activated imine in (2.12) forms the dihydropyrimidine ring which requires a final oxidation to afford the aromatic ring, Scheme 2.4. Thus, ligand (2.8) has the atomic composition of ligand (2.7) with the loss of two hydrogen atoms.
Scheme 2.4. Proposed mechanism for the rearrangement of the bis-imine (2.7) to the quaterpyridine ligand (2.8) catalyzed by Co(II) ion.

The results obtained during the course of this research project demonstrate that our bis-imine (2.7) is highly reactive, not at all surprising since both aromatic groups attached are electron deficient pyridine rings. All attempts to crystallize this ligand for characterization by single crystal X-ray diffraction have failed, even from dry solvents and under inert conditions. Crystallization from dry methanol at room temperature afforded single crystals of compound (2.14), in which interestingly, a molecule of methanol has added across the imine bond. The molecular structure of this compound (Figure 2.13) was determined by X-ray crystallography.
The molecule sits on a crystallographic centre of symmetry and the outer pyridine rings are disordered between two close lying positions. The molecule is roughly planar with the exception of the two methoxy groups which protrude on either side. Two hydrogen bonds from each NH group stabilize the molecular conformation. One is to a bipyridine N atom (N---H 1.81(3) Å, N---H-N 140(2)°) and holds the former imine bond at ca. 14° to the bipyridine plane. The other is to the disordered terminal pyridine ring (N---H: 2.20(3) Å, N---H-N 103(2)° and N---H: 2.40(3) Å, N---H-N 100(2)°). There is an anomeric effect within the NH-C-OMe systems. Thus, the N-C(OMe) bond (1.431(3) Å) is of similar length to the C-OMe (1.435(2) Å) bond, in contrast to the usual trend of N-C bonds being longer than O-C bonds. The H atom attached to the amino group was located in the structure solution, and the bonding geometry at N is close to planar (sum of angles at N: 357(3)°). Nevertheless, it should also be noted that the shortest bond from the amino group is to the pyridine ring (1.382(3) Å), indicating that this lone pair is also conjugated with the aromatic ring. Table 2.5 summarizes the selected bond lengths [Å] and bond angles [°] for compound (2.14).
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<td>O(1)-C(12)</td>
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Table 2.5. Selected bond lengths [Å] and bond angles [°] for compound (2.14).

Reaction of the bis-imine ligand (2.7, L2) with Cu(II) triflate in dry acetonitrile gave a green precipitate characterized as a 1:1 complex by C,H,N microanalysis, but no suitable single crystals could be grown to fully confirm the molecular structure. Mass spectra showed fragments due to Cu(L2)(triflate) and Cu(L2). The corresponding reaction with Ag(I) triflate also gave a 1:1 complex. Mass spectra showed an [Ag(L2)]+ fragment. A brown 2:1 complex of ligand (L2) with Cu(II) triflate has also been prepared by using stoichiometric amounts of the reactant. Microanalysis confirmed the composition and mass spectrometry showed a Cu(L2)(triflate) ion. It was not possible to obtain crystals for X-ray diffraction experiments, so the structural
assignments are tentative. The 2:1 complex is assigned as structure (2.15), in which each Cu(II) is coordinated by three N atoms, one from the pyridine, one from the bipyridine and one from the imine. This is analogous to the structure of the previously reported Cu(II) amide complex (2.4), Figure 2.14.

![Image](2.15)

**Figure 2.15.** The proposed structure of Cu\textsubscript{2}(L\textsubscript{2})(triflate)\textsubscript{4} derivated from the structure of Cu\textsubscript{2}(L\textsubscript{1})(hfac)\textsubscript{2}.

The high reactivity of the imine to nucleophilic attack, either from water or intramolecularly from a pyridine nitrogen or amine, means that if reactions are carried out in wet solvents in air, then a range of different and unique products can be obtained. For example, hydrolysis of one imine group in (L\textsubscript{2}) releases an amino group which can add to the remaining imine group and form the fused dihydro-1,3-diazepine compound (2.16, L\textsubscript{2}'), Scheme 2.6. Indeed, crystals of this substance have been isolated from acetonitrile solution, and reaction of the bis-imine (L\textsubscript{2}) with zinc(II) hexafluoroacetoacetonate in wet acetonitrile yielded the metal complex of (2.19) whose structure has been confirmed by X-ray crystallography. In contrast, reaction with zinc(II)(hfac)\textsubscript{2} in acetonitrile yielded crystals containing the oxidized ligand (2.18), which can be formed by addition of water to one imine, followed by attack of the formed amine on the other imine, and completed by air oxidation (Scheme 2.6). Finally, as previously discussed, in the presence of cobalt(II) perchlorate, the ligand rearranged and crystals of the cobalt(II) complex (2.13) of a
quaterpyridine-like ligand were isolated and structurally characterized by crystallography.

Scheme 2.6. Proposed mechanism for the rearrangement of the bis-imine (2.7) affording two new ligands (2.16) and (2.18).

During the preparation of the bis-imine (2.7), an initial orange precipitate that contains the diazepine (2.16) along with another material, tentatively assigned as the free base of cation (2.10), formed by intramolecular attack by a pyridine N atom on the imine.

Figure 2.15. Molecular structures of complexes (2.17) and (2.19).

The crystal structures of compound (2.16) and complexes (2.17) and (2.19) were determined by Prof. Helen S. Evans on a STOE image plate diffractometer at low temperature. Crystals of the dihydroadiazepine ligand (2.16) (Figure 2.16) was a twin which contains two independent molecules. The bipyridine rings lie at 26.2 and 32.9° to each other and the isolated pyridine ring lies at 66-79° to the bipyridine rings of their respective molecules. The molecule possesses a
centre of symmetry and the pyridine ring is disordered over two positions. However, the two conformations are distinctly different, which may be related to the optimization of molecular packing dominated by all four N-H bonds forming intermolecular hydrogen bonds to pyridine N atoms.

![ORTEP representation of the molecular structure of (2.16)](image)

**Figure 2.16.** ORTEP representation of the molecular structure of (2.16) showing the atomic labelling Scheme. There are two independent molecules found in the unit cell. Thermal ellipsoids are plotted at 50%.

In the diazepine rings, the three atoms not belonging to the pyridine system deviate from the best plane of the other four, with one N and one C atom displaced to one side of the plane, and the second N atom to the other side of the plane. Four carbons at the ring fusion and one amino N atom lie roughly in a plane and an amino N atom and the methine C atom are displaced from it in the same direction (molecule 1: N3 0.703(2), C11 0.987(2) Å; molecule 2: N8 0.921(2), C27 0.963(3) Å). The isolated pyridine ring is oriented differently in the two molecules; the torsion angles between the pyridine N atom and the “in plane” amino N atom are 174.34(18) and 79.1(2)°. This dihydrodipyridodiazepine ring system has only been reported before as cyclic urea and thiourea derivatives. Table 2.6 summarizes selected bond lengths [Å] and bond angles [°] for compound (2.16).
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</table>

Table 2.6. Selected bond lengths [Å] and bond angles [°] for compound (2.16).

Crystals isolated from reaction of the bis-imine (2.7) and zinc(II)(hfac)$_2$ by slow evaporation afforded two different compounds. The first one, complex (2.17), was shown by crystallography to contain zinc(II) bound to ligand (2.16), one hfac anion and, surprisingly, one trifluoroacetate anion derived by hydrolysis of another hfac anion, Figure 2.17. Table 2.7 summarizes selected bond lengths [Å] and bond angles [°] for complex (2.17).
Figure 2.17. ORTEP representation of the molecular structure of (2.17) showing the atomic labelling Scheme. Thermal ellipsoids are plotted at 50%.

<table>
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Table 2.7. Selected bond lengths [Å] and bond angles [°] for complex (2.17).

The bipyridine ligand, the trifluoroacetate and one oxygen atom of the hfac form a distorted
square planar arrangement around the zinc, with the second hfac O atom forming a contact from an axial position. The axial Zn-O contact (2.209 Å) is significantly longer than the other two Zn-O distances (Zn-O(hfac):1.941 Å, Zn-O(trifluoroacetate):2.010 Å). The Zn-N distances are in the range of 1.987 to 1.956 Å. The fluorine positions on the trifluoroacetate are disordered. The diazepinobipyridine system is planar with the exception of the carbon atom carrying the isolated pyridine ring, which lies out of plane to form an envelope-type conformation for the central seven-membered ring, and the isolated pyridine ring lies at 66° to the bipyridine’s best plane. The binding of zinc(II) promotes the planarity of the bipyridine system, and removes the repulsion between nitrogen lone pairs which would be partly responsible for the non-planarity of the bipyridine in the free ligand. The zinc(II) ion probably catalyses the hydrolysis of hfac as shown in Scheme 2.7.

Scheme 2.7. Proposed mechanism for hydrolysis of the hfac catalysed by Zn(II).

A second Zn(II) complex (2.19) isolated from the reaction of Zn(II)(hfac)_2 and the bis-imine were also obtained and the structure of complex (2.19) was obviously different from that of the complex (2.17). This interesting phenomenon is probably due to the difference of time that these two compounds were exposed to water and oxygen. Crystallography shows that complex (2.19) contains a Zn(II) ion complexed by two hfac ions and the unexpected oxidized ligand (2.18), with composition “bis(imine)+H_2O·4H”, Figure 2.18. Table 2.10 summarizes selected bond lengths [Å] and bond angles [°] for complex (2.19).
Figure 2.18. ORTEP representation of the molecular structure of (2.19) showing the atomic labelling Scheme. Thermal ellipsoids are plotted at 50%.

Instead of the 5-coordinate geometry of the Zn(II) ion, the Zn(II) ion of complex (2.19) is 6-coordinate and possesses a distorted octahedral geometry. The Zn-N bond lengths are 2.127(3) and 2.155(3) Å, and the bond lengths from Zn to the hfac O atoms are in the range 2.074(3)-2.118(3) Å. In contrast to ligand (2.16) in complex (2.17), the bipyridine rings lie at 26.29(18)° to each other, due to the reduced flexibility of the diazepine ring, which contains an endocyclic amidine group acylated with a picolinoyl group. The latter lies roughly planar with the amide N atom and its two attached carbon atoms. The pyridine attached to the C atom of the amidine is almost coplanar with this group, and lies at 85.8(2)° to the other pyridyl substituent. The N-C bond lengths in the N=C-N-C(=O) system are 1.257(5), 1.438(5) and 1.374(5) Å respectively, indicating that the amide N atom makes a stronger conjugation with the carbonyl than the imine group. There is a surprisingly short 1,5 contact between the nicotinoyl ring N atom and the imine C atom 2.650(5) Å, which would correspond to incipient attach by a lone pair on the C=N double bond. The two nitrogen atoms in the diazepine ring are displaced in opposite
directions, and by the largest amounts, from the best plane through the diazepine ring. Table 2.8 summarizes the selected bond lengths and bond angles for complex (2.19).

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<td>Zn(1)-N(2)-C(6)</td>
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<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table 2.8. Selected bond lengths [Å] and bond angles [°] for complex (2.19).

To summarize, two novel ligands have been prepared by exploiting the functionality of 3,3'-diamino-2,2'-bipyridine. The magnetic properties of the Cu tetramer (2.5) have promise as a building block for the self-assembly of molecule-based magnetic materials, in particular if the terminal chloride could be replaced by suitable bridging ligands, such as cyanide. The imine ligand (2.7) is perhaps the most interesting system for further study due to its high reactivity. Future studies could be directed to fully exploit the chemistry of this ligand (2.7).
Chapter 3 - Experimental for bipyridine project

General information:

All reagents were purchased from commercial suppliers (Fisher-Aldrich, Acros, Strem, CALEDON, Fluka and BDH). Reactions that were expected to be sensitive to air or moisture were performed under an inert atmosphere of argon or nitrogen. All glassware and syringes were dried in an oven above 100 °C, and then cooled in a dry box before use. All temperatures are in °C. Low temperature baths were prepared with acetone/dry ice for -78 °C and ice/water for 0 °C. A constant temperature silicon oil bath was used for heating reaction mixtures at temperatures above room temperature. Air sensitive reagents and solutions were transferred via syringes and were introduced under argon or nitrogen. Removal of solvent was normally accomplished using a reduced pressure rotary evaporator (10-15 mmHg) and vacuum pump (0.3-0.5 mmHg). Reagent-grade solvents were used for all extractions and work-up procedures. Distilled water was used for all aqueous workups and all aqueous solutions. Tetrahydrofuran (THF) and benzene were distilled from sodium benzophenone ketyl. Dichloromethane and diethyl ether were distilled from CaH₂. Dry methanol and ethanol were distilled from magnesium and a catalytic amount of iodine. Unless otherwise stated, coordination chemistry was generally carried out using regular solvents in air at room temperature.

Thin layer chromatography (TLC) was carried out on Merck pre-coated silica gel 60 F254, aluminium sheets, 200µm thick, 25mm (width) x 50mm (length). Fourier transform infrared spectra (FT-IR) were recorded on a Bomem MB-100 spectrometer as neat films between NaCl plates, or as KBr discs. Low resolution mass spectra (MS) were recorded on a Carlo Erba/Kratos GC/MS Concept 1S double focusing mass spectrometer interfaced to a Kratos DART acquisition
system and a Sun SPARC workstation. Samples were introduced through a direct inlet system. Ions were generated using electron impact (EI) at 70ev or Fast Atom Bombardment (FAB) sources and were reported as m/z values for the parent peak and major fragments. $^1$H-NMR and $^{13}$C-NMR spectra were obtained on Bruker DPX-300/ Bruker DPX-600 digital FT NMR spectrometer with deuterated chloroform as solvent unless otherwise stated. Chemical shifts for NMR were determined relative to the internal standard tetramethylsilane (0.00 ppm) and CDCl$_3$ (7.26 ppm) for $^1$H-NMR spectroscopy, and CDCl$_3$ (77.00 ppm) for $^{13}$C-NMR spectroscopy. All $^1$H-NMR data listed have the following order: chemical shift (ppm), (multiplicity, number of protons, coupling constants, assignment). Multiplicity is designed using following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet); m (multiplet), br (broad). The $^{13}$C-NMR data listed in chemical shift (ppm).

3.1 Experimental Section for bipyridine project

3.1.1 Procedure for the activation of Copper Powder

20 g of copper powder (1-3μm) was stirred with a solution of 2% iodine in acetone (200 mL) until the color turned light yellow. The resulting grayish pink powder was filtered off and stirred with a 1:1 solution of concentrated hydrochloric acid: acetone (100 mL). The residual copper powder was filtered off and washed with acetone several times. The dry pink copper powder was used directly in the next step and the remainder was stored in a desiccator for future use.

3.1.2 Synthesis of 3,3'-dinitro-2,2'-bipyridine

![Chemical Reaction](image)

2-chloro-3-nitropyridine (10.00 g, 63.09 mmol) was dissolved in distilled DMF (200 mL)
under argon until a clear, a yellow solution was formed. 10 g of freshly activated copper powder was then added. The mixture was heated to 150 °C and stirred for approximately 2.5 h. The progress of the reaction was monitored by TLC (CH₂Cl₂). Once no more starting material was detected the solution was cooled and diluted with 200 mL of cold water to afford the crude product as brown precipitate. The solid was collected by filtration, washed with concentrated ammonia hydroxide (200 mL) and the resulting residue was extracted twice with 150 mL portions of 1,4-dioxane. Removal of the solvent under vacuum afforded a green-brown solid. Re-crystallization from ethanol gave pale yellow crystals of 3,3'-dinitro-2,2'-bipyridine. Yield (4.91 g, 63%), m.p. 205-206 °C.

^1^H-NMR (CDCl₃, ppm): 8.89 (dd, J = 4.7, J = 1.7, 2H, 6,6'-H), 8.59 (dd, J = 8.4, J = 1.5, 2H, 4,4'-H), 7.65 (m, 2H, 5,5'-H).

^13^C-NMR (CDCl₃, ppm): 152.91 (6,6'-C), 150.72 (2,2'-C), 144.01 (3,3'-C), 133.12 (4,4'-C), 124.61 (5,5'-C).

3.1.3 Synthesis of 3,3'-diamino-2,2'-bipyridine

![Chemical Structure](attachment:image.png)

3,3'-dinitro-2,2'-bipyridine (0.602 g, 2.44 mmol) was added to a hot solution of SnCl₂ (4.16 g, 2.20 mmol) in concentrated HCl (37.5%, 10.00 mL) and refluxed for 0.5h. The pH value was adjusted to 12~13 with aqueous 5 M NaOH solution while still keeping the solution hot (care was taken not to let the solution cool down otherwise an insoluble precipitate is formed and the reaction fails). After cooling, the solution was extracted with chloroform and dried with Na₂SO₄. Removal of the solvent under vacuum afforded the product as a yellow solid. Yield
(0.40 g, 88%), m. p. 133-134 °C.

$^1$H-NMR (CDCl$_3$, ppm): 7.98 (dd, $J_{4.6} = 7.0$, $J_{5.6} = 3.0$, 2H, 6,6'-H), 7.04 (m, 4H, 4,4'-H and 5,5'-H), 6.39 (s, 4H, 2 NH$_2$).

$^{13}$C-NMR (CDCl$_3$, ppm): 143.82 (3,3'-C), 140.61 (2,2'-C), 135.72 (6,6'-C), 123.91 (4,4'-C), 122.92 (5,5'-C).

3.1.4 Preparation of 2-pyridinecarbonyl chloride$^{[49]}$

![Chemical structure image](image)

2-picoline acid (1.23 g, 10 mmol) was dissolved in distilled dichloroethane (10 mL) under nitrogen and the temperature was raised to 50 °C. Distilled SOCl$_2$ (10 mL) was added dropwise to afford a white mixture. Two drops of distilled DMF were then added and the mixture turned clear within a few minutes. The mixture was then heated to 80 °C for 2h under nitrogen with continuous stirring. Removal of solvent under vacuum afforded the product as a light yellow solid. Yield (1.19 g, 84%). This product was used directly without any purification.

$^1$H-NMR (CDCl$_3$, ppm): 8.84 (d, 1H), 8.14 (d, 1H), 7.92 (t, 1H), 7.60 (t, 1H).

IR (KBr, cm$^{-1}$): 3094, 1734 (s, C=O), 1611, 1460, 1407, 1258, 1087, 750.

MS (EI, m/z): 106 [M-Cl]$^+$.

3.1.5 Synthesis of 2,2'-bipyridine-3,3'-(2-pyridinecarboxamide)$^{[50]}$

![Chemical structure image](image)

To a solution of 2-pyridinecarbonyl chloride (1.19 g, 8.41 mmol) in distilled
dichloromethane (10 mL) was added 3,3'-diamino-2,2'-bipyridine (0.781 g, 4.20 mmol). The resulting clear solution was slowly dropped into triethylamine (1.80 mL, 12.6 mmol) at 0 °C to afford a yellow solid. The mixture was stirred at 0 °C for 2h and then heated to 45 °C for 3h. After cooling, a solid was obtained that was isolated by filtration, washed with saturated aqueous NaHCO₃ solution, water, acetone and diethylether and dried under vacuum to afford the product as a pale yellow crystalline powder. Yield (1.25 g, 51%).

1H-NMR (CDCl₃, ppm): 14.72 (s, 2H, CONH), 9.35 (d, 2H, J = 8.4), 8.76 (d, 2H, J = 3.6), 8.63 (d, 2H, J = 3.6), 8.27 (d, 2H, J = 7.8), 7.90 (t, 2H), 7.48 (m, 4H).

13C-NMR(CDCl₃, ppm): 164.01, 150.65, 148.52, 143.22, 141.46, 137.37, 136.01, 129.95, 126.37, 124.03, 122.73.

HMS-EI: C₂₂H₁₆N₆O₂ calcd. 396.1335 m/z, found 396.1332 m/z.

IR (KBr, cm⁻¹): 3449 (NH), 2929, 2363, 1676 (C=O) s, 1564 s, 1511 s, 1434 s, 1387 s, 1296 s, 1227 s, 1139, 1084 s, 999 s, 932 s, 904 s, 805 s, 739 s, 693 s.

m.p. (dec): 218 °C.

C,H,N: C₂₂H₁₆N₆O₂ calcd C 66.65%, H 4.07%, N 21.20%, found C 66.74%, H 3.72%, N 20.80%.

3.1.6 Synthesis of N'-bis(2-pyridylmethyl)[2,2'-bipyridine]-3,3'-diimine[^48]

3,3'-diamino-2,2'-bipyridine (1.50 g, 8.05 mmol) and p-toluene-sulfonic acid (0.113 g,
0.650 mmol) were dissolved in dry toluene (30 mL) to which 2-pyridine-aldehyde (1.73 g, 16.1 mmol) and 4 Å molecular sieves were added. The solution was refluxed using a Dean Stark apparatus for a period of 5 days. The resulting solution was cooled and the solid was discarded by filtration. The filtrate was evaporated to dryness to afford a dark red sticky solid. This solid was dissolved in CH₂Cl₂ (5 mL) and slowly added to 500 mL of cold n-pentane with continuous stirring over a period of 5 h. The resulting precipitate was collected by filtration and dried under vacuum to afford a brown powder. Yield (1.18 g, 40%), m.p. dec. 80-81 °C.

¹H-NMR(CDCl₃, ppm): 8.71 (2H, dd, J = 4.7, 1.2 Hz, 2 x 6-H, bipy), 8.51 (d, J = 4.7 Hz, 2H, 2 x 6-H, pyr), 8.34 (s, 2H, 2 x CH imine), 7.79 (2H, d, J = 7.8 Hz, 2 x 3-H, pyr), 7.69 (dd, J = 7.8, 1.2 Hz, 2H, 2 x 4-H, pyr), 7.47 (dd, J = 7.8, 1.2 Hz, 2H, 2 x 4-H, bipy), 7.43 (dd, J = 7.8, 4.6 Hz, 2H, 2 x 5-H, bipy), 7.30 (dd, J = 7.8, 4.7 Hz, 2H, 2 x 5-H, pyr).

¹³C-NMR(CDCl₃, ppm): 162.3 (2 x C, imine), 154.1 (2 x 2-C pyr), 151.5 (2 x 2-C bipy), 149.4 (2 x 6-C, pyr), 147.5 (2 x 6-C, bipy), 146.1 (2 x 3-C, bipy), 136.7 (2 x 4-C, pyr), 125.7 (2 x 3-H, pyr), 125.3 (2 x 4-C, bipy), 124.1 (2 x 5-C, pyr), 121.6 (2 x 5-C, bipy).

IR (KBr, cm⁻¹): 3053, 1630, 1566, 1501, 1458, 1418, 1401, 1224, 1188, 993, 879, 797, 756, 622.

MS (EI, m/z): 364 ([M]+, 100%).

HMS (EI): C₂₂H₁₆N₆, calcd. 364.1436, found 364.1435.

CHN: C₂₂H₁₆N₆ calcd. C 72.50% H 4.43% N 23.07%; found C 71.97% H 4.43% N 23.43%.
3.1.7 Coordination Complexes of the 2,2'-bipyridine carboxamide Ligand (L₁)

Copper(II)

[Cu₂(L₁)(hfac)] (2.4): Cu(II)(hfac)₂ (0.248 g, 0.502 mmol) was dissolved in MeOH (5 mL) with continuous stirring. The amide ligand (0.198 g, 0.502 mmol) was then added to the resulting solution in one portion. The mixture was stirred for 1 day at room temperature and the resulting precipitate was collected by filtration, washed with n-pentane to afford the complex as a green powder. Yield (0.305 g, 65%). Single crystals suitable for X-ray diffraction were grown via slow evaporation from acetonitrile at room temperature.

IR (KBr, cm⁻¹): 3408, 2361, 1638 (C=O) s, 1600 s, 1557, 1528, 1495, 1476, 423, 1349 s, 1300, 1257 s, 1209 s, 1147 s, 1088, 1047, 996, 902, 803, 753, 691, 669, 587.

MS (FAB, m/z): 727 [Cu₂(L₁)(hfac)]⁺ 100%, 520 [Cu₂(L₁)]⁺ 40%, 458 [Cu(L₁)]⁺ 40%.

CHN: C₂₂H₁₄N₆O₂Cu₂Cl₂: calcld C 44.61, H 2.38, N 14.19; found C 44.82, H 2.41, N 14.25.

[Cu₂(L₁)Cl₂] (2.5): Cu(II) chloride dihydrate (0.170 g, 1.00 mmol) was dissolved in MeOH (5 mL) with continuous stirring. The amide ligand (0.198 g, 0.501 mmol) was then added to the resulting solution in one portion. The mixture was stirred for 1 day at room temperature after which time a green precipitate was obtained. The solid was filtered and washed with n-pentane to
afford the complex as a green powder. Yield (0.084g, 28%). Single crystals suitable for X-ray diffraction were grown via slow evaporation from acetonitrile at room temperature.

IR (KBr, cm\(^{-1}\)): 3472, 3073, 2673, 2363, 1624 (C=O) s, 1589 s, 1528 s, 1466, 1440, 1405, 1357, 1324, 1299, 1233, 1154, 1082, 1022, 888, 812, 750, 682, 644.

MS (FAB, m/z): 593 [Cu\(_2\)(L\(_1\))Cl\(_2\)]\(^+\) 20%, 557 [Cu\(_2\)(L\(_1\))Cl]\(^+\) 70%.

CHN:

X-ray Crystallography. X-ray crystallographic data for compounds (2.4), (2.5) and (2.16) were collected and solved by Prof. M. Pilkington on a Bruker Apex II CCD diffractometer with graphite monochomated Mo K\(\alpha\) radiation (\(\lambda = 0.71073\ \text{Å}\)). X-ray crystallographic data for compounds (2.13), (2.16), (2.17), (2.19) and (5.16) were collected and solved by Prof. Helen-Stoeckli Evans, University of Neuchâtel, on a Stoe Mark II-Image Plate Diffraction System using Mo K\(\alpha\) graphite monochromated radiation (\(\lambda = 0.71073\ \text{Å}\)). In all cases, the structures were solved by Direct methods using the SHELXTL V6.14 package\(^{[51]}\) and the SHELXS-97 program.\(^{[52]}\) The refinement and all further calculations were carried out using the SHELXTL package\(^{[51]}\) and the SHELXL-97 program.\(^{[53]}\) The H-atoms were included in calculated positions and treated as riding atoms using default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F\(^2\).
3.1.8 Coordination complexes of the bis-diimine ligand (L₂)

Cobalt(II)

A few mg’s of the ligand bis-imine (L₂) were dissolved in wet acetonitrile and an excess of Co(II) perchlorate hexahydrate was added to the solution which was left to evaporate slowly at room temperature in air. After a few months, dark red needle crystals appeared which were characterized by X-ray crystallography to be a Co(II) complex of a terpy-like ligand.

Zinc(II)

Complexes (2.17) and (2.19): Zn(II) hexafluoroacetylacetonate dihydrate (0.516 g, 1.00 mmol) was added to a solution of the bis-imine (2.7, L₂) (0.364 g, 1.00 mmol) in methanol (5 mL). The mixture was stirred for 0.5h and then heated to 60 °C for overnight. The solvent was removed and the residue was dissolved in CH₂Cl₂ (3 mL) and slowly dropped into cold n-pentane at 0 °C. The resulting yellow precipitate was collected by filtration and washed with cold n-pentane to afford the complex as a yellow powder. Yield 0.453g. Two different types of single crystals were grown via slow evaporation from acetonitrile and their molecular structures...
were determined by X-ray crystallography.

Co(II) acetate (0.089 g, 0.50 mmol) was added to a solution of the bis-imine (2.7, L₂) (0.182 g, 0.501 mmol) in acetonitrile (5 mL). The mixture was stirred for 3h at which time a dark brown precipitate was formed. The complex was collected by filtration and washed with diethyl ether to afford the product as a brown powder. Yield 0.107 g. No suitable single crystals could be grown for characterization of the molecular structure by X-ray crystallography.

IR (KBr, cm⁻¹): 3387, 3256, 2362, 1593, 1467, 1417, 1343, 1207, 1087, 1022, 945, 799, 761, 666, 618.

MS (FAB): 725 [M⁺]; 668 [M-(CH₃CO₂)]⁺; 609 [M-(CH₃CO₂)₂]⁺.

UV-Vis (MeOH): 432, 297, 259 nm.

Co(II) chloride hexahydrate (0.238 g, 1.00 mmol) was added to a solution of N,N'-bis(2-pyridylmethyl)[2,2'-bipyridine]-3,3'-diimine (0.364 g, 1.00 mmol) in acetonitrile (5 mL). The mixture was stirred for 0.5h and a brown precipitate was obtained. The product was collected by filtration and washed with diethyl ether to afford the complex as a brown powder. Yield 0.453 g. No suitable single crystals could be grown for characterization of the molecular structure by X-ray crystallography.

IR (KBr, cm⁻¹): 3481, 3448, 3421, 3339, 3117, 3078, 2363, 2337, 1636, 1598, 1470, 1424, 1207, 1156, 1122, 1089, 1022, 906, 880, 743, 668.


UV-Vis (MeOH): 432, 297, 247 nm.

Co(II) perchlorate hexahydrate (0.366 g, 1.00 mmol) was added to a solution of the bis-imine (2.7, L₂) (0.364 g, 1.00 mmol) in acetonitrile (5 mL). The mixture was stirred at room
temperature for 24h and then refluxed for 24h. The solvent was then removed under vacuum to give a dark green powder, Yield 0.695 g. No suitable single crystals could be grown for characterization of the molecular structure by X-ray crystallography.

**IR (KBr, cm⁻¹):**  3349 s, 3082 s, 2363, 1636, 1598, 1525, 1473 s, 1330, 1209, 1087 s, 909, 766, 628.

**MS (FAB, m/z):**  708 [Co₂(L₂')(ClO₄)]⁺, 609 [Co₂(L₂')]⁺, 522 [Co(L₂')(ClO₄)]⁺, 423 [Co(L₂)]⁺, 334 [Co(L₂')]⁺.

**UV-Vis (MeOH):**  439, 303, 260 nm.

**Copper(I)**

Cu(I) chloride (0.0991 g, 1.00 mmol) was added to a solution of the *bis*-imine (2.7, L₂) (0.364 g, 1.00 mmol) in acetonitrile (5 mL). The reaction mixture was stirred for 1h, after which time a green precipitate was obtained. The product was filtered and washed with ether to afford a green powder. Yield 0.364 g. No suitable single crystals could be grown for characterization of the molecular structure by X-ray crystallography.

**IR (KBr, cm⁻¹):**  3320, 3065, 2363, 1628, 1590 s, 1459, 1350, 1299, 1202 s, 1150, 1095, 899, 803, 775, 647.

**MS (FAB, m/z):**  613 [Cu₂(L₂')Cl₂(H₂O)₈]⁺, 490 [Cu₂(L₂)]⁺, 427 [Cu(L₂)]⁺, 373 [Cu(L₂')Cl]⁺, 338 [Cu(L₂')]⁺.

**UV-Vis (MeOH):**  421, 288, 246 nm.

**Copper(II)**

Cu(II) chloride dihydrate (0.043 g, 0.25 mmol) was added to a solution of the *bis*-imine (2.7, L₂) (0.091 g, 0.25 mmol) in methanol (5 mL). The mixture was stirred for 2h at room temperature
after which time a green precipitate was obtained. The complex was collected by filtration and washed with diethyl ether to afford a green powder. Yield 0.103 g. No suitable single crystals could be grown for characterization of the molecular structure by X-ray crystallography.

IR (KBr, cm⁻¹): 3391, 3265, 3069, 2369, 1701, 1596, 1519, 1462, 1345, 1305, 1204, 1156, 1126, 805, 719, 685, 649.

MS (FAB, m/z): 613 [Cu₂(L₂')Cl₂(H₂O)₈]⁺, 545 [Cu₂(L₂')Cl₂(H₂O)₈]⁺, 478 [Cu(L₂')Cl₂(H₂O)₈]⁺, 427 [Cu(L₂)]⁺, 373 [Cu(L₂')Cl]⁺, 338 [Cu(L₂')]⁺.

UV-Vis (MeOH): 423, 285, 245 nm.

Cu(II) hexafluoroacetylacetonate hydrate (0.248 g, 0.500 mmol) was added to a solution of the bis-imine (2.7, L₂) (0.182 g, 0.500 mmol) in acetonitrile (5 mL). The mixture was stirred for 0.5h after which time a yellow precipitate was formed. The complex was collected by filtration and washed with diethyl ether to afford a yellow powder. Yield 0.030 g. No suitable single crystals could be grown for characterization of the molecular structure by X-ray crystallography.

IR (KBr, cm⁻¹): 321, 1664 s, 1598, 1549, 1528 s, 1497, 1470, 1427, 1337, 1260 s, 1201 s, 1144 s, 1085, 801, 667, 583.

MS (FAB, m/z): 814 [Cu₂(L₂')(hfac)₂]⁺, 609 [Cu₂(L₂')(hfac)]⁺, 545 [Cu(L₂')(hfac)]⁺, 338 [Cu(L₂')]⁺.

UV-Vis (MeOH): 422, 286, 242 nm.

Cu(II) perchlorate hexahydrate (0.371 g, 1.00 mmol) was added to a solution of the bis-imine (2.7, L₂) (0.364 g, 1.00 mmol) in acetonitrile (5 mL). The mixture was stirred for 2h, after which time a green precipitate was formed. The precipitate was collected by filtration and washed with diethyl ether to afford the complex as a green powder. Yield 0.284 g. No suitable
single crystals could be grown for characterization of the molecular structure by X-ray crystallography.

IR (KBr, cm⁻¹): 3338, 3082, 2363, 1598, 1466, 1306, 1208, 1094, 808, 716, 626.

MS (FAB, m/z): 777 [Cu₂(L₂')₂(ClO₄)]⁺, 712 [Cu(L₂')₂(ClO₄)]⁺, 613 [Cu(L₂)₂]⁺, 437 [Cu(L₂')(ClO₄)]⁺, 338 [Cu(L₂')]⁺.

UV-Vis (MeOH): 452, 288, 246 nm.

Cu(II) triflate (0.20 g, 0.55 mmol) was added to a solution of the bis-imine (2.7, L₂) (0.20 g, 0.55 mmol) in acetonitrile (5 mL). The mixture was stirred for 2 h after which time a green precipitate was formed. The complex was collected by filtration and washed with diethyl ether to afford the complex as a green powder, Yield 0.305 g. No suitable single crystals could be grown for characterization of the molecular structure by X-ray crystallography.

IR (KBr, cm⁻¹): 3449, 3313, 2363, 1599, 1524, 1467, 1430, 1256 s, 1164 s, 1031 s, 888, 807, 767, 639.

MS (FAB, m/z): 762 [Cu(L₂')₂(CF₃SO₃)]⁺, 613 [Cu(L₂')₂]⁺, 487 [Cu(L₂')(CF₃SO₃)]⁺, 427 [Cu(L₂)]⁺, 338 [Cu(L₂')]⁺.

UV-Vis (MeOH): 423, 288, 247 nm.

**Manganese(II)**

Mn(II) hexafluoroacetylacetonate trihydrate (0.469 g, 1.00 mmol) was added to a solution of the bis-imine (2.7, L₂) (0.364 g, 1.00 mmol) in a solution of 1:1 CH₂Cl₂ and methanol (5 mL). The mixture was stirred for 1 h and then heated to 60 °C overnight. The solvent was removed under vacuum, and the residue was dissolved in CH₂Cl₂ (3 mL). The solution was then dropped into 300 mL of cold n-pentane under ice bath to yield a yellow precipitate. The solid was
collected by filtration and washed with cold pentane to afford the complex as a brown powder. Yield 0.607 g. No suitable single crystals could be grown for characterization of the molecular structure by X-ray crystallography.

**IR (KBr, cm⁻¹):**

3320, 2362, 1677, 1651, 1596, 1525, 1501, 1463, 1428, 1257, 1200, 1144, 1098, 802, 725, 665, 582.

**MS (FAB, m/z):**

1196 [Mn(L₂)₂(hfac)₂]⁺, 744 [Mn(L₂′)(hfac)₂]⁺, 626 [Mn(L₂)(hfac)]⁺, 537 [Mn(L₂′)(hfac)]⁺, 329 [Mn(L₂′)]⁺.

**UV-Vis (MeOH):** 405, 304, 244 nm.

**Nickel (II)**

Ni(II) acetate tetrahydrate (0.249 g, 1.00 mmol) was added to a solution of the bis-imine (2.7, L₂) (0.364 g, 1.00 mmol) in acetonitrile (5 mL). The mixture was stirred for 1 h after which time a yellow precipitate was obtained. The solid was then collected by filtration and washed with (wet or dry) diethyl ether to afford the complex as a yellow powder. Yield 0.484 g. No suitable single crystals could be grown for characterization of the molecular structure by X-ray crystallography.

**IR (KBr, cm⁻¹):**

3259, 2363, 1592, 1567, 1463, 1418, 1340, 1207, 1152, 1122, 809, 763, 728, 672 cm⁻¹.

**MS (FAB, m/z):**

449 [Ni(L₂′)(CH₃CO₂)₂]⁺, 392 [Ni(L₂′)(CH₃CO₂)]⁺, 333 [Ni(L₂′)]⁺.

**UV-Vis (MeOH):** 409, 284, 246 nm.

Ni(II) hexafluoroacetylacetonate (0.473 g, 1.00 mmol) was added to a solution of the *bis*-imine (2.7, L₂) (0.364 g, 1.00 mmol) in methanol (5 mL). The mixture was stirred for 0.5 h after which time a yellow precipitate was isolated. The resulting solid was collected by filtration.
and washed with diethyl ether to afford the complex as a yellow powder. Yield 0.501 g. No suitable single crystals could be grown for characterization of the molecular structure by X-ray crystallography.

IR (KBr, cm⁻¹): 3258, 2364, 1647 s, 1592, 1552, 1502 s, 1441, 1341, 1309, 1258 s, 1201 s, 1148 s, 1083, 794, 760, 671, 586.

MS (FAB, m/z): 1057 [Ni₂(L2)(hfac)]⁺, 693 [Ni₂(L2)(MeOH)]⁺, 661 [Ni(L2)(hfac)(MeOH)]⁺, 629 [Ni(L2)(hfac)]⁺, 422 [Ni(L2)]⁺.

UV-Vis (MeOH): 396, 304, 246 nm.

Silver(I)

Ag(I) triflate (0.141 g, 0.551 mmol) was added to a solution of the bis-imine (2.7, L₂) (0.200 g, 0.550 mmol) in acetonitrile (5 mL). The mixture was stirred at room temperature for 1 day after which time a yellow precipitate was formed. The solid was collected by filtration and washed with diethyl ether to afford the complex as yellow powder. Yield 0.190 g. No suitable single crystals could be grown for characterization of the molecular structure by X-ray crystallography.

IR (KBr, cm⁻¹): 3451, 2363, 2339, 1627, 1588, 1567, 1474, 1442, 1262, 1159, 1104, 1032, 1007, 905, 813, 774, 639.

MS (FAB, m/z): 729 [Ag₂(L₂)(CF₃SO₃)]⁺, 579 [Ag₂(L₂)]⁺, 471 [Ag(L₂)]⁺.

UV-Vis (MeOH): 433, 284, 246 nm.
4.1 Magnetism

Magnetism is one of the phenomena by which materials exert an attractive or repulsive force on external magnetic fields. Magnetism arises from the movement of electrical charge, either from the movement of electrons in an electric current, or from the quantum-mechanical spin and orbital motion of electrons. Electrons are fundamental subatomic particles that carry a negative electric charge and possess an intrinsic angular momentum, or spin. Spin states can be characterized by a quantum number $m_s = \pm 1/2$, commonly known as 'spin up' or 'spin down'. For those paired electrons, each will possess a spin state with a magnetic moment which is equal in magnitude but opposite in sign to its orbital counterpart (Figure 4.1). Thus, the magnetic moment generated by one electron is cancelled out by the magnetic moment from the second electron in the same molecular orbital. As a result, the presence of unpaired electrons turns out to be the prerequisite for observing magnetic behaviour.

\[ \mu = -g\beta m_s, \ m_s = \pm 1/2 \ (h/2\pi) \]

Figure 4.1. Relationship between electronic magnetic moment $\mu$ and spin state $\pm m_s$, where $g$ is the g-factor which is a proportionality constant approximately equal to 2 and $\beta$ is the Bohr magneton.

Magnetic behaviour is dependent upon the interactions of spin and/or orbital angular momentum involving adjacent atoms, and it can be determined by placing the sample in an
external magnetic field and measuring its magnetic induction $B$ (Equation 4.1). $B$ is related to the magnetization $M$ induced in the sample in the presence of an external field, $H$.

$$B = H + 4\pi M \quad (4.1)$$

Magnetization can be thought of as the extent to which a magnet has been affected by an external field. It is defined as the net sum of previous randomly arranged individual magnetic moments in the presence of an external field, and it will be cancelled out in the absence of an external field. The ability of the individual moments of a substance to align with an external field, the magnetic susceptibility $\chi$, is defined as in Equation 4.2.

$$\chi = M/H \quad (4.2)$$

The gram susceptibility, $\chi_g$, is obtained by dividing the experimental value of volume susceptibility, $\chi_v$, by the density of the substance being measured, $\rho$. The molar magnetic susceptibility, $\chi_M$, can then be obtained by multiplying the gram susceptibility $\chi_g$ by the molar mass of the substance under study. In the absence of other interactions between spins, there are two types of responses to an external field, attraction and repulsion. A negative $\chi_M$ value represents diamagnetic behaviour, which means the sample is repelling the magnetic field. Diamagnetism results from the repulsion between the external field, $H$, and the induced field within the sample. It is the weakest magnetic behaviour and usually has a value on the order of $-10^{-6}$ emu/mol. Generally, it is temperature and field independent, and is exhibited by all materials. On the other hand, a positive $\chi_M$ value represents paramagnetic behavior. Paramagnetism is due to the alignment of the magnetic moments of unpaired electrons in the presence of an external field so that the generated field has a trend of moving towards regions of higher field strength. Paramagnetism is temperature dependent, field independent and its
magnitude typically is on the order of $10^{-3}/10^{-4}$ emu/mol at room temperature. The total magnetic susceptibility for a magnetic molecule is the sum of its diamagnetic and paramagnetic susceptibilities (Equation 4.3).

$$\chi_{\text{obs}} = \chi_{\text{dia}} + \chi_{\text{para}} \quad (4.3)^{[54]}$$

### 4.1.1 Paramagnetism

Inorganic chemists are interested in paramagnetic components of magnetic behavior because they can shed light on the electronic structure of coordination compounds. In 1910, it was demonstrated that the temperature dependence of a paramagnetic substance obeys the Curie Law, that is, the magnetic susceptibility of a paramagnetic material is inversely proportional to temperature (Equation 4.4, Figure 4.2, $\theta = 0$) (C, Curie constant; $N$, the Avogadro constant; $S$, the ground state spin multiplicity; $k$, the Boltzmann constant).

$$\chi = C/T = N g^2 \beta^2 S(S+1)/3kT \quad (4.4)^{[54]}$$

![Figure 4.2. Plot of $1/\chi$ vs $T$ showing ideal Curie and Curie-Weiss magnetic behaviour.](image)

Magnetic materials whose susceptibilities exhibit a temperature dependence based on Equation 4.4 are said to display ideal Curie behaviour, which is rare and generally only occurs in the absence of any magnetic interactions between neighboring paramagnetic units among other factors. The vast majority of paramagnetic substances feature spin-spin interactions between
molecules in the solid state. There are several methods to take such intermolecular interactions into consideration and the simplest is with the Curie-Weiss Law (Equation 4.5):

\[
\chi = C/(T-\theta)
\]

(4.5)\(^{[54]}\)

where the sign of the Weiss constant, \(\theta\), or Curie temperature, is dependent on the nature of the intermolecular magnetic interactions. \(\theta\) is positive if all of the spins tend to align parallel to each other and the interaction is referred to as ferromagnetic. On the contrary, \(\theta\) is negative if the spins tend to align antiparallel and the interaction is referred to as antiferromagnetic. \(\theta\) can be determined by plotting \(1/\chi\) versus temperature and the intersection at \(x\)-axis is the \(\theta\) value. In general, these interactions are very weak and persist only in the presence of an external magnetic field and disappear when the field is removed. The Curie-Weiss law says nothing about the specific nature of the interactions and is used as a qualitative estimate of the magnetism and sign of these interactions. The magnetic susceptibility of different compounds will behave according to a Curie-Weiss law in different temperature ranges with different values of \(C\) and \(\theta\).

There are two types of intramolecular magnetic interactions between neighboring paramagnetic units within a paramagnetic molecule: ferromagnetic interactions where the unpaired electrons align parallel to one another and, antiferromagnetic interactions where the unpaired electrons align antiparallel to one another. The strength of the spin-spin interaction between atom A and atom B is characterized by \(J\), the exchange interaction parameter, using the Heisenberg spin Hamiltonian (Equation 4.6, where \(\hat{S}\) is the spin operator).

\[
\hat{H} = -2JS_A \cdot \hat{S}_B
\]

(4.6)\(^{[54]}\)

For a bimetallic system when \(S = 1/2\) for each metal ion, or any molecular system containing two weakly coupled unpaired electrons, the Bleaney-Bowers equation (Equation 4.7) can be
obtained by applying a Boltzman distribution to the energies of the spin states determined from the spin Hamiltonian (Equation 4.6). The temperature dependence of magnetic susceptibility $\chi$ for a two-spin bimetallic molecular system can be measured, and a best fit can be obtained with the Bleaney-Bowers equation using the experimental $\chi$ data. Subsequently, the $J$ value can be determined by fitting the experimental $\chi$ data to the Bleaney-Bowers model. $J$ is positive for a ferromagnetic interaction and is negative for an antiferromagnetic interaction.

\[
\chi = \frac{2Ng^2\beta^2}{kT} \left[ \frac{3 + \exp\left( -\frac{2J}{kT} \right)}{kT} \right] 
\]

\[\text{(4.7)}\]

![Figure 4.3. $\chi T$ vs $T$ curves for different $J$ values for paramagnetic systems containing two unpaired electrons.}\[54\]

The temperature dependence $\chi T$ vs $T$ for different $J$ values for a bimetallic complex containing two $S = 1/2$ metal ions is presented in Figure 4.3. Ferromagnetic behaviour gives an increasing $\chi T$ value with decreasing temperature due to the thermal depopulation of the diamagnetic singlet excited state and population of ground triplet states. The limiting value at low temperature is approximately 1.00 emu·K/mol ($\chi T = 2Ng^2\beta^2/3k$). Antiferromagnetic behaviour gives a gradually decreasing $\chi T$ value with decreasing temperature, and $\chi T$ tends to a
value of zero due to the complete population of the diamagnetic singlet state. A temperature independent \( \chi T \) value is obtained when \( J = 0 \), consistent with a Curie paramagnet (\( \chi T = 0.75 \)).

4.1.2 Magnetic long range order

The existence of intramolecular magnetic interactions does not guarantee the exhibition of long range magnetic order, which characterizes the entire magnetic interactions of a system in which remote portions of the same sample exhibit correlated behavior physically. At a certain temperature, the long range 2-D/3-D magnetic ordering differs fundamentally from intramolecular neighboring spin-spin magnetic interactions. Actually, many systems displaying intramolecular ferromagnetic interactions as indicated by the sign and magnitude of \( J \) at room temperature are Curie paramagnets with spins randomly distributed in the absence of an external magnetic field.

![Diagram](image1.png)

**Figure 4.4.** (a) Magnetic domains randomly distributed so that the net magnetization is zero, (b) magnetic domains aligned parallel so that the net magnetization is not zero.

Ferromagnets display zero magnetization in the absence of an external field at high temperature, and this is simply due to the formation of magnetic domains. Magnetic domains are areas separated by so-called domain walls, and each of the domains has a uniform direction of the magnetization (Figure 4.4a). Within the domain, the magnetic field is intense, but in a bulk sample the material is usually unmagnetized because the domains are oriented randomly at room temperature. One important parameter for ferromagnets is the critical temperature, \( T_c \), the
temperature below which such magnetic domains, or spins, are aligned parallel so that the net magnetization is no longer zero and the previously paramagnetic species exhibits a ferromagnetic ordering, Figure 4.4b. For antiferromagnetism, the spins tend to align antiparallel below a certain temperature so that the previously paramagnetic species exhibits an antiferromagnetic ordering. Paramagnets display antiferromagnetism at low temperature, and the transition temperature is called the Néel temperature, $T_N$.

![Diagram](image)

**Figure 4.5.** Magnetic susceptibility curves vs Temperature for paramagnetism, ferromagnetism, ferrimagnetism and antiferromagnetism upon long range order.

The temperature dependence of magnetic susceptibilities for paramagnetic, ferromagnetic, ferrimagnetic and antiferromagnetic behaviours are given in Figure 4.5. Ideal paramagnetic response of the $\chi_M T$ curve is temperature independent so that a straight line is obtained; ferromagnets have an increasing curve of $\chi_M T$ upon decreasing temperature; antiferromagnets have a downward curvature upon decreasing temperature. Besides these three, there is also a 'ferrimagnetism', which refers to such magnetic materials in which the unequal magnetic moments of the atoms on different sublattices are opposite to each other so that a net magnetic moment will remain. Ferrimagnets display first a downward curvature and then an upward curvature and are typically polymetallic complexes containing more than one spin centres with
unequal spin states.

A distinguishing characteristic of ferromagnets and ferrimagnets is the presence of a hysteresis loop. The hysteresis loop can be obtained by plotting magnetization \( M \) of a ferromagnet versus the applied field \( H \) (Figure 4.6). That is, when applying a sufficiently large magnetic field, the magnetization becomes saturated at \( M_s \); when the magnetic field is switched off, the magnetization does not vanish, but assumes a certain value referred to as the remnant magnetization, \( M_R \). Zero magnetization can be achieved by applying a coercive field, \( H_c \), in the opposite direction. Actually, it is the existence of this magnetic hysteresis loop that confers a memory effect on the material.

![Figure 4.6. An ideal hysteresis loop, where \( M_s \) is the magnetization at saturation.](image)

### 4.2 Molecule-based magnets

Magnetic materials traditionally used for information storage are metallic alloys or oxides. However, magnets can also be molecular compounds. The assembly of magnetic materials from molecular precursors via conventional synthetic organic and/or inorganic chemistry is now recognized as an independent field within inorganic chemistry and is referred to as “molecular magnetism”. Molecular magnetism is based on the magnetic behaviour of single molecules in contrast with traditional magnets, or permanent magnets, which are based on the assembling...
behaviour of metals, usually iron, cobalt and nickel. The use of molecules or molecular assemblies for information processing is one of the most appealing aims of modern molecular chemistry due to their potentially extensive storage abilities. A fundamental underlying concept is that of bistability – the ability of the molecular system to occur in two different electronic states\cite{55,56,57}. Usually, one of these states is the state of lower energy and another state is a metastable state in which the system can be efficiently trapped. One can associate a bit of information with each of these states, and thereby create a binary code, provided that there is a way to address each state. In a memory device, the reading of the states of the system can be done by measuring a physical property, e.g. optical or magnetic, which distinguishes clearly the two states. For chemists, the challenge is to design bistable molecular compounds, then to understand the physical property distinguishing the two states, and eventually to optimize these compounds in such a way that the bistability range is easily accessible. Memory devices are expected to work at room temperature, i.e. 293 K (20 °C) should fall within the bistability range of the system.

One class of molecular magnetic compounds attracting interest from a commercial perspective is spin crossover (SCO) compounds. Like molecule-based magnets, spin crossover compounds display a memory effect and can potentially be used in devices. The primary objectives of this project are to prepare and characterize novel precursors to molecule-based magnets, especially spin crossover compounds. In order to put this research in context, it is useful to review some of the highlights within the field of spin crossover chemistry.

4.3 Spin crossover compounds

4.3.1 High spin and low spin states
The spin crossover (SCO) phenomenon was first discovered by Cambi and co-workers in the 1930’s.\cite{Cambi} Since then, the development of the field has led to one of the most promising research topics at the interface of coordination chemistry and magnetochemistry. In recent years, progress in this area has rapidly advanced leading to an increased understanding of the phenomenon itself as well as the fundamental properties associated with it. To date, a range of compounds have been prepared and the SCO phenomenon has been reported to occur in more than one physical state that include solids, solutions as well as a polymeric matrix.\cite{Cambi}

Spin crossover is most commonly observed in the solid state and is referred to as a certain type of molecular magnetism where the spin-state and magnetic moment of a central $d$ block ion can be changed by external constraints such as temperature, pressure, light and magnetic field. It is usually accompanied by change in colour, molecular structure and magnetic properties. A spin crossover transition occurs as a consequence of the energy splitting of the $5d$ orbitals into the $t_{2g}$ and $e_g$ sets by an octahedral ligand field. Certain transition metal ions with configurations of $3d^4$ to $3d^7$ may switch between the high-spin state (HS) and low-spin state (LS), depending on the nature of the ligand field around the metal ion. The electronic liability of transition metal complexes in which a reversible change of the spin multiplicity of the metal ion may be induced together with the memory effect arising from the possible bistable behaviour, make these systems potentially suitable for practical applications in the area of molecular switches, display devices and information storage. The possible advantages of using SCO materials lie in: i) the short addressing times (picosecond scale on the molecular level); ii) photostability over successive cycles; iii) low addressing power (on the order of mW cm$^{-2}$) and iv) high storage densities.
To date, spin crossover properties have been detected in complexes containing Cr(II), Mn(II), Mn(III), Fe(II), Fe(III), Co(II) or Co(III) metal ions. Among these, Fe(II) spin crossover compounds are the most widely studied since they provide the best examples of molecular bistability.\(^{[59]}\) In 1964, Baker and Bobonich reported the first class of Fe(II) SCO compounds of stoichiometry \([\text{Fe(phen)}_2(\text{NCX})_2]\) (\(X = \text{S, Se}\)) and \([\text{Fe(bipy)}_2(\text{NCS})_2]\).\(^{[60]}\) These compounds were, however, not fully characterized magnetically and the spin transition between the \(S = 0\) and \(S = 2\) spin states was not reported until these compounds were revisited three years later, where magnetic susceptibility and Mössbauer spectroscopy were used to establish the nature of their spin transitions.\(^{[60]}\)

Studies have shown that the high-spin state and low-spin state have different magnetic, optical and structural properties from each other. For intermediate magnetic fields, the energy difference \((\Delta E_{\text{hl}}^{\circ})\) between the lowest vibronic levels of the potential wells of the two states may be sufficiently small such that application of some relatively minor external perturbation effects a change in the state. This phenomenon is known as a spin crossover (SCO) or spin transition (ST) and its origin is illustrated in Figure 4.7. The metal–donor atom distance is remarkably sensitive to spin-state. SCO is often accompanied by an increase in atomic distance between metal ions and coordination ions from LS to HS states. For systems in the solid state, this change in the molecular dimensions may also bring about fundamental changes in the crystal lattice.
Figure 4.7. Representation of the potential wells for the $^1A_1$ and $^5T_2$ states of a Fe(II) SCO system, the nuclear coordinate being the metal–donor atom distance.\(^{[55]}\)

The energy difference between HS and LS states, $\Delta E^o_{HL}$, is close to the thermal energy, $k_BT$, and therefore can be overcome when $\Delta E^o_{HL} = k_BT$ is achieved by an external stimulus, such as changing temperature, pressure or electromagnetic radiation; thus for an octahedral metal ion, the electrons can be promoted or excited to the higher energy level $e_g$ orbitals. In weak fields, the ground state is HS alone and the spin multiplicity is a maximum, and the $d$ electrons are distributed over both the $t_{2g}$ and $e_g$ sets. In contrast, strong fields stabilize the LS state with a minimum multiplicity; the $t_{2g}$ set being completely occupied before electrons are added to the $e_g$ set. Take the $d^6$ Fe(II) for example: the two states are illustrated by $[\text{Fe(H}_2\text{O})_6]^{2+}$, which with the configuration $t_{2g}^4e_g^2$ has four unpaired electrons ($S = 2$) and thus is strongly paramagnetic, and $[\text{Fe(CN)}_6]^{4-}$ with the configuration of $t_{2g}^6e_g^0$, which has no unpaired electrons ($S = 0$) and thus is diamagnetic (Figure 4.8).
**Figure 4.8.** Electronic configuration for a $d^6$ Fe(II) ion in the LS state, in the HS state and equilibrium between these two states in the case of thermal SCO. $P$ is the pairing energy.

### 4.3.2 Cooperativity

Spin crossover behaviour is observed for systems in both solution and the solid states, although the one system will not necessarily display the SCO transition in both phases. In solution, interactions between the molecules undergoing spin change are virtually negligible and thus the course of the transition can be described using a temperature dependent Boltzmann distribution over all HS vibronic states and the LS state. The thermal transition is a molecular process and not subject to cooperative interactions. That is, an interaction of the constituent subunits of a system causing a conformational change in one subunit to be transmitted to all others. In this instance, the transition occurs essentially at the molecular level without the constraints of lattice interactions.
Figure 4.9. The nature of ST curves for SCO systems in the solid state: (a) gradual; (b) abrupt; (c) with hysteresis; (d) with steps; (e) incomplete.\textsuperscript{[55]}

For solid systems, lattice effects play a role and the full range of behaviour illustrated by the curves of Figure 4.8 a–e have been observed. The transition may be gradual and continuous over an extended temperature range (Figure 4.9a), or it may be abrupt and occur within a narrow temperature range (Figure 4.9b). The transition may be associated with a thermal hysteresis loop (Figure 4.9c) or be a two-step process (Figure 4.9d). In certain instances, the transition may also be incomplete (Figure 4.9e).

The cooperativities stand for the extent to which the physical and chemical property changes in a molecule during a SCO process causes corresponding changes in its neighbouring molecules. When it is low, the transition will be a gradual/continuous process. The transition becomes more abrupt as cooperativity increases, and sometimes can be associated with a phase change and thermal hysteresis. A transition temperature, $T_{1/2}$, is defined at which the fractions of HS and LS species are equal. For transitions displaying hysteresis, two transition temperatures, $T_{1/2\uparrow}$ and $T_{1/2\downarrow}$, define the width of the hysteresis loop.

It has been observed that dehydration of the spin crossover compound can affect its spin
crossover properties. Bonhommeau et al. discovered that the dehydrated form of 
([Fe(pyrazine){Pt(CN)₄}]\_nH₂O, \( n = 2-3 \)) displays a complete hysteresis loop after losing two 
water molecules, Figure 4.10. The most interesting aspect of this research lies in the fact that a 
large improvement in spin crossover behaviour is observed after dehydration and the transition 
centre is shifted so that it falls within room temperature, which is crucial for the realization of 
any commercial applications.

\[ \chi_M T/\text{cm}^3\text{Kmol}^{-1} \]

\[ T/K \]

**Figure 4.10.** Graph of \( \chi_M T \) versus \( T \) for [Fe(pyrazine){Pt(CN)₄}] in the cooling and heating modes before and after thermal treatment at 430 K.

In the solid state during the SCO transition, there is an electron-phonon coupling between 
molecules changing spin state, resulting in different degrees of cooperative interactions, Figure 
4.9. Experimental proof for the existence of cooperative interactions during SCO processes in 
solids has been observed by applying metal dilution effects. This involves the partial 
replacement of an Fe(II), (without altering the crystal structure), with a foreign diamagnetic 
metal ion, e.g. Zn(II), which has the \( d^{10} \) electron configuration and thus is magnetically silent. 
This was carried out for the above example (Figure 4.10) and is reported to affect the SCO curve 
\( \gamma_{HS}(T) \) in two ways: (i) it becomes more gradual and (ii) it is displaced progressively to lower 
temperatures with decreasing iron concentration. In fact, at sufficiently high dilution, the SCO
curve reflects a simple Boltzmann distribution of the separate spin states indicative of vanishing cooperative interactions, and resembles the curve for the system in the liquid states. Further proof for the existence of cooperative interactions comes from optical spectroscopy of decaying long-lived HS states generated by light. Both features are indicative of vanishing cooperative interactions in a diluted crystal, where the average Fe(II)–Fe(II) distance has become so large that the metal centres are too far away and can not communicate with each other any more. These results indicate that the close proximity of neighbouring molecules is important for communication and, in turn, optimal for spin crossover properties. One strategy to help control the way molecules assemble in the solid state is to use hydrogen bonds to direct the solid-state packing. In this respect, hydrogen bonding is another way to link neighbouring complexes either directly or via bridging solvent molecules or anions. An additional promising means of enhancing cooperativity is also to utilize π-π stacking interactions. There is also evidence to suggest that the short enough distance between chalcogen atoms can also affect the SCO hysteresis loop. Takahashi et al. prepared the first example of an Fe(II) SCO complex involving a 1,3-dithiole ligand, Fe(II)(DPyDT)\(_2\)(NCS)\(_2\)-0.5MeOH (DPyDT = di(2-pyridyl)methylidene-1,3-dithiol-2-ylidene), for which the S⋯S contacts play a key role in an abrupt spin transition of both the low- and high-temperature phases.

Since the elastic interaction between SCO sites within a crystal lattice is the predominant factor influencing cooperativity, two methods have been explored to assemble SCO compounds with long-lived metastable states. The first is referred to as the polymeric approach and the second, the supramolecular approach. The former uses chemical bonds to connect neighbouring SCO sites, i.e. bridging ligands and has afforded a range of 1-D, 2-D and 3-D
magnetic materials; the latter is concerned with the use of non-covalent interactions such as hydrogen bonds and \( \pi-\pi \) stacking for the self-assembly of supramolecular compounds with spin crossover properties.\(^{[63]}\)

Reviewing the spin crossover compounds reported in the chemical literature reveals that a thorough understanding of the cooperative behaviour in a SCO transition is the key to designing useful materials for possible applications. In general, cooperativity in molecular solids is influenced by intermolecular interactions such as \( \pi-\pi \) stacking, hydrogen bonding, the coordination bond and even inter-chalcogen-atom interactions. In other words, it is these interactions that dictate the communication between neighbouring SCO centres, and influence the structural changes that occur in the molecule undergoing the SCO. Cooperativity leads to two of the most significant features of SCO systems, namely thermal hysteresis and the resulting bistability.

**4.3.3 Light-Induced Excited Spin-State Trapping (LIESST)**

Fe(II) spin crossover compounds which exhibit bistability between the high-spin state and low-spin state have attracted great interest since the transition can be triggered not only by temperature, pressure and magnetic field, but also by irradiation. The light-induced excited spin-state trapping (LIESST) was discovered by Decurtins et al., who observed a light-induced LS\( \rightarrow \)HS transition involving quantitative trapping of the molecules in the excited HS state at low temperature.\(^{[64]}\) The possibility of inducing a SCO by irradiation offers potential for the future realization of optical switches and magneto-optical storage devices. The major drawback however is that unlike the thermal SCO transition, LIESST is only efficient at cryogenic temperatures below 50 K, a property that has to be overcome before these properties can be
exploited commercially.\textsuperscript{[64]} Recently Bonhommeau \textit{et al.} have demonstrated that it is possible to trigger SCO by light at room temperature using a nanosecond laser of 8-nanosecond pulses ($\lambda = 532$ nm) with pulse energies of about 1 mJ to irradiate the complex [Fe(C$_4$H$_4$N$_2$)]{Pt(CN)$_4$}], for both ascending and descending branches of the hysteresis loop.\textsuperscript{[61]} Both the LS$\rightarrow$HS and HS$\rightarrow$LS transitions were followed by a distinctive color change in the visible region, as well as by measuring their Raman spectra in the 620-720 cm$^{-1}$ frequency range before and after application of the pulses, Figure 4.11.\textsuperscript{[61]}

![Figure 4.11. Proportion of HS Fe(II) ions before (blank) and after (black) a one-shot laser pulse of irradiation on the ascending and descending branches of the hysteresis loop for [Fe(pyrazine)]{Pt(CN)$_4$}]. The insets show the Raman spectra recorded before and after irradiation.\textsuperscript{[61]}

4.4 A review of the N$_3$O$_2$ macrocyclic ligand (L)

It has been found in recent years that spin crossover properties occur in Fe(II) metal complexes assembled from N-substituted heterocyclic ligands, such as triazoles, tetrazoles and imidazoles.\textsuperscript{[65]} In this respect, the pentadentate macrocyclic ligand (L) (Figure 4.12) with N$_3$O$_2$ donor atoms has also attracted renewed interest thirty years on from its initial synthesis by Nelson.\textsuperscript{[66]}

83
In 1986, a Japanese group revisited this compound and prepared the Fe(II) complex \([\text{Fe}(\text{L})(\text{CN})_2]\cdot\text{H}_2\text{O}\) via the Schiff-base condensation of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine using the Fe(II) as the metal template.\(^{[67]}\) Upon normal cooling and warming, a spin crossover transition was observed with the characteristic temperatures of \(T_{1/2\downarrow} = 207 \text{ K}\) and \(T_{1/2\uparrow} = 222 \text{ K}\) affording a hysteresis loop of 15 K in width. The thermally controlled, reversible high-spin (\(S = 2\)) to low-spin (\(S = 0\)) transition is now well established for this complex. In contrast to these observations, more recent magnetic studies applying a faster cooling method uncovered a two-step transition: from pure LS to an approximately 1:1 ratio of HS:LS mixture centred around 157 K.\(^{[67]}\) This was achieved by suddenly decreasing the temperature from 250 K to 160 K, and the transition was almost complete at around 150 K. Upon rapid warming, this complex went from pure LS state to HS:LS = 1:1 at around 160 K, and this state was retained until the temperature reached 207 K, when the curve is in accordance with what is obtained at the normal cooling rate. These studies show that a two-step transition is obtained that is under thermal control. Since a \(d^6\) electron configuration is precluded for Fe(II) with \(D_{3h}\) symmetry, it was proposed that in the LS form, the Fe(II) might be 6-coordinated with one oxygen atom uncoordinated and in the HS state, the Fe(II) could adopt a 7-coordinated structure.\(^{[68]}\) Unfortunately, no single crystal data was available at this time to prove or disprove this suggestion, as all of the above measurements were carried out on powder samples. This serves to highlight the importance of having single crystal data in order to elucidate the
molecular structure and interactions between neighbouring molecules to fully interpret the magnetic data.

In 2001, the single crystal data for the [Fe(L)(CN)₂]·H₂O complex in the HS state was obtained and characterized by Sato et al. [69]

![Figure 4.13. ORTEP view for complex [Fe(L)(CN)₂]·H₂O at high spin (270K) state.][69]

It is thereby demonstrated that in the HS state, the Fe(II) is in a pentagonal bipyramidal coordination environment where the N₃O₂ macrocycle occupies a pentagonal girdle around the metal ion and the CN⁻ ligands are axially coordinated, functioning as terminal bridging groups. The complete structure remains unsolved for the LS complex since the single crystals crack at lower temperatures. There is, however, data to suggest that the distances between the Fe(II) and the two imine nitrogen atoms and the distances between the Fe(II) and the two oxygen atoms are not identical in the LS complex and that the whole structure is not absolutely symmetric. The magnetic properties of a single crystal of [Fe(L)(CN)₂]·H₂O were investigated. Upon cooling, a $T_{1/2}$ of 159 K was first observed. In the warming mode, $\chi_m T = 3.2$ emu·K mol⁻¹ was observed at 172 K. As a result, a thermal hysteresis of 13 K was determined for a single crystal of this compound. Upon further warming, the $\chi_m T$ value decreased to 1.7 emu·K/mol at 207 K and then
increased to 3.4 emu·K/mol at 225 K, Figure 4.14, which is approximately the same as was observed for the powder form by Nelson et al. 30 years earlier.\textsuperscript{[66]}

Figure 4.14. $\chi_m T$ versus $T$ plots for complex [Fe(L)(CN)$_2$]·H$_2$O. (1): Cooling mode of first cycle. (2): Warming mode of first cycle. (3): Cooling mode of second cycle. (4): Warming mode of second cycle. The $\chi_m T$ versus $T$ plot in the inset was recorded in the warming mode.\textsuperscript{[69]}

During these single crystal measurements, Sato et al. observed a 'frozen-in' high-spin state using a liquid helium temperature cavity inside the SQUID magnetometer to quench the sample rapidly.\textsuperscript{[69]} When the sample was rapidly cooled (over a few seconds), the $\chi_m T$ value of 3.5 emu·K mol$^{-1}$ indicated the presence of a HS state that could be retained for several days and the characteristic HS$\leftrightarrow$LS transition was not observed until the crystal was slowly warmed up to 150 K. This phenomenon is really encouraging since the bistable states of spin crossover usually exist in the temperature range below 80 K. Subsequently, a Hg-Xe lamp ($\lambda = 550$ nm, 1.5 mW/cm$^2$) was applied for a LIESST experiment on the sample and a critical temperature of $T_c = 130$ K for the SCO transition was recorded which is the highest reported to date.\textsuperscript{[69]}

Since the initial discovery of this pentagonal bipyramidal complex by Nelson, a few other complexes of this macrocyclic ligand have reported. Several metal ions have been verified as
effective templates for the synthesis. To-date three mononuclear species have been reported: 

\[
[\text{Fe(III)(L)(CN)}_2\cdot\text{H}_2\text{O}]^{[68,69]} \quad [\text{Mn(II)(L)(NCS)}_2]^{[66]} \quad \text{and} \quad [\text{Mg(II)(L)(H}_2\text{O)}_2]\text{(ClO}_4\text{)}_2.\]^{[70]}

Lanthanide metal ions are also reported to be efficient templates, but no single crystal structural data is available to corroborate these findings.\(^{[71,72]}\) As explained previously, molecular materials with 1-, 2- and 3-D structures are of great interest in the field of molecular magnetism since they can also display a molecular hysteresis.\(^{[73]}\) One effective approach to prepare these compounds is via the self-assembly of two building blocks, one of which possesses terminal ligands capable of acting as linkers between metal ions such as \(\text{CN}^-\), while another has available coordination spots, or terminal groups that can be easily substituted, such as \(\text{Cl}^-\). In order to achieve magnetic properties derived either from the 'communication' between the metal centres or from the isolated molecules themselves, these building blocks are typically transition metal complexes. Following this strategy, the \([\text{Mn(II)(L)Cl}_2]\) unit has been assembled together with hexacyanometallate precursors of stoichiometry \(A_3[M^{\text{III}}(\text{CN})_6] \quad (A^+ = \text{K}^+, \text{NMe}_4^+; M^{\text{III}} = \text{Cr(III)}, \text{Fe(III)}, \text{or K}_4[\text{Fe(II)(CN)}_6], \text{or K}_2[M^{\text{II}}(\text{CN})_4] \quad (M^{\text{II}} = \text{Ni(II)}, \text{Pd(II)}, \text{Pt(II)}).\)\(^{[74]}\) In this way, Decurtins \textit{et al.} have successfully constructed a number of multidimensional complexes that include discrete heterometallic assemblies, heterometallic linear chains and heterometallic 2-D layers.\(^{[74]}\)
Chapter 5 – Results and Discussion for the macrocycle project

The objective of this research project is to prepare two compounds (5.5) and (5.15), Figure 5.1, that can be assembled into a binuclear N₃O₂ macrocyclic compound by applying the template synthetic methodology devised by Nelson in the 1970’s.[66]

\[
\text{Figure 5.1. The molecular structures of the two target building blocks, (5.5) and (5.15).}
\]

Dinuclear spin crossover compounds of iron(II) and cobalt(II) are currently receiving great interest largely because of fundamental questions concerning the synergy between the transition and intramolecular exchange coupling, the latter for instance occurring between \(d^5-d^5\) centres in iron(II)-iron(II) compounds across covalent bridging ligands of various types and geometries.[75] In surveying, the advances made in the past was in terms of intradinuclear bridging ligands, and what remains unclear is the influence of antiferromagnetic exchange across the various bridges on the spin-transition mechanism. The assembly of new dinuclear spin crossover complexes for which there are either ferromagnetic or antiferromagnetic interactions between the two dinuclear centres will shed light in this area and lead to a greater understanding of these interactions and their SCO behaviour. In order to address this, our strategy is to prepare and characterize dinuclear building blocks and exploit their chemistry for the preparation of magnetic materials. We are particularly focusing on targeting spin crossover compounds and studying their magnetic properties so as to gain a better understanding with regard to the structure of the HS-LS
molecules and the effect cooperativity between two metal centres has on the nature of the SCO transitions. Only when these interactions are fully understood and elucidated can we begin to rationally design SCO materials with a more predictable set of properties for device applications.

5.1 The synthesis and characterization of 4-pyridyl-2,6-diacetylpypyridine (5.5).

The first step in the project was to develop a suitable synthetic strategy for the preparation of two new compounds (5.5) and (5.15). During the first part of this project, attention was focused on compound (5.5), which contains an additional pyridine ring that is appended to the 4-position of diacetyl pyridine, a precursor for the preparation of the macrocycle. It was proposed that the pyridine functionality could be used as an additional linker to transition metal ions. The strategy we adopted to prepare the 4-pyridyl-2,6-diacetylpyridine (5.5) involves a Suzuki coupling, Scheme 5.1.

![Scheme 5.1. Synthetic route for the preparation of 4-pyridyl-2,6-diacetylpyridine (5.5).](image)

4-pyridyl-2,6-diacetylpyridine (5.5) was prepared by treatment of the appropriately 4-substituted 2,6-diacetylpyridine, where X= Cl/Br, with 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pyridine using Pd(Ph3)4 as the catalyst. The successful synthesis of compound (5.5) was verified by ¹H-NMR, ¹³C-NMR, IR and mass spectroscopy.
Figure 5.2. 300 MHz $^1$H NMR spectrum of 4-pyridyl-2,6-diacetylpyridine (5.5).

The 300 MHz $^1$H-NMR spectrum of compound (5.5) is shown in Figure 5.2. Since the whole molecule is nicely symmetrical the NMR spectrum is straightforward to interpret. The doublet at 8.93 ppm is assigned to the protons at the C$_8$ and C$_8'$ positions on the successfully substituted 4-pyridyl group. The following singlet at 8.56 ppm is attributed to the C$_4$ and C$_4'$ protons of the dimethylketone pyridine. The last upfield doublet at 8.21 ppm is assigned to the C$_7$ and C$_7'$ protons of the substituted pyridine ring. The singlet at 2.87 ppm is characteristic for the dimethylketone CH$_3$ group and is shifted slightly with respect to the acetyl peaks in the starting material, most likely as a consequence of the electron withdrawing nature of the newly appended
pyridine ring. All of the proton signals have the correct integration ratio to support the structure.

The $^{13}$C-NMR spectrum of compound (5.5) has a peak at 199.08 ppm, which can be assigned to the methyl ketone carbonyl carbon. Peaks at 153.80 and 150.47 ppm are assigned to carbons C$_3$, C$_3'$ and C$_8$, C$_8'$, respectively. Peaks at 132.17 and 132.04 ppm are assigned to carbons C$_5$, C$_5'$ and C$_6$, C$_6'$, respectively. The set of peaks at 128.43 and 122.25 ppm were attributed to C$_7$, C$_7'$ and C$_4$, C$_4'$, respectively. The final peak at 25.72 ppm was assigned to the two methyl groups adjacent to the ketone functionality. The high resolution mass spectrum (EI) for compound (5.5) shows a parent ion at $m/z = 240.0896$ that is in excellent agreement with the calculated mass of 240.0899 for C$_{14}$H$_{12}$N$_2$O$_2$. Furthermore, a fragment ion was observed at $m/z = 212$ corresponding to the loss of one carbonyl group and a second ion at $m/z = 198$ can be attributed to the additional loss of a methyl group. A fragment ion at $m/z = 162$ was also observed corresponding to the loss of the 4-substituted pyridine ring. An intense stretch in the IR spectrum at 1698 cm$^{-1}$ can be attributed to the C=O groups of the dimethyketone functionality.

Compound (5.5) is a new ligand that possesses great potential for the preparation of new coordination compounds. Unfortunately, the yield from the Suzuki coupling reaction was so low (8%) that only small amounts of this compound could be prepared for characterization and scaling up this reaction was problematic. In order to address this problem, we prepared the 4-bromo derivative thinking that the coupling reaction would go a little easier, as bromine is a better leaving group. In this case, the yield was only very slightly improved (11%). We then decided to try the coupling reaction with the ester (5.10) instead of the methyl ketone. The ester can then be converted to the ketone following the procedure outlined in Scheme 5.2.
Scheme 5.2. Synthetic strategy for the preparation of (5.5).

When this reaction was carried out on a small scale in the laboratory, the yield was improved to 33%. Scaling up the synthesis, however, was still problematic and numerous small scale reactions would have needed to be employed in order to generate enough product to proceed any further. Considering these problems we then decided to change our strategy and target the symmetrical compound (5.15) since the preparation of this compound appeared to be more straightforward and less time consuming.

5.2 The preparation and coordination chemistry of a novel N$_3$O$_2$ macrocycle ligand (5.15).

Scheme 5.3. Synthetic route for the preparation of 2,2',6,6'-tetraacetyl-4,4'-bipyridine (5.15).

Although the acid chloride compound (5.14) has been reported before, the tetraacetyl
compound, 2,2',6,6'-tetraacetyl-4,4'-bipyridine (5.15), has not been reported in the chemical literature. The synthetic route for the preparation of the macrocycle is outlined in Scheme 5.3.

The known tetraacid (5.13) was converted to tetrachloroformyl-4,4'-bipyridine (5.14) by reaction with thionyl chloride in DMF. Reaction of (5.14) with 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum’s acid) followed by hydrolysis and decarboxylation afforded 2,2',6,6'-tetraacetyl-4,4'-bipyridine (5.15) following the procedure of Abdelaziz et al, Schemes 5.3 and 5.4.[77]

![Scheme 5.4](image1.png)

**Scheme 5.4.** General synthetic strategy for transforming an acid chloride into a ketone.

![Scheme 5.5](image2.png)

**Scheme 5.5.** The proposed reaction mechanism for transforming an acid chloride into a ketone.

The proposed mechanism for this reaction is shown in Scheme 5.5. Compound (5.18) was obtained as the intermediate in the first step of this reaction which was in turn hydrolysed by the addition of 2N HCl and further decarboxylated by refluxing in a (1:1) acetic acid/water mixture for 16h. The product was isolated as a pale yellow solid in 32% yield after a recrystallization from acetone. The structure of this compound was characterized by $^1$H- and $^{13}$C-NMR, IR and
Due to the high-symmetry of the molecule, the 300 MHz $^1$H-NMR is very simple and just shows two signals, the singlet at 8.56 ppm for the pyridyl protons at C$_3$, C$_3'$ and C$_5$, C$_5'$ and the peak at 2.85 ppm for protons of the two methyl groups on the C$_8$ carbons.

**Figure 5.3.** 300 MHz $^1$H-NMR spectrum of 2,2',6,6'-tetraacetyl-4,4'-bipyridine (5.15).
Figure 5.4. 600 MHz $^{13}$C-NMR spectrum of 2,2',6,6'-tetraacetyl-4,4'-bipyridine (5.15).

The 600 MHz $^{13}$C-NMR is shown in Figure 5.4 and has a peak at 198.81 ppm assigned to carbonyl group. The peak at 153.98 ppm can be assigned to the C$_2$ and C$_6$ carbons. The next peak at 146.68 ppm is attributed to the C$_4$ carbon. The remaining peak at 122.27 ppm is assigned to the C$_3$ and C$_5$ carbons. A peak corresponding to the two methyl groups is observed at 25.72 ppm. The IR spectrum shows the intense carbonyl stretch for the two methyl ketones at 1704 cm$^{-1}$. The EI mass spectrum showed a peak at m/z = 324 consistent with the molecular weight of this compound. Peaks at m/z = 309 and 282 can be assigned due to the loss of one methyl group followed by a carbonyl group. The high resolution EI mass spectrum gave a peak at m/z = 324.1110 which fits perfectly with the calculated value of 324.1110 for C$_{18}$H$_{16}$N$_2$O$_4$. 
Scheme 5.6. Synthetic route for the dinuclear macrocycle {[Mn(N$_3$O$_2$)]ClH$_2$O$_2$Cl}$_2$$\cdot$2Cl$\cdot$10.5H$_2$O (5.16).

The dimeric macrocycle {[Mn(N$_3$O$_2$)]ClH$_2$O$_2$Cl}$_2$$\cdot$2Cl$\cdot$10.5H$_2$O (5.16) was prepared by a metal templated Schiff-base condensation reaction. Treatment of the 2,2',6,6'-tetraacetyl-4,4'-bipyridine (5.15) with two equivalents of 3,6-dioxaoctane-1,8-diamine in the presence of two equivalents of MnCl$_2$$\cdot$4H$_2$O (Scheme 5.6) afforded compound (5.16) as a brown solid. Single crystals of this compound were grown from a H-tube via slow evaporation of a MeOH/H$_2$O solution. The molecular structure of this compound was determined by Prof. H. S. Evans by X-ray diffraction and consists of two covalently tethered N$_3$O$_2$ pentadentate macrocycles chelated to Mn(II) metal ions, together with four chloride anions (two coordinated and two uncoordinated, one of which is disordered over two sites) and two coordinated water molecules. The molecular structure together with the atomic numbering scheme is shown in Figure 5.5. Both Mn(II) ions are in a pentagonal bipyramidal environment, with the macrocycles occupying the equatorial plane and a bound water molecule and chloride ion in the axial positions. The dihedral angle between the two planes of the pyridine rings is 41°. The two macrocyclic rings are nearly planar. The maximum deviations of contributing atoms from the MnN$_3$O$_2$ least squares plane are 0.1 Å N(3) and 0.1 Å N(6). The distance between the two Mn(II) ions in the molecule is 11.2 Å.
<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
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<tr>
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<td>Mn(2)-N(4)</td>
<td>2.124(5)</td>
</tr>
<tr>
<td>Mn(1)-N(2)</td>
<td>2.182(5)</td>
<td>Mn(2)-N(5)</td>
<td>2.194(5)</td>
</tr>
<tr>
<td>Mn(1)-N(3)</td>
<td>2.184(5)</td>
<td>Mn(2)-N(6)</td>
<td>2.180(5)</td>
</tr>
<tr>
<td>Mn(1)-O(1)</td>
<td>2.242(4)</td>
<td>Mn(2)-O(3)</td>
<td>2.273(4)</td>
</tr>
<tr>
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</tr>
<tr>
<td>Mn(1)-Cl(1)</td>
<td>2.474(2)</td>
<td>Mn(2)-Cl(2)</td>
<td>2.465(2)</td>
</tr>
<tr>
<td>N(3)-Mn(1)-N(3)</td>
<td>72.52(18)</td>
<td>N(4)-Mn(2)-N(6)</td>
<td>72.95(17)</td>
</tr>
<tr>
<td>N(3)-Mn(1)-O(2)</td>
<td>72.14(17)</td>
<td>N(6)-Mn(2)-O(4)</td>
<td>71.77(15)</td>
</tr>
<tr>
<td>O(2)-Mn(1)-O(1)</td>
<td>71.07(15)</td>
<td>O(4)-Mn(2)-O(3)</td>
<td>70.95(14)</td>
</tr>
<tr>
<td>O(1W)-Mn(1)-Cl(1)</td>
<td>178.99(17)</td>
<td>O(2W)-Mn(2)-Cl(2)</td>
<td>174.05(15)</td>
</tr>
</tbody>
</table>

Table 5.1. Selected bond lengths [Å] and bond angles [°] for the complex (5.16).

Figure 5.5. ORTEP[45] representation of the molecular structure of compound (5.16) (ellipsoids at 50% probability). The Cl⁻ counter ions are omitted for clarity.

The packing diagram reveals that the molecules are stacked in a slightly offset arrangement down the a-axis (Figure 5.6).
The shortest distance between neighbouring pyridine rings is 5.46 Å. Intermolecular contacts between Cl\(^-\) anions and neighbouring hydrogen atoms are in the range 2.87 – 3.11 Å and are shown as dashed lines. Compound (5.16) was magnetically characterized by Dr. A. Alberola who measured the temperature dependence of the magnetic susceptibility. A typical \(1/\chi \text{ vs } T\) for this compound is shown in Figure 5.7. The susceptibility of the sample rises monotonically as the temperature is lowered following a typical Curie-Weiss behaviour. The presence of two Mn(II) per molecule is confirmed by a Curie constant of 8.741 emu-K/mol (as expected for \(S = 5/2\) and \(g = 2\)) and a value for the Weiss constant of \(\theta = -2.89\) K, Figure 5.7.
Figure 5.7. $1/\chi$ vs T plot including a fit to the Curie-Weiss law for compound (5.16).

A best fit described by the solid line done was performed by Dr Alberola and is shown as a solid line in Figure 5.8. The $\chi T$ product is fairly stable between 270 and 45 K giving a value of 8.58 emu·K/mol and decreases below 40 K to reach a value of 1.9 at 2·K. This decrease can arise from either inter- or intra-dimer coupling. A single parameter curve fit to the expression for $\chi$ in compound (5.16) yielded $J_{ex} = -0.51$ K with $g = 2$, which is in very good agreement with the estimate from the mean-field theory (Figure 4) and is suggestive that the intradimer coupling is dominant. However, the weak nature of these interactions makes it impossible to completely rule out that inter-dimer interactions could also play a role in the magnetic properties.
To summarize, we have prepared two organic ligands as precursors to new dinuclear building blocks. A novel dimeric N\textsubscript{3}O\textsubscript{2} macrocycle containing Mn(II) metal ions has been assembled and magnetically characterized. We have extended the strategy for the preparation of the cobalt macrocycle which has an identical mass spectrum to that of the Mn(II). Attempts to crystallize the Co(II) macrocycle compound for further characterization is currently underway in the group. Magnetic measurements on the Mn(II) macrocycle reveal that there is communication between the two metal centres in the form of antiferromagnetic exchange interactions. In this respect, this should be an ideal compound for studying the effects antiferromagnetic exchange interactions have on SCO transitions in the Fe(II) analogues. We initially chose to work with Mn(II) and Co(II) metal ions since their coordination compounds are stable with respect to air and moisture. Fe(II) compounds have to be treated a little more carefully as they can readily be oxidized by traces of oxygen. A collaboration is currently underway with Dr. Antonio Alberola at the University of Cambridge who has recently prepared the Fe(II) analogue and attempts to crystallize the

Figure 5.8. $\chi T$ vs $T$ plot and fit.
thiocyanate derivate for magnetic studies are currently underway and will be reported in due course. Attempts to prepare multidimensional magnetic materials by crystallizing the cobalt(II) and manganese(II) macrocycles together with an appropriate Fe(CN)$_6$ salt afforded precipitates, but no single crystals have been obtained to date.
Chapter 6 – Experimental for the macrocycle project

General information:

See Chapter 3 for general information.

6.1 Experimental

6.1.1 Synthesis of dimethyl 4-chloropyridine-2,6-dicarboxylate\textsuperscript{[80]}

\[
\begin{array}{c}
\text{HOO}_{\text{H}} \text{C} \text{O} \text{N} \text{C} \text{O} \text{O}_{\text{H}} \text{C} \text{O} \text{H} \text{C} \text{O} \text{O} \\
\text{Cl} \text{N} \text{C} \text{O} \text{O}_{\text{H}} \text{C} \text{O} \text{H} \text{C} \text{O} \text{O} \\
\end{array}
\]

4-hydroxypyridine-2,6-dicarboxylic acid (2.61 g, 13.0 mmol) was added to a 3-necked flask under argon. Phenylphosphonic dichloride (7.20 mL, 52.0 mmol) was added slowly using a syringe with continuous stirring at room temperature, and the mixture was heated to 120 °C for 2h. The reaction system was then cooled and distilled methanol (40 mL) was added slowly to produce a large amount of white precipitate. The resulting mixture was stirred vigorously for 1h and the solvent was removed under vacuum. The residue was dissolved in chloroform (100 mL) and then the solution was washed twice with water, half-saturated sodium bicarbonate solution and the organic phase was dried with anhydrous MgSO\textsubscript{4}. Removal of solvent under vacuum afforded a yellow solid, which was re-crystallized from distilled methanol to afford (5.1) as colorless needles. Yield (1.78 g, 60%).

\(^1\text{H-NMR (CDCl}_3, \text{ppm)}: \delta = 8.30 (s, 2H, 2 \text{ py-H}), 4.04 (s, 6H, 2 \text{ CH}_3).

\(^{13}\text{C-NMR (CDCl}_3, \text{ppm)}: \delta = 164.65 (C=O), 149.91, 147.34, 128.71, 54.05.
6.1.2 Synthesis of 4-chloropyridine-2,6-dicarboxylic acid\textsuperscript{[80]}

\begin{align*}
\text{Cl} & \text{H}_2\text{COOC} & \text{Cl} & \text{H}_2\text{COOC} \\
\text{N} & \text{COOCH}_3 & \text{N} & \text{COOCH}_3 \\
(5.1) & & (5.2)
\end{align*}

\[ \begin{array}{c}
1. \text{NaOH} \\
2. 25\% \text{HCl}
\end{array} \]

Dimethyl 4-chloropyridine-2,6-dicarboxylate (1.78 g, 7.76 mmol) was refluxed in an aqueous solution of 5 M NaOH (35 mL) for 1h. After cooling, the solution was acidified to pH = 2 with 25\% aqueous HCl solution. The white precipitate was then collected by filtration and dried under vacuum to obtain the product as a white powder. Yield (1.19 g, 76\%).

$^1$H-NMR (DMSO, ppm): \( \delta = 8.17 \text{ (s, 2H)} \).

$^{13}$C-NMR (DMSO, ppm): \( \delta = 164.93 \text{ (C=O)}, 150.38, 145.69, 127.63 \).

6.1.3 Synthesis of 4-chloropyridine-2,6-dicarboxylic dichloride\textsuperscript{[81]}

\begin{align*}
\text{Cl} & \text{Cl} & \text{HOOC} & \text{COOH} \\
\text{N} & \text{COOH} & \text{N} & \text{COOH} \\
(5.2) & & (5.3)
\end{align*}

\[ \text{DMF/SOCl}_2 \]

A mixture of distilled DMF (5 mL) and distilled SOCl\textsubscript{2} (20 mL, excess) was stirred vigorously under argon for 5 min. The solution was then added to 4-chloropyridine-2,6-dicarboxylic acid (2.01 g, 10.0 mmol) in a 3-necked flask under argon with continuous stirring. The resulting yellow solution was refluxed for 2h, and then cooled under argon. The solvent and remaining SOCl\textsubscript{2} were removed under high vacuum. The resulting light yellow solid was then dissolved in dry toluene and the solvent was evaporated under high vacuum. This treatment was repeated twice to remove the last trace of SOCl\textsubscript{2} to afford the product as a pale yellow solid. Yield (1.60 g, 67\%).

$^1$H-NMR (CDCl\textsubscript{3}, ppm): \( \delta = 8.23 \text{ (s, 2H)} \).
$^{13}$C-NMR (CDCl$_3$, ppm): $\delta = 169.00$ (C=O), 150.47, 148.32, 129.33.

6.1.4 Synthesis of 4-chloro-2,6-diacylpyridine$^{[76]}$

$$
\begin{array}{c}
\text{Cl} \\
\text{CO} \\
\text{N} \\
\text{Cl}
\end{array}
\quad + 
\begin{array}{c}
\text{CO}_2
\end{array}
\quad \xrightarrow{1. \text{Pyridine}}
\begin{array}{c}
\text{Cl} \\
\text{CO}
\end{array}
$$

To a solution of 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid, 4.61 g, 40.4 mmol) in distilled CH$_2$Cl$_2$ (35 mL) and distilled pyridine (8.92 mL, 111 mmol) was added 4-chloropyridine-2,6-dicarboxylic dichloride (4.82 g, 20.2 mmol) in one portion. A dark brown solution formed immediately and that was stirred at 0 °C for one hour and at room temperature for another hour. The resulting mixture was diluted with distilled CH$_2$Cl$_2$ (50 mL) and then poured into 2 N HCl aqueous solution containing crushed ice (50 mL). The organic layer was separated and the aqueous solution was extracted several times with CH$_2$Cl$_2$. The organic layer was collected, washed with 2 N HCl (2 x 50 mL) and dried with anhydrous Na$_2$SO$_4$. The solvent was removed to afford 5.90 g of an intermediated as a dark brown solid, which was then refluxed in a 1:1 acetic acid/H$_2$O solution (500 mL) at 115 °C for 16h. The reaction mixture was diluted with H$_2$O, and then extracted into CH$_2$Cl$_2$ (6 x 50 mL). The combined organic layers were washed with an aqueous solution of 5% NaHCO$_3$ and then dried with Na$_2$SO$_4$. Removal of the solvent under vacuum afforded the product as a yellow solid. Yield (1.83 g, 46%).

$^1$H-NMR (CDCl$_3$, ppm): $\delta = 8.18$ (s, 2H, py-H), 2.78 (s, 6H, 2 CH$_3$).

$^{13}$C-NMR (CDCl$_3$, ppm): $\delta = 198.18$ (C=O), 153.87, 146.93, 124.97, 25.78.
6.1.5 Synthesis of 4-pyridyl-2,6-diacetylpyridine (method 1)[77]

To a 3-necked flask under argon was added 4-chloro-2,6-diacetylpyridine (0.20 g, 1.0 mmol) and distilled toluene (10 mL). 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pyridine (0.21 g, 1.0 mmol) and Cs$_2$CO$_3$ (0.42 g, 1.3 mmol) were then added to the yellow solution with continuous stirring. Pd(PPh$_3$)$_4$ (0.06 g, 0.05 mmol) was added to the reaction mixture and the solution was refluxed at 100 °C for 24h and the reaction was monitored by TLC (CH$_2$Cl$_2$:hexane=1:3). The solvent was removed under high vacuum, and then the residue was dissolved in chloroform (200 mL). The solution was washed with water, dried with anhydrous Na$_2$SO$_4$ and filtered through celite to remove any other catalyst. The chloroform was removed, and the residue was dissolved in diethyl ether. The resulting solution was filtered and the solvent was removed. Sonication with hexane was applied twice to remove any traces of catalyst. The solid was filtered off to afford the product as a light yellow solid. Yield (0.02 g, 8%).

$^1$H-NMR (CDCl$_3$, ppm): $\delta = 8.93$ (d, 2H, $J = 6$ Hz), 8.56 (s, 2H), 8.21(d, 2H, $J = 6.3$ Hz), 2.87 (s, 6H, CH$_3$).

$^{13}$C-NMR (CDCl$_3$, ppm): $\delta = 199.08$ (C=O), 153.80 (C$_3$), 150.47 (C$_8$), 132.17 (C$_5$), 132.04 (C$_6$), 128.43 (C$_7$), 122.25 (C$_4$), 25.72 (CH$_3$).

IR (KBr, cm$^{-1}$): 3498, 2982, 2364, 1698 (C=O) s, 1623, 1594, 1536, 1424, 1365 s, 1238, 1202, 1155 s, 1031 s, 959, 876, 828, 803, 725, 648, 600, 563.
Mass spectrum (EI): \( C_{14}H_{12}N_{2}O_{2} \), calcd. m/z = 240.0899, found m/z = 240.0896.

m.p.: 194-197 °C.

6.1.6 Synthesis of dimethyl 4-bromopyridine-2,6-dicarboxylate\[^{78}\]

\[
\begin{array}{c}
\text{OH} \\
\text{HOOC} \\
\text{N} \\
\text{COOH}
\end{array} \xrightarrow{1. \text{PBr}_5} \begin{array}{c}
\text{Br} \\
\text{Br} \\
\text{H}_2\text{COOC} \\
\text{COOCH}_3
\end{array}
\]

A mixture of chelidamic acid (2.00 g, 10.0 mmol) and phosphorus pentabromide (17.0 g, 39.5 mmol) in \( \text{CCl}_4 \) (30 mL) was heated at 80 °C for 12h. After cooling to room temperature, distilled methanol (10 mL) was added dropwise with vigorous stirring until the reaction mixture reached room temperature again. The liquid was mostly removed under vacuum, and the residue was treated with ice water (100 mL), and stirred for 1h. The resulting precipitate was collected by filtration to obtain the product as a white powder. Yield (2.28 g, 83%).

\[ ^1\text{H NMR (CDCl}_3, \text{ppm):} \quad \delta = 8.46 \text{ (s, 2H, py-H), 4.03 (s, 6H, CH}_3 \text{).} \]

\[ ^{13}\text{C NMR (CDCl}_3, \text{ppm):} \quad \delta = 164.02 \text{ (C=O), 149.11, 135.16, 131.35, 25.34.} \]

m.p.: 167-168 °C.

6.1.7 Synthesis of 4-bromopyridine-2,6-dicarboxylic acid\[^{80}\]

Dimethyl 4-bromopyridine-2,6-dicarboxylate (2.34 g, 8.65mmol) was refluxed in 5 M \( \text{NaOH} \) solution (40 mL) for 1h. The solution was cooled, and then was acidified to pH = 2 with an aqueous solution of 25% HCl. The white precipitate was collected by filtration and dried under vacuum to offord a white powder. Yield (1.94 g, 91%).

\[ ^1\text{H NMR (DMSO, ppm):} \quad \delta = 8.35 \text{ (s, 2H).} \]
\[^{13}\text{C} \text{NMR (DMSO, ppm):} \quad \delta = 164.58, 149.81, 134.29, 130.25.\]

6.1.8 Synthesis of 4-bromopyridine-2,6-dicarboxylic dichloride\[^{[81]}\]

![Chemical structure](image)

A mixture of distilled DMF (5 mL) and distilled SOCl\(_2\) (20 mL, excess) was stirred vigorously under argon for 5 min. The solution was then added to 4-bromopyridine-2,6-dicarboxylic acid (1.94 g, 7.89 mmol) in a 3-necked flask under argon with continuous stirring. The resulting yellow solution was refluxed for 2h, and then cooled under argon. The solvent and remaining SOCl\(_2\) were removed under high vacuum. The resulting light yellow solid was then dissolved in dry toluene and the solvent was evaporated under high vacuum. This treatment was repeated twice to remove any last traces of SOCl\(_2\) to afford the product as a pale yellow solid. Yield (1.94 g, 87%).

\[^{1}\text{H} \text{NMR (CDCl}_3\text{, ppm):} \quad \delta = 8.31 \text{ (s, 2H).}\]

\[^{13}\text{C} \text{NMR (CDCl}_3\text{, ppm):} \quad \delta = 168.60, 150.12, 147.95, 132.42.\]

6.1.9 Synthesis of 4-bromo-2,6-diacetylpypyridine\[^{[76]}\]

To a solution of 2,2'-dimethyl-1,3-dioxane-4,6-dione (Meldrum’s acid, 1.64 g, 11.4 mmol) in distilled CH\(_2\)Cl\(_2\) (12 mL) and distilled pyridine (2.90 mL, 35.9 mmol) was added 4-bromopyridine-2,6-dicarboxylic dichloride (4.82 g, 20.2 mmol) in one portion. A dark brown solution formed immediately that was first stirred at 0 °C for one hour and then at room
temperature for another hour. The resulting mixture was diluted with distilled CH$_2$Cl$_2$ (30 mL) and then poured into an aqueous 2 N HCl solution containing crushed ice (24 mL). The organic layer was separated and the aqueous solution was extracted several times with CH$_2$Cl$_2$. The organic layer was collected, washed with 2 N HCl (2 x 20 mL) and dried with anhydrous Na$_2$SO$_4$. The solvent was removed to afford a dark brown solid, which was then refluxed in a 1:1 acetic acid/H$_2$O solution (100 mL) at 115 °C for 16h. The reaction mixture was diluted with H$_2$O, and then extracted with CH$_2$Cl$_2$ several times. The combined organic layers were washed with an aqueous 5% NaHCO$_3$ solution and dried with Na$_2$SO$_4$. Removal of the solvent under vacuum afforded the product as a yellow solid. Yield (0.91 g, 55%).

$^1$H NMR (CDCl$_3$, ppm): $\delta = 8.18$ (s, 2H, py-H), 2.78 (s, 6H, CH$_3$).

$^{13}$C NMR (CDCl$_3$, ppm): $\delta = 198.16, 153.88, 146.93, 124.97, 25.64$.

Mass spectrum (EI): C$_9$H$_8$NO$_2$Br, m/z = 241/243.

### 6.1.10 Synthesis of 4-pyridyl-2,6-diacetylpyridine (method 2)$^{[77]}$

To a 3-necked flask under argon was added 4-bromo-2,6-diacetylpyridine (0.204 g, 1.00 mmol) and distilled toluene (10 mL). 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pyridine (0.21 g, 1.0 mmol) and Cs$_2$CO$_3$ (0.368 g, 1.13 mmol) were then added to the yellow solution with continuous stirring. Pd(PPh$_3$)$_4$ (0.0346 g, 0.0315 mmol) was added to the reaction mixture and the solution was refluxed at 100 °C for 24h and the reaction was monitored by TLC (CH$_2$Cl$_2$:hexane = 1:3). The solvent was
removed under high vacuum, and then the residue was dissolved in chloroform (200 mL). The solution was washed with water, dried with anhydrous Na₂SO₄ and filtered through celite to remove the catalyst. The chloroform was removed under vacuum, and the residue was dissolved in diethyl ether. The resulting solution was filtered and the solvent was removed. Sonication in hexane was repeated twice to remove any last traces of catalyst. The solid was filtered off to afford the product as a pale yellow solid. Yield (0.0264 g, 11%).

\[ \text{\textsuperscript{1}H-NMR (CDCl₃, ppm):} \delta = 8.93 \text{ (d, 2H, } J = 6 \text{ Hz), 8.56 (s, 2H), 8.21 (d, 2H, } J = 6.3 \text{ Hz),} \]
\[ 2.87 \text{ (s, 6H, CH}_3 \text{).} \]

\[ \text{\textsuperscript{13}C-NMR (CDCl₃, ppm):} \delta = 199.08 \text{ (C=O), 153.80, 150.47, 132.17, 132.04, 128.43,} \]
\[ 122.25, 25.72. \]

\[ \text{IR (KBr, cm}^{-1}):\text{ 3498, 2982, 2364, 1698 (C=O) s, 1623, 1594, 1536, 1424,} \]
\[ 1365 \text{ s, 1238, 1202, 1155 s, 1031 s, 959, 876, 828, 803, 725, 648,} \]
\[ 600, 563. \]

\[ \text{Mass spectrum (EI):} \text{ C}_{14}\text{H}_{12}\text{N}_{2}\text{O}_{2}, \text{ calcd. m/z = 240.0899, found m/z = 240.0896 m/z.} \]

\[ \text{m.p.:} 194-197 ^\circ \text{C.} \]

6.1.11 Synthesis of dimethyl 4-pyridyl-2,6-dicarboxylate pyridine (method 1)\[77\]

To a 3-necked flask under argon was added dimethyl 4-bromopyridine-2,6-dicarboxylate (0.55 g, 2.0 mmol) and distilled DMF (20 mL). 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-y1)-pyridine (0.41 g, 2.0 mmol) and Cs₂CO₃ (0.82 g,
2.5 mmol) were then added to the yellow solution with continuous stirring. Pd(PPh₃)₄ (0.0233 g, 0.0105 mmol) was added and the reaction mixture was refluxed for 22h and the reaction was monitored by TLC (CH₂Cl₂:hexane = 1:3). The solvent was removed under vacuum. The residue was dissolved in chloroform and the solution was then filtered through. The resulting solution was washed with water and dried with anhydrous Na₂SO₄. Removal of the solvent under vacuum afforded the crude product as a pale yellow solid, which was sonicated in hexane to remove any last traces of catalyst. The solid was collected by filtration to afford the product as a yellow solid. Yield (0.10 g, 18%).

¹H-NMR (CDCl₃, ppm): \( \delta = 8.90 \text{ (d, } 2\text{H, } J = 3.9 \text{ Hz), 8.61 } (\text{s, } 2\text{H), 7.95 } (\text{d, } 2\text{H, } J = 5.7 \text{ Hz), 4.09 } (\text{s, } 6\text{H).} \)

¹³C-NMR (CDCl₃, ppm): \( \delta = 164.77 \text{ (C=O), 149.71, 147.11, 125.68, 53.86.} \)

Mass spectrum(m/z): C₁₄H₁₂N₂O₄, m/z = 272.

6.1.12 Synthesis of dimethyl 4-pyridyl-2,6-dicarboxylate pyridine (method 2) [77]

To a 3-necked flask under argon was added dimethyl 4-chloropyridine-2,6-dicarboxylate (0.46 g, 2.0 mmol) and distilled DMF (15 mL). 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pyridine (0.41 g, 2.0 mmol) and Cs₂CO₃ (0.82 g, 2.5 mmol) and Pd(PPh₃)₄ (0.035 g, 0.015 mmol) were added subsequently to the yellow solution under continuous stirring. The reaction mixture was refluxed for 22h and monitored by TLC (CH₂Cl₂:hexane = 1:3). The solvent was removed under vacuum. The residue was dissolved in
chloroform and the solution was then filtered through celite. The resulting solution was washed with water and dried with anhydrous Na$_2$SO$_4$. Removal of the solvent under vacuum afforded a pale yellow solid as the crude product, which was sonicated in hexane to remove any last traces of catalyst. The solid was collected by filtration to afford the product as a yellow solid. Yield (0.18 g, 33%).

$^1$H-NMR (CDCl$_3$, ppm):  $\delta = 8.90$ (d, 2H, $J = 3.9$ Hz), 8.61 (s, 2H), 7.95 (d, 2H, $J = 5.7$ Hz), 4.09 (s, 6H).

$^{13}$C-NMR (CDCl$_3$, ppm):  $\delta = 164.77$, 149.71, 147.11, 125.68, 53.86.

Mass spectrum:  C$_{14}$H$_{12}$N$_2$O$_4$, m/z = 272.

6.1.13 Synthesis of 4-pyridyl-dicarboxylic acid pyridine$^{[80]}$

![Chemical structure diagram]

Dimethyl 4-pyridyl-2,6-dicarboxylate pyridine (0.23 g, 0.85 mmol) was refluxed in a 5 M aqueous NaOH solution (20 mL) for 1h. After cooling, the solution was acidified to pH = 2 with 25% aqueous HCl solution. The white precipitate was filtered off and dried under vacuum to afford the product as a white powder. Yield (0.19 g, 91%).

$^1$H-NMR (DMSO, ppm):  $\delta = 8.76$ (d, 2H, $J = 6.3$ Hz), 8.55 (s, 2H), 7.95 (d, 2H, $J = 3.3$ Hz)

Mass spectrum:  C$_{12}$H$_8$N$_2$O$_4$, m/z = 244.

IR (KBr, cm$^{-1}$):  3460 (OH), 3246, 3124, 2982, 2783, 2417, 2352, 2074, 2009, 1727 (C=O), 1613, 1513, 1382, 1236, 1091, 1018, 899, 809.
6.1.14 Synthesis of 2,2',6,6'-tetramethyl-4,4'-bipyridine

\[
\begin{array}{c}
\text{2} \\
\text{Na/THF} \\
\text{2. SO}_2 \\
\end{array} \\
\rightarrow \\
\begin{array}{c}
\text{2,2',6,6'-tetramethyl-4,4'-bipyridine} \\
(5.12)
\end{array}
\]

Dry hexane (100 mL) was added to Na (30%-35% in paraffin wax) (13.87 g, 196.0 mmol) under argon, and the mixture was sonicated for 20 min. The solvent was then removed with a syringe and the operation was repeated twice. Distilled THF (80 mL) and 2,6-lutidine (10 mL, 86 mmol) were added to the reaction mixture, that was stirred vigorously under argon overnight to afford a light yellow solution. SO₂ gas was then passed over the reaction mixture slowly over a period of 5h. The reaction mixture was then quenched with ethanol (100 mL), and the pH of the solution was adjusted to approximately 8 with an aqueous solution of 12 M NaOH. The resulting mixture was extracted with CH₂Cl₂ (6 x 50 mL), and the organic layers were combined. Removal of the solvent under vacuum afforded the crude product as a pale yellow solid, which was re-crystallized from water to afford the product as a white solid. Yield (15.54 g, 85%).

\(^1\)H-NMR (CDCl₃, ppm): \(\delta = 7.19\) (s, 4H, py-H), 2.62 (s, 12H, CH₃).

\(^{13}\)C-NMR (CDCl₃, ppm): \(\delta = 158.56, 146.84, 118.19, 24.56\).

6.1.15 Synthesis of 2,2',6,6'-tetracarboxylic-4,4'-bipyridine

\[
\begin{array}{c}
\text{2,2',6,6'-tetramethyl-4,4'-bipyridine} \\
(5.12)
\end{array} \\
\rightarrow \\
\begin{array}{c}
\text{2,2',6,6'-tetracarboxylic-4,4'-bipyridine} \\
(5.13)
\end{array}
\]

2,2',6,6'-tetramethyl-4,4'-bipyridine (1.95 g, 9.20 mmol) was dissolved in concentrated H₂SO₄ solution (M = 18 mol/L, 32 mL) in ice bath, and then CrO₃ (11.02 g, 11.02 mmol) was cautiously added in portions over 3h with continuous stirring. The resulting reaction mixture was slowly heated to 75 °C and then kept at that temperature for 2h. The resulting dark green sticky
solution was poured into ice water (200 mL) with continuous stirring. The resulting white precipitate was collected by filtration and dried under vacuum to afford the product as a white solid. Yield (2.05 g, 67%).

\[ ^1H-\text{NMR (DMSO, ppm)}: \delta = 13.62 \text{ (s, 4H, COOH)}, 8.61 \text{ (s, 4H, py-H)}. \]

\[ ^{13}C-\text{NMR (DMSO, ppm)}: \delta = 165.81, 150.06, 146.71, 125.82. \]

6.1.16 Synthesis of 2,2',6,6'-tetrachloroformyl-4,4'-bipyridine \[^{82}\]

To a solution of distilled SOCl\(_2\) (12 mL) was added 2,2',6,6'-tetracarboxylic-4,4'-bipyridine (2.80 g, 8.43 mmol) and two drops of distilled DMF under argon. The resulting reaction mixture was refluxed for 4h. The solvent was removed under high vacuum to afford the product as a pale green solid. Yield (3.03 g, 89%).

\[ ^1H-\text{NMR (CDCl}_3, \text{ppm)}: \delta = 8.62 \text{ (s, 4H, py-H)}. \]

\[ ^{13}C-\text{NMR (CDCl}_3, \text{ppm)}: \delta = 169.23, 150.81, 146.78, 126.16. \]

6.1.17 Synthesis of 2,2',6,6'-tetraacetyl-4,4'-bipyridine \[^{77}\]

To a solution of 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum’s acid, 4.45 g, 30.9 mmol) in distilled CH\(_2\)Cl\(_2\) (25 mL) and distilled pyridine (6.20 mL, 76.9 mmol) was added 2,2',6,6'-tetrachloroformyl-4,4'-bipyridine (3.03 g, 7.46 mmol) in one portion. A dark brown
solution formed immediately and that was stirred at 0 °C for one hour and at room temperature for another hour, respectively. The resulting reaction mixture was diluted with distilled CH₂Cl₂ (40 mL), and then poured into 2 N HCl aqueous solution containing crushed ice (50 mL). The organic layer was separated and the aqueous solution was extracted with CH₂Cl₂ (6 x 50 mL). The organic layers were combined, washed with 2 N HCl (2 x 50 mL) and dried with anhydrous Na₂SO₄. The solvent was removed to afford the intermediate as a dark brown solid (5.05 g), which was then refluxed in acetic acid: H₂O = 1:1 solution (500 mL) at 115 °C for 16h. The resulting reaction mixture was then diluted with H₂O (200 mL), and extracted in CH₂Cl₂ (6 x 50 mL). The combined organic layers were washed with an aqueous 5% NaHCO₃ solution and dried with anhydrous Na₂SO₄. Removal of solvent under vacuum afforded the product as a yellow solid. Yield (0.77 g, 32%).

¹H-NMR (CDCl₃, ppm):  δ = 8.56 (s, 4H, py-H), 2.85 (s, 12H, CH₃).

¹³C-NMR (CDCl₃, ppm):  δ = 198.77, 154.00, 146.71, 122.27, 25.69.

IR (KBr, cm⁻¹):  3426, 2920, 1704 s (C=O), 1637, 1592, 1410, 1364 s, 1303, 1236, 1131, 1100, 960, 895, 797, 599.

MS (El, m/z):  C₁₈H₁₆N₂O₄ calcd. m/z = 324.1110, found m/z = 324.1110.

m.p.:  266-268 °C.

**6.1.18 Synthesis of {[Mn(N₃O₂)]ClH₂O}₂·2Cl·10.5H₂O**[^83]

2,2',6,6'-tetraacetyl-4,4'-bipyridine (0.162 g, 0.504 mmol) was added to a solution of
MnCl$_2$·4H$_2$O (0.148 g, 1.00 mmol) in MeOH (10 mL), and the resulting solution was heated to approximately 50 °C with continuous stirring. A solution of 3,6-dioxaoctano-1,8-diamine (0.198 g, 1.00 mmol) in MeOH (5 mL) was then added. The reaction mixture was then refluxed for 6h, and then concentrated to half of the volume under vacuum. A solid was precipitated via the addition of diethyl ether. The brown solid was collected by filtration and washed with diethyl ether. Yield (0.16 g, 42%). Small orange plates suitable for X-ray crystallography were grown via slow evaporation of a methanol/water solution at room temperature.

IR (KBr, cm$^{-1}$): 3424 br (OH), 2983, 2929, 2366, 1646 (C=N) s, 1597 s, 1421, 1376, 1248, 1215, 1106-1073 s (C-O-C), 877, 660 (py).


**Susceptibility Measurements:** Variable-temperature magnetic susceptibility data were collected on a powdered sample of $\{[\text{Mn(N}_3\text{O}_2)]\text{ClH}_2\text{O}\}_2\cdot2\text{Cl} \cdot 10.5\text{H}_2\text{O}$ with the use of a Quantum Design SQUID magnetometer in an applied field of 5000 G between 2 and 270 K. Data were corrected for both sample diamagnetism (Pascal's constants) and the sample holder.

**X-ray Crystallography:** Intensity data were collected at 173 K on a Stoe Mark II-Image Plate Diffraction System using Mo K$_\alpha$ graphite monochomated radiation. Image plate distance 100 mm, $\omega$ rotation scans 0-180° $\phi$ 0° and 0 - 50° at 90°, step = 1.0°, with an exposure time of 4 mins per image, 2 range 2.29 - 59.53°, $d_{\min}$ - $d_{\max}$ = 17.779-0.716 Å. A semi-empirical absorption correction using the program PLATON/MULABS$^{[84]}$ was applied to the data for $\{[\text{Mn(N}_3\text{O}_2)]\text{ClH}_2\text{O}\}_2\cdot2\text{Cl} \cdot 10.5\text{H}_2\text{O}$. The structure was solved by Direct methods using the program SHELXS-97.$^{[52]}$ The refinement and all further calculations were carried out using SHELXL-97.$^{[53]}$ The H-atoms were included in calculated positions and treated as riding atoms.
using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on $F^2$. There is disordered solvent present in this structure. PLATON/SQUEEZE$^{[84]}$ was used to correct the data for the presence of the disordered solvent.

6.1.19 Synthesis of $\{[\text{Co(N}_3\text{O}_2])\text{ClH}_2\text{O}\}_2\cdot 2\text{Cl}^{[83]}$

![Chemical structure](image)

2,2',6,6'-tetraacetyl-4,4'-bipyridine (0.170 g, 0.525 mmol) was added to a solution of CoCl$_2$·6H$_2$O (0.240 g, 1.01 mmol) in MeOH (10 mL), and the resulting solution was heated to approximately 50 °C with continuous stirring. A solution of 3,6-dioxaoccano-1,8-diamine (0.152 g, 1.03 mmol) in MeOH (5 mL) was then added. The reaction mixture was then refluxed for 6h, and then concentrated to half of the volume under vacuum. A solid was precipitated via the addition of diethyl ether. The yellow solid was collected by filtration and washed with diethyl ether. Yield (0.20 g, 47%).

IR (KBr, cm$^{-1}$): 3448, 3386, 3124, 3028, 2926, 2885, 2555, 2422, 2364 s, 2121, 1793, 1774, 1645 (C=N) s, 1603, 1562, 1321, 1279, 1221, 1120, 1093 C-O-C s, 1045, 957, 899, 874, 798, 671 (py).

Chapter 7 - References


48. J. Wang, B. Djukic, M. Pilkington, unpublished work.


Appendix 1-X-ray crystallographic data

X-ray Crystallographic Data for compounds 2.4, 2.5 and 2.16 were collected on a Bruker Apex II CCD system with graphite monochromated Mo Kα radiation.

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\(^a\) R = Σ||F_o| - |F_c||Σ|F_o|; \(^b\) Rw = [Σw(|F_o|^2-|F_c|^2)^2]/Σw|F_o|^4]^{1/2}.
X-ray Crystallographic data for compounds **2.13**, **2.14** **2.17** **2.19** and **5.16** were collected on a Stoe Mark II-Image Plate Diffraction System using Mo Kα graphite monochromated radiation.

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<td>1646.7(2)</td>
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<td>ρ_{calcld} (g cm⁻³)</td>
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<td>μ (mm⁻¹)</td>
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<td>0.0465</td>
<td>0.0799</td>
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<tr>
<td>R_w(Fo²)ᵇ</td>
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<td>0.0833</td>
<td>0.1349</td>
<td>0.1291</td>
<td>0.1988</td>
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</table>

ⁿR = \sum |F_o| - |F_c|/\sum |F_o|; ᵇR_w = [\Sigma w(|F_o|^2 - |F_c|^2)^2]^{1/2}.
Rational Design of a Covalently Tethered Dinuclear [Mn\(^{II}\)(N\(_2\)O\(_2\))Cl(OH\(_2\))]\(^{2+}\) Macroyclic Building Block: Synthesis, Structure, and Magnetic Properties

Jian Wang,¹ Brianna Slater,¹ Antonio Alberola,² Helen Stoeckli-Evans,³ Fereidoon S. Razavi,¹ and Melanie Pilkington*¹

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Received November 20, 2006

A novel dimeric Mn\(^{II}\) complex \{[Mn(N\(_2\)O\(_2\))Cl(OH\(_2\))]\(^{2+}\)\(\cdot\)2Cl\(\cdot\)2MeOH\(\cdot\)2H\(_2\)O\} (2) of a macrocyclic Schiff base ligand derived from the condensation of 2,2’6,6’-tetracetyl-4,4’-bipyridine with 3,6-dioxoacetanilide and 1,8-diamine in the presence of a stoichiometric amount of Mn\(^{II}\) has been prepared and characterized. The X-ray analysis of 2 reveals that the two Mn ions assume a pentagonal-bipyramidal geometry, with the macrocycle occupying the pentagonal plane and the axial positions being filled by a halide ion and a H\(_2\)O molecule. Magnetic susceptibility data (2–270 K) reveal the occurrence of weak antiferromagnetic interactions between covalently tethered Mn\(^{II}\)–Mn\(^{II}\) dimeric units.

In recent years, developing new synthetic strategies for the preparation of molecule-based magnetic materials has become an important area of research.¹ One synthetic rationale commonly employed is the use of organic molecules, e.g., macrocycles, to block several of the coordination sites of the assembling paramagnetic cations. Macrocyclic ligands are usually coordinated into the equatorial plane of the metal ions, leaving two free axial positions that can be occupied by bridging ligands, which, in turn, can function as organic linkers between adjacent paramagnetic metal centers.²,³

In 1977, Nelson reported metal complexes of a 15-membered Schiff base macrocyclic ligand.¹,⁴ Interest in this macrocyclic ligand has gained momentum in recent years given that the Fe\(^{II}\) complex [Fe\(^{II}\)(L)\(\cdot\)(CN)\(_2\)]\(\cdot\)H\(_2\)O exhibits spin-crossover behavior \(S = 0 \leftrightarrow S = 2\) including a LIESST effect, with a high relaxation time of 130 K.⁴ A number of divalent cations have been successfully employed as metal templates for the formation of the N\(_2\)O\(_2\) macrocycle,¹,⁴ but no successful transmetalation reactions have been reported to date for complexes of this particular macrocycle. Nevertheless, mononuclear complexes have recently become popular as connection devices for self-assembly, a strategy that has been successfully exploited for the preparation of magnetic clusters as well as 1- and 2-D coordination polymers.⁵ Given these advances, a new class of compound incorporating Nelson’s N\(_2\)O\(_2\) macrocycle should serve as a useful building block for exploitation in the field of supramolecular chemistry.

We report herein the synthesis, structure, and magnetic properties of a new bimetallic Schiff base compound comprised of two covalently tethered N\(_2\)O\(_2\) pentadentate macrocycles built around a 4,4’-bipyridine moiety \{[Mn(N\(_2\)O\(_2\))Cl(OH\(_2\))]\(^{2+}\)\(\cdot\)H\(_2\)O\}\(\cdot\)2Cl\(\cdot\)H\(_2\)O\(\cdot\)(2H\(_2\)O) (2). Synthetic routes to covalently tethered macrocycles are relatively uncommon in the chemical literature. Nevertheless, their potential as ligand systems for

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preparing compounds with intermolecular magnetic interactions when bridging ligands are installed provides an attractive approach for the preparation of extended systems that could yield novel materials such as molecule-based magnets.

The preparation and crystal growth of 2 is as follows. 2,2',6,6'-Tetraacetyl-4,4'-bipyridine (6; 0.162 g, 0.50 mmol) was added to a solution of MnCl₂·4H₂O (0.148 g, 1.00 mmol) in methanol (MeOH; 10 mL). The mixture was kept at 50 °C, and a solution of 3,6-dioxaoctane-1,8-diamine (0.198 g, 1.00 mmol) in MeOH (5 mL) was added with continuous stirring. The resulting solution was then refluxed for 6 h, after which the solvent was partially removed and the resulting solid was isolated by filtration, washed with diethyl ether, and air-dried to afford the product as an orange/brown solid. Yield: 42%. IR (KBr, cm⁻¹): 3423 br (OH), 2928–2883 s, 1646 s (C=O), 1105–1073 s (C–O–C), 1597 s, 877 m, 660 w (py). MS (FAB): m/z 763 [M – H]⁺, 728 [M – 2H₂O]⁺ (100%). Anal. Calcld for CₓHₓNₓOₓClₓMnₓ: C, 35.1; H, 6.4; N, 8.2. Found: C, 35.4; H, 6.4; N, 8.1. Small orange plates suitable for X-ray crystallography were grown via slow evaporation of a MeOH solution at room temperature.

Intensity data were collected at 173 K on a Stoe Mark II image plate diffractometer system using graphite-monochromated Mo Kα radiation. A semiempirical absorption correction using the program PLATON/MULABS was applied to the data for 2. The structure was solved by direct methods using the program SHELX-97. The refinement and all further calculations were carried out using SHELXL-97. PLATON/SQUEEZE was used to correct the data for the presence of the disordered solvent.

Table 1. Crystallographic Data for Compound 2

<table>
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<th>Parameter</th>
<th>Value</th>
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<td>Mw</td>
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<td>T, K</td>
<td>173(2)</td>
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<td>λ, Å</td>
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<td>Space group</td>
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<td>b, Å</td>
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<td>c, Å</td>
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<td>71.07(15)</td>
</tr>
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<td>F₀</td>
<td>72.95(17)</td>
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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 2

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<th>Distance (Å)</th>
<th>Bond Angle (deg)</th>
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<td>Mn2–N6</td>
</tr>
<tr>
<td>Mn1–O1</td>
<td>2.242(4)</td>
<td>Mn2–O3</td>
</tr>
<tr>
<td>Mn1–O2</td>
<td>2.277(4)</td>
<td>Mn2–O4</td>
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<tr>
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<td>71.07(15)</td>
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<td>O1W–Mn1–Cl1</td>
<td>178.99(17)</td>
<td>O2W–Mn2–Cl2</td>
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</table>

Figure 1. ORTEP representation of the molecular structure of 2 (ellipsoids at 30% probability). The Cl⁻ counterions are omitted for clarity.

The synthetic route for the preparation of the macrocycle is outlined in Scheme 1. The known tetraacid 3 was converted to tetrachloroformyl-4,4'-bipyridine (4) by reaction with trichloromethane in N,N-dimethylformamide. The reaction of 4 with 2,2-dimethyl-1,3-dioxane-4,6-dione (5, Meldrum's acid) followed by hydrolysis and decarboxylation afforded 6. Compound 6 then undergoes a metal-templated Schiff base condensation reaction together with 3,6-dioxaoctane-1,8-diamine to give the desired covalently tethered macrocycle. A ν(C=N) stretching mode was observed at 1646 cm⁻¹ in the IR spectrum of 2 that supports imine formation. A peak in the fast atom bombardment (FAB) mass spectrum at m/z 763 is also consistent with the loss of a proton from the [Mn₂(N₂O₂)Cl₂(H₂O)₂]²⁺ species.

The molecular structure of 2 was determined by X-ray crystallography and consists of two tethered N₂O₂ pentadentate macrocycles chelated to Mn₁ metal ions, together with four Cl⁻ anions (two coordinated and two uncoordinated, one of which is disordered over two sites) and two coordinated water molecules. The molecular structure together with the atomic numbering scheme is shown in Figure 1. Selected bond distances and angles are given in Table 2.

Both Mn₁ ions are in a pentagonal-bipyramidal environment, with the macrocycles occupying the equatorial plane.
and a bound water molecule and Cl\(^-\) ion in the axial positions. The dihedral angle between the two planes of the pyridine rings is 41°. The two macrocyclic rings are nearly planar. The maximum deviations of contributing atoms from the Mn\((\text{N}_3\text{O}_2)\) least-squares plane are 0.1 Å (N3) and 0.1 Å (N6). The distance between the two Mn\(^{II}\) ions in the molecule is 11.2 Å. The packing diagram reveals that centrosymmetric pairs of molecules are stacked along the c axis (Figure 2). The shortest distance between neighboring pyridine rings is 5.46 Å. Intermolecular contacts between Cl\(^-\) anions and neighboring H atoms are in the range of 2.87–3.11 Å and are shown as dashed lines. Compound 2 was magnetically characterized by following the temperature dependence of the magnetic susceptibility.\(^{(13)}\) The susceptibility of the sample rises monotonically as the temperature is decreased following a typical Curie–Weiss behavior, from which the Curie constant C could be determined. The presence of two Mn\(^{II}\) ions per molecule is confirmed by a Curie constant of 8.741 emu\(K/\text{Oe}\cdot\text{mol}\) (as expected for two \(S = \frac{5}{2}\) and \(g = 2\)) and a value for the Weiss constant of \(\theta = -2.89\) K (Figure 3). As shown in Figure 4, the \(\chi T\) product is fairly constant between 270 and 45 K at 8.58 emu\(K/\text{Oe}\cdot\text{mol}\) and decreases below 40 K to reach a value of 1.9 emu\(K/\text{Oe}\cdot\text{mol}\) at 2 K. This decrease can arise from either inter- or intradimer coupling. In our view, the dimers are magnetically well isolated, and at the simplest level, we can apply the results

\(\chi = \frac{N g^2 \beta^2}{3 k T} \frac{55 + 30 e^{-5/k T} + 14 e^{-9/k T} + 5 e^{-12/k T} + e^{-14/k T}}{11 + 9 e^{-5/k T} + 7 e^{-9/k T} + 5 e^{-12/k T} + 3 e^{-14/k T} + e^{-15/k T}}\)

A single parameter curve fit to the expression for \(\chi\) in compound 2 yielded \(J_{\text{ex}} = -0.51\) K with \(g = 2\), which is in very good agreement with the estimate from the mean-field theory (Figure 4) and is suggestive that the intradimer coupling is dominant. However, the weak nature of these interactions makes it impossible to completely rule out that interdimer interactions could also play a role in the magnetic properties.

To summarize, we have developed a new synthetic strategy to a magnetic building block comprising two covalently tethered pentadentate Mn\(^{II}\) macrocycles. Structural characterization reveals that the Mn\(^{II}\) ions contain labile axial ligands that can be readily replaced by bridging ligands, e.g., cyanide. Work along these lines is currently in progress and will be reported in due course.

Acknowledgment. This work was supported by the NSERC, CRC, Brock University (BUSRA, International Seed Funds), and the MEC (Ramón y Cajal research contract to A.A.).

Supporting Information Available: X-ray crystallographic files in CIF format for compound 1. This material is available free of charge via the Internet at http://pubs.acs.org.

IC062212O
The Preparation of a Highly Reactive 3,3'-Disubstituted-2,2'-Bipyridine Ligand and its Rearrangement to a Novel Quaterpyridine Analogue.

Jian Wang, Melanie Pilkington, Helen Stoeckli-Evans, Stuart Onions, Joan. K. Halfpenny and John D. Wallis

A remarkable one-pot transformation of a new 3,3'-disubstituted-2,2'-bipyridine to a quaterpyridine type ligand is presented whose Co(II) coordination complex has been structurally characterised by X-ray Crystallography.

The usual approach to coordination chemistry involves the study of how ligands of known structures can form coordination complexes from metal ions. But here we have prepared a bis-imine 1 with pyridine-2-carbaldehyde. The susceptibility of this ligand to nucleophilic attack at an imine functionality adds an extra dimension to reactions of its solutions with metal ions, especially since this attack can be intramolecular from a pyridine N atom.

The bis-imine 2 was prepared by reaction of the 3,3'-diamino-2,2'-bipyridine with two equivalents of pyridine-2-carbaldehyde in toluene in the presence of 4 Å molecular sieves. The ligand is stable if kept in a dry box at room temperature. With six sp² N atoms, there are several possibilities for coordinating metal ions, e.g. via the bipyridine and/or via the iminopyridine groupings. It is known that 3,3'-disubstituted 2,2'-bipyridines can coordinate by their ring N atoms, even when the substituents make no attractive interaction e.g. methyl. There is also the possibility of the bipyridine group adopting a trans conformation which opens other opportunities for metal ion coordination. However here we report a most remarkable transformation. Reaction with cobalt(II) perchlorate in wet acetonitrile at room temperature led to the isolation of the metal complex of the rearranged ligand 2 which contains four contiguous heterocycles - three pyridines and one pyrido(2,3-d)pyrimidine in which a pyrimidine N atom is the coordinating centre (Figure 1).

![Figure 1](image-url)

Thus, this complex ligand was obtained in one simple step, in contrast to ligands such as quaterpyridine which require Pd catalysed coupling chemistry. X-ray crystallography shows that ligand 2 coordinates the cobalt ion in a planar tetradeionate fashion with one acetoniitrile and one water molecule occupying the axial coordination sites. The four Co-N distance lies in the range 2.107(7) Å - 2.160(7) Å, as the N-Co-N angles lie in the range 74.2(3)-76.5(3)°. The tetradeinate ligand is close to perfect planarity, the maximum angle between any of the four ring systems is 5.7(4)°. The formation of this ligand from the bis-imine 1 can be rationalised by the mechanism shown in Scheme 1. Thus, intramolecular attack of a bipyridine N atom on the imine belonging to the second ring creates a pyridinium cation fused to a dihydropyrimidine 4. The pyridinium ring is then opened by water to give aldehyde 5 with a tetrahydropyrimidine ring. The latter opens to form an amine and an imine, and the former drives the formation of a new pyridine ring in 6. Finally a further addition of an amino to an imine forms the dihydropyrimidine ring which requires a final oxidation to form the aromatic ring.
This pyridine ring lies roughly perpendicular to the bipyridine system. The longest ring bond in this molecule is from the pyridinium N atom to the methine C atom (1.504 Å), and there is the expected widening of the angle at N in the pyridinium ring (123.9°) compared to the other pyridine rings (117.6-117.7°). The primary amino group makes a shorter bond (1.343 Å) to its pyridinium ring than the secondary amino group to its pyridine ring (1.381 Å). This secondary amino group adopts a pyramidal structure, but the lone pair can make to anomic interaction, and lies roughly parallel to the bond to the isolated pyridine ring.

These results suggest that there is considerable scope for the synthesis of novel metal binding species by carrying out one-pot procedures involving the coordination chemistry on chemically reactive ligands. For comparison, Manivannan recently noted the formation of 4′-(2-pyridyl)terpyridine by coordination of copper(II) to the imine of 2-aminoethylpyridine and 2-acetylpyridine. We believe this conversion involves tautomerism to provide the imine of 1-aminoethylpyridine and pyridine-2-carbaldehyde and thus additional building blocks for construction of the product.

Notes and references

1. Crystal data for Co(II) complex of 2: C5H5N+CoO2ClO4. M = 679.3, monoclinic, a = 14.311(2), b = 13.4071(16), c = 14.598(2) Å, β = 103.464(17)°, V = 2723.9(7) Å³, D = 1.66 g cm⁻³, space group Cc, Z = 4, μ(MoKα) = 0.71073, T = 173(2) K, 8587 measured refs, 4930 unique, final R₁ = 0.055 for 2656 refs with 1 > 2σ(I).

2. Crystal data for 4: C12H11N2Cl, M = 311.77, monoclinic, a = 12.9931(15), b = 12.4406(14), c = 9.5280(11) Å, β = 109.248(7)°, V = 1454.0(3) Å³, D = 1.424 g cm⁻³, space group P2₁/c, Z = 4, μ(MoKα) = 0.71073, T = 100 K, 15114 measured refs, 4458 unique, final R₁ = 0.0437 for 3731 refs with 1 > 2σ(I).

1. A. Name, B. Name and C. Name, Journal Title, 2000, 35, 3523; A. Name, B. Name and C. Name, Journal Title, 2000, 35, 3523.


6. The bispyridyldimine I has been fully characterised by HRMS and correct elemental analysis: δH (600 MHz, CDCl3): 8.71 (2H, dd, J = 4.7, 1.2 Hz, 2 x 6-H, bipy), 8.51 (2H, d, J = 4.7 Hz, 2 x 6-H, pyr), 8.34 (2H, s, 2 x CH imine), 7.79 (2H, d, J = 7.8 Hz, 2 x 3-H, pyr), 7.69 (2H, dd, J = 7.8, 1.2 Hz, 2 x 4-H, pyr), 7.47 (2H, dd, J = 7.8, 1.2 Hz, 2 x 4-H, bipy), 7.43 (2H, dd, J = 7.8, 4.6 Hz, 2 x 5-H, bipy), 7.30 (2H, d, J = 7.8, 4.7 Hz, 2 x 5-H, pyr), δC (600 MHz, CDCl3): 162.3 (2 x C imine), 154.1 (2 x C-pyr), 151.5 (2 x C-bipy), 149.4 (2 x 6-C-pyr), 147.5 (2 x 6-C-bipy), 146.1 (2 x 3-C-pyr), 136.7 (2 x 4-C-pyr), 125.7 (2 x 3-H, pyr), 125.3 (2 x 4-C-bipy), 124.1 (2 x 5-C-pyr), 121.6 (2 x 5-C-bipy), v(NO(KBr)): 3053, 1630, 1566, 1501, 1458, 1418, 1401, 1224, 1188 (SH), found: 364.1364, C₂₁H₁₈N₄ requires 364.1436. C₂₃H₂₅N₄ requires 346.1436. C₃₃H₃₂N₄ requires 364.43. C₇₂H₉₂N₁₂ requires 72.50 H 4.43 N 23.07 %; found C 71.97 H 4.43 N 23.43 %.