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**MAGNETO-STRUCTURAL CORRELATIONS OF NOVEL
COPPER(II) MOLECULAR MATERIALS**

by

CHRISTOPHER A. WHITE, B.Sc.

A thesis submitted to
The Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements of the degree of
Doctor of Philosophy

Department of Chemistry

Carleton University
Ottawa, Ontario
May, 1999

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Christopher A. White, B.Sc.

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Chair, Department of Chemistry

Thesis Supervisor

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Carleton University
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ABSTRACT

The novel π -donor bridging ligands, 1,3-dicyanamidobenzene dianion (*meta*-dicyd²⁻) and 1,3-dicyanamidotoluene dianion (Me-*meta*-dicyd²⁻) were synthesized and fully characterized both spectroscopically and crystallographically. Eight 1-D chains namely $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\cdot(\text{H}_2\text{O})_n$ (1), $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{CF}_3\text{SO}_3]_{2n}$ (2), $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BF}_4]_{2n}$ (3), $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{PF}_6]_{2n}$ (4), $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{Br}]_{2n}$ (5), $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{Cl}]_{2n}$ (6), $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-Me-meta-dicyd}]_n[\text{BPh}_4]_{2n}\cdot(\text{H}_2\text{O})_n$ (7), and $[\{\text{Cu}(\text{bpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{CF}_3\text{SO}_3]_{2n}\cdot(2\text{H}_2\text{O})_n$ (8) incorporate these ligands. All have been characterized by IR spectroscopy, elemental analysis and solid state magnetic susceptibility and (1) has been characterized by X-ray crystallography revealing a low-symmetry, alternating chain structure exhibiting unique magnetic properties. Chains (1)-(4) and (8) all displayed a weak ferromagnetic ground state upon which was superimposed a dominant antiferromagnetic interaction. Chains (5) and (6) exhibited similar antiferromagnetic interactions further strengthened by antiferromagnetic interchain interactions. The methyl substituted dicyd²⁻ chain (7) perturbed the structure of (1) resulting in a loss of the weak ferromagnetic ground state. Following this, a material was synthesized and characterized, having the stoichiometry $[\text{Cu}_{12}(\text{meta-dicyd})_{11}(\text{C}_3\text{H}_6\text{O})_{12}(\text{CF}_3\text{SO}_3)_2]_n$. This material revealed 3-D ordering with residual magnetization at zero applied field and magnetic properties owing to either ferrimagnetism or spin canting as observed in the 1-D chains. Finally, a homoleptic alternating chain, $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$, was synthesized and fully characterized. This

rare example of an alternating equatorial-equatorial / equatorial-axial bridged system, exhibited strong antiferromagnetic behaviour with a magnetic exchange constant value, $J = -90 \text{ cm}^{-1}$.

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*This work is dedicated to my wife, Dawn,
to my son Ethan, and to my parents,
Michele and Derrick White*

*"It is, I think, an ascertained fact, that ponderable matter is not
essential to the existence of physical lines of magnetic force."*

Michael Faraday

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LIST OF ABBREVIATIONS

Me	methyl
Ph	phenyl
trpy	2,2':6',2''-terpyridine
bpy	2,2'-bipyridine
trif	trifluoromethane sulfonate
<i>para</i> -dicyd ²⁻	1,4-dicyanamidobenzene dianion
<i>meta</i> -dicyd ²⁻	1,3-dicyanamidobenzene dianion
Me- <i>meta</i> -dicyd ²⁻	1,3-dicyanamidotoluene dianion
H ₂ - <i>meta</i> -dicyd	1,3-H ₂ -dicyanamidobenzene
H ₂ -Me- <i>meta</i> -dicyd	1,3-H ₂ -dicyanamidotoluene
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
TCNE	tetracyanoethylene
DMSO	dimethylsulfoxide
DMF	N,N-dimethylformamide
TMS	tetramethylsilane
IR	Infrared
NMR	Nuclear Magnetic Resonance
MS	Mass Spectrometry

CHAPTER 1

INTRODUCTION

1.1 Background

The multidisciplinary field of molecular magnetism has evolved a great deal in the last twenty years.^{1,2} It involves synthetic chemists, solid state physicists, theoreticians, material scientists as well as life science researchers, all of whom are fervently discovering novel molecular magnetic materials with interesting properties. Magnets themselves are by no means a recent discovery for since the advent of the compass, they have been a part of our lives for centuries. Conventional magnets are a crucial part of our society found in every electric motor, generator, loudspeaker, microphone, and data storage device, as well as being integral parts in frictionless bearings, switches, magnetic resonance imaging instruments and magnetic shielding devices. Molecular magnetic solids, however, are novel in the sense that they can be synthesized using organic molecules, they can be made using common solvents at ambient temperatures and they do not require a three dimensional network to exhibit magnetic properties.³

The search for an air stable, molecule-based ferromagnetic system that orders at or above room temperature, is a major driving force in the field of magnetochemistry. Admittedly, magnetochemists accept the fact that even if this quest were fulfilled, neither organic nor organometallic based magnets will ever be able to replace powerful conventional magnets as they do not have the same density of spins as metal based magnets.⁴ This being the case, the future for these molecular magnetic materials is far from bleak. Having properties such as low density,

flexibility, processibility at low temperatures, high strength, tuning of properties via chemistry, solubility, low environmental contamination, redox chemistry, compatibility with other polymers for composites, biocompatibility, high magnetic susceptibility, high magnetization, low magnetic anisotropy, transparency and semiconducting/insulating properties will see their application, depending on the specific nature of their design, employed in a variety of specialty uses.

One such use is being researched by Olivier Khan where iron-1,2,4-triazoles are being designed as magnetic storage devices.^{4,5} The premise is that the iron atoms are held in place by the organic framework of the triazoles, thus greatly stabilizing the structure of the material. This stability in turn allows the unpaired electrons of the iron atoms to point in one of two directions – one being a low energy state and the other a high energy state. This could be considered akin to today's binary (one's and zero's) storage system one would find on a computer disk or compact disc. This same material has also been proposed to be an electronic wallet where credits (money) could be switched on or off using heat. One of the properties of these iron-1,2,4-triazoles is that they change colour when in these different spins states – from white to purple depending on the state thus indicating the amount of credits remaining in ones account.

Another interesting avenue of research is being performed by Joel Miller, one of the co-discoverers of the first room temperature ferromagnetic material, vanadium-TCNE (tetracyanoethylene).⁶ This material has a critical temperature of 373 K and a magnetization almost equivalent to that of iron.⁷ Its only drawback, as alluded to at the beginning of the second paragraph, is that it is extremely unstable in air. Attempts

to correct this problem are currently underway. A suitable application for this and other similar magnetic materials, could be as electromagnetic shielding for high voltage power lines and/or magnetically sensitive devices. A power line or integrated circuit (IC), coated with these materials, would keep electromagnetic radiation from leaking to the ground below or penetrating into the intricate architecture of the IC, respectively.⁴

There are other factors which add to the challenge of the aforementioned search. Systems that combine two or more functional properties such as magneto-optics, superconductivity, and magnetism, and the design and characterization of mesoscopic molecules possessing large magnetic moments or the search for molecules exhibiting spin cross-over phenomena are examples of just such challenges.

Work done by Phil Langley and Jürg Hulliger have probed these challenges, and succeeded in trapping molecular magnets inside of nanometer diameter tubes.⁸ They postulate that magnetically doped nanotubes could halve the wavelength of light passing through them thereby transforming infrared light into ultraviolet light. Incorporation of these materials into magneto-optical storage devices (compact discs) would thus double their storage capacity.

Without a doubt, high temperature molecular magnetic materials will definitely find applications in today's world. The greatest advantage of this field of study is the abundant applications and needs for this avenue of research. Crutchley et al have, for the past decade, been exploring the nature of metal-metal coupling mediated by 1,4-dicyanamidobenzene dianion (*para*-dicyd²⁻) derivatives.⁹ It was shown that dinuclear complexes of this bridging ligand, with metal-metal distances of approximately 13 Å,

exhibit strong antiferromagnetic coupling in both ruthenium(III) and copper(II) complexes. This thesis will explore the metal-metal coupling and in particular, the magnetic exchange, of copper complexes by purposefully synthesizing a new bridging ligand, namely 1,3-dicyanamidobenzene dianion (*meta*-dicyd²⁻). Using both the superexchange model¹⁰ and the McConnell spin-polarization model¹¹, and supported by physical characterizations and molecular modeling, one dimensional copper(II) systems and a copper(II) material incorporating the *meta*-dicyd²⁻ bridging ligand will be examined. Furthermore, a reinvestigation into thiocyanate (SCN) chemistry will reveal a new homoleptic copper(II) linear chain system that may lead to the development of Cu-SCN 3-D networks based on Prussian Blue magnetic material analogues.

This introduction will briefly review the characteristics that make up a molecular magnetic solid thereby clearly defining the complexity and diversity that can be found in these materials. A brief look at the magnetochemistry of these systems, the models that will be used, and the theoretical basis for ligand synthesis will also be covered.

1.2 Introduction to Magnetism

A molecular magnetic material can be formed by free radicals, transition metal ions, rare earth ions or any combination of these linked by diamagnetic ligands.^{1,12} However, only free radicals can form magnetic molecular solids by themselves. Transition metal ions and rare earth ions require either magnetic or diamagnetic ligands to stabilize the molecular system. All of these components and their magnetic

properties must be taken into account when attempting to establish the basis of magnetism in any molecular solid.

In molecular solids, the degree of localization of the magnetic moments varies strongly between individual compounds. Magnetic moments can be fully localized, as is the case in many transition metal ion and rare earth ion systems, or they can be fully delocalized in conduction bands, as found in molecular conductors. Magnetic moments can also be delocalized within the molecule, but not the solid, as seen in metal-organic clusters or many free radicals. Essentially, a given material's magnetic properties will be governed by the degree of delocalization of its magnetic moments.

Because the permanent dipole moments of most atomic nuclei are too small to produce significant effects above temperatures of few mK, magnetism is primarily due to moving electrons. Therefore, any theory on magnetism must deal with the electronic structure of the atoms and ions making up the magnetic material.^{1,3,12} This introduction will elaborate on two fundamental concepts which are of basic importance when trying to understand magnetic phenomena in solids. The most basic of all is that distinct magnetic moments can be associated with a particular atom or ion in a solid and the other that these moments can interact with each other. These interactions need not necessarily be isotropic and, depending on the arrangement of the molecules and atoms in the solid and on the anisotropy, can lead to a rich variety of magnetic phenomena.

Two kinds of magnetic systems can be defined when examining magnetic interactions. The simplest being that the individual magnetic moments behave independently. Here, it is the external magnetic field which is responsible for ordering

the system. The other system shows mutual interactions between the moments which can result in magnetic ordering. Realistically, when considering a solid, both these types of magnetic systems should be included. These magnetic interactions have quantum mechanical origin and derive from electronic repulsion and from the influence of the Pauli principle. Two main classes of quantum mechanical coupling (or, from this point forward, exchange coupling) can be distinguished. Direct exchange operates between unpaired electrons on ions or molecules that are close enough to have significant overlap of their wavefunctions. Indirect exchange couples magnetic moments over considerable distances mediated by a non-magnetic moiety. In the case of insulators, the intermediary can be a diamagnetic atom, an ion or a molecule and the coupling is known as *superexchange*. With conducting solids, the intermediary are, in general, conducting electrons and the coupling is known as *RKKY* (named for Ruderman, Kittel, Kasuya and Yosida).¹⁴ While the latter yields interesting insight into magnetic properties of solids, the scope of this thesis deals primarily with the phenomena associated with superexchange.

Long range interaction between moments on ions, too far apart for direct exchange, but coupled via an intervening non-magnetic ligand, was first explained by Kramers¹⁵ in terms of superexchange. The key point of this interaction, having been fully developed by Anderson,¹⁶ is simply that the spin moments of the interacting metal ions couple with each other via the ligand orbitals. The nature of the metal centers and the bridging ligand, will determine whether the electron-transfer or hole-transfer superexchange mechanism will take place. The electron conduction pathway is favoured when the energies of the metal *d*-orbitals are best matched to the energy

of the ligand's lowest unoccupied molecular orbital (LUMO). Conversely, when the metal d -orbitals are energy matched to the energy of the ligand's highest occupied molecular orbital (HOMO), the hole-transfer superexchange mechanism predominates. In fact, the latter has been shown to be the dominant superexchange mechanism in past studies incorporating the dicyd²⁻ family of bridging ligands.¹⁷ In the simplest case, consider a system composed of two metal ions M_A and M_B , each possessing one unpaired electron in a non-degenerate orbital bridged by a diamagnetic ligand.

In all cases presented in this thesis, the metal ions are too far apart to interact directly and therefore, the orbitals of the bridging ligand play an important role. In the LMCT state, the unpaired electrons can couple only if their spins are opposite. The mixing of the ground state with the LMCT excited state stabilizes a new ground state in which the electrons are antiparallel. The optimization of superexchange, represented in the above equation, requires that the magnetic orbitals (those containing the unpaired electrons) overlap directly with the single ligand molecular orbital – the superexchange pathway. In order for this to occur, the magnetic orbitals must have the same symmetry and be as energetically matched as possible to the ligand molecular orbital. Such has been the case with Cu(II), Pd(II), Ni(II) and pivotally Ru(III) systems bridged by the dicyd²⁻ moiety.

A slightly different situation arises when the non-degenerate orbitals in the metals are orthogonal. This results in the stabilization of the parallel alignment of the

magnetic moments on each metal ion. In general, superexchange is the consequence of anti-parallel interactions (antiferromagnetic) and parallel interactions (ferromagnetic) where the antiferromagnetic interactions usually dominate.

The relative orientation of two electrons magnetic moments dictate their degree of electrostatic interaction. This can be expressed as coupling between the respective spins and depends only on the distance separating them (the distance between the two ions). Assuming that the interaction is isotropic, the interaction Hamiltonian for metal ions A and B , bridged by a diamagnetic ligand, L and separated by a distance r_{AB} , possessing

spins S_A and S_B , can be written

$$H = -2J \sum_{A>B} (r_{AB}) S_A \cdot S_B \quad (1)$$

where J is the exchange parameter. For direct molecular (intra-atomic) exchange, J is, in general, positive and leads to Hund's rule. This results in the parallel alignment of the magnetic moments and is called *ferromagnetic*, shown in figure 1.1.

Figure 1.1 – Singlet to triplet energy gap for two ferromagnetically coupled, $S = \frac{1}{2}$ metal ions

For direct inter-atomic exchange, J can either be positive or negative depending on the balance between coulombic and kinetic energy. Negative values of J favour an

antiparallel alignment of the magnetic moments and the interaction is called *antiferromagnetic*.

Figure 1.2 –Triplet to singlet energy gap for two antiferromagnetically coupled, $S = \frac{1}{2}$ metal ions.

Whether a singlet or a triplet ground state is formed depends on the relative magnitude of both the ferromagnetic (J_F) and antiferromagnetic (J_{AF}) terms expressed as

$$2J = J_F - J_{AF} \quad (2)$$

where J_F represents the total spin pairing energy and J_{AF} is the energy released as a result of spin coupling. Both types of magnetic interactions will be covered in more detail in sections 1.4.3 and 1.4.4, respectively.

1.3 Magnetism (Magnetic Ordering)

Magnetic moments and interactions are necessary, but not sufficient, conditions for magnetic ordering. Thermodynamically, three conditions must be met for a system to be considered magnetically ordered at zero applied magnetic field. First, the system must contain magnetic moments; second, there must be magnetic interactions between these moments; and third, the correlation length, which is the length along which two spins are magnetically correlated, approaches infinity as the

temperature approaches the *critical temperature*, T_c . Although systems which don't satisfy the third condition may still exhibit interesting magnetic properties, they cannot be considered ordered.¹ The correlation length is a measure of the ordering present in a system below its critical temperature. Obviously, it is temperature dependent and generally increases as the temperature decreases until its divergence to infinity at T_c . Furthermore, in ferromagnetic systems, a spontaneous magnetization, M_s , arises at T_c and can be considered the order parameter of the transition as it demonstrates how much of the system is ordered below T_c . This is shown pictorially in Figure 1.3.

Figure 1.3 – Representation of the process of magnetic ordering.

The divergence of the correlation length at T_c is important as it ensures that the magnetic system will be volume independent at $T \leq T_c$. Consequently, a high spin molecule is not a ferromagnet, independent of its size and total spin moment, since the size of the molecule establishes an upper limit for the correlation length. The same holds true for antiferromagnets with the magnetic interactions aligning neighbouring spin moments antiparallel thus resulting in an average magnetization equal to zero below T_c .¹⁷

1.4 Basic Magnetic Phenomena

The presence of magnetic moments is the only condition necessary for a material to exhibit magnetic behaviour (diamagnetism, paramagnetism). However, the absence of magnetic interactions in a magnetic substance is the exception rather than the rule since there is usually an appreciable exchange coupling between the substance's magnetic moments (ferromagnetism, antiferromagnetism, ferrimagnetism, etc).

Figure 1.4 – A two-dimensional spin alignment for various magnetic systems.

Any occurrence of magnetic interactions in the material implies a cooperative magnetism, which can dominate assuming the thermal energy of the moments in the paramagnetic regime are sufficiently quenched. Basic magnetic phenomena in the absence of magnetic interaction will be introduced first, which will set the groundwork for introducing magnetic phenomena in interacting systems.

1.4.1 Diamagnetism

Diamagnetism is an extremely important and fundamental property of all matter which cannot be ignored. It arises from the interaction of paired electrons with an applied magnetic field and is independent of both applied field strength and temperature. Typical values for the molar susceptibility of a diamagnetic material range from -1 to -100×10^{-6} emu/mol. In the scope of this thesis, diamagnetic susceptibilities serve only as correction factors of an experimentally determined susceptibility. Pascal's constants^{1,12} provide a method for this correction and one can calculate the diamagnetic contribution of the experimental susceptibility using the formula

$$\chi_{dia} = \chi_{atoms} + \chi_{bonds} \quad (3)$$

With χ_{dia} having been determined, the measured susceptibility can be corrected for using the equation,

$$\chi_{measured} = \chi_{dia} + \chi_{para} \quad (4)$$

1.4.2 Paramagnetism

The molar magnetic susceptibility of certain classes of compounds follows, to a first approximation, the law

$$\chi_M = \frac{C}{T} \quad (5)$$

where T is the absolute temperature and C , the Curie constant, is positive, and can be expressed as

$$C = \frac{Ng^2\beta^2}{3k}[S(S+1)] \quad (6)$$

where N is Avogadro's number, g is the Landé factor, β is the Bohr magneton, k is the Boltzmann constant and S is the spin quantum number. Equation (5) is known as the Curie Law and applies to substances where all their magnetic moments are in the ground state and do not interact with one another.

Later experiments showed that the susceptibility of certain materials was better fit to the Curie-Weiss Law

$$\chi_M = \frac{C}{T - \theta} \quad (7)$$

where C and T are the same as in the Curie Law, and θ is the Weiss constant which accounts for the interaction of neighbouring magnetic moments. In order to use equations (5) and (7) correctly, values for χ need to be corrected for the diamagnetic contributions using equation (4). Usually the diamagnetic correction can be ignored or roughly calculated as paramagnetic susceptibilities can be from 10^2 to 10^4 times greater than diamagnetic susceptibilities and increase further with decreasing temperature. However, complexes with large ligands, many and/or large counter-ions and few paramagnetic ions could give false results if the diamagnetic correction was ignored.

If a plot of χ^{-1} vs. T were made for a system obeying the Curie-Weiss law (figure 1.5), a straight line would result with a slope equal to C^{-1} and the x-intercept

Figure 1.5 – The inverse of χ as a function of T for systems exhibiting Curie and Curie-Weiss behaviour.

equal to θ . For values of $\theta < 0$, this indicates intermolecular interactions of an antiferromagnetic nature and, conversely, $\theta > 0$ indicates ferromagnetic interactions; both are limited to a temperature range where $T > \theta$. Another type of plot that could be employed in Curie-Weiss type systems is the χT vs. T plot (figure 1.6).

Figure 1.6 – A χT vs. T plot for systems obeying the Curie-Weiss law with $C=0.375 \text{ emu K mol}^{-1}$

This is a very good way, as will be shown much later on, for elucidating the magnetic behaviour of a given compound especially if the system is one which exhibits weak magnetic coupling of any type.

1.4.3 Ferromagnetism

As previously mentioned, ferromagnetism is a cooperative magnetism that leads to long-range parallel alignment of all the magnetic moments in the compound. A ferromagnetic substance usually divides itself into *domains*¹⁸ in order to minimize its total free energy. As a result of the parallel alignment of the moments, a *spontaneous magnetization* occurs in each domain, even in the absence of an applied external magnetic field.

Figure 1.7 – Magnetization process for a sample that was cooled below its T_c in the absence (left) and presence (right) of a magnetic field.

The direction of the spontaneous magnetization may vary from one domain to the other and can be altered by the application of an external magnetic field. In fact, the external magnetic field is just a tool used to enhance the ordering that already exists microscopically. Magnetic saturation occurs when the maximum domain alignment is achieved.

Within a domain, the magnitude of the spontaneous magnetization is weakly dependent on the strength of the applied magnetic field and can only be significantly reduced by increasing the temperature, eventually falling to zero at T_c . Above T_c , a ferromagnet will behave as a Curie-Weiss paramagnet as shown schematically in figure 1.8.

Figure 1.8 – Curie-Weiss paramagnetic behaviour is observed above T_c and ferromagnetic ordering is observed below T_c .

Examining figure 1.8, it would appear that the Curie-Weiss law predicts that $\theta = T_c$. In fact, this is an upper-limit for T_c that cannot be reached as short-range interactions and the quantum nature of the moments tend to reduce the critical temperature.

The first genuine molecular compound displaying a ferromagnetic transition, chlorobis(diethyl-dithiocarbamate)iron(III), $T_c = 2.46$ K, was discovered in 1967. However, the relatively recent discovery of $[\text{Fe}(\text{Me}_5\text{C}_2)_2][\text{TCNE}]$, $T_c = 4.8$ K, in 1988 marked the turning point in molecular magnetism, provoking magnetochemists the world over to push for the elusive $T_c > 298$ K ferromagnet.¹⁹

1.4.4 Antiferromagnetism

Similar to ferromagnetism, antiferromagnetism is a result of cooperative interactions that lead to long-range order. However, with antiferromagnetism, the interactions tend to orient the magnetic moments antiparallel to each other resulting in no spontaneous magnetization. Above T_c , called the Néel temperature (T_N) for antiferromagnets, thermal energy destroys any magnetic ordering reverting the material's magnetic characteristics to those that follow the Curie-Weiss law. Because nature tends to align magnetic moments antiparallel, rather than parallel, to one another, antiferromagnetism is much more common than ferromagnetism. Although molecular magnetism seems to be much more concerned with ferromagnetism, there is a genuine interest in antiferromagnetism because it deals with extended magnetic interactions between molecules.

Figure 1.9 – Magnetic susceptibility and inverse susceptibility as a function of temperature for an antiferromagnetic system.

The magnetic ordering of many inorganic systems, where magnetic interactions propagate between ionic or covalent bonds, can be understood using the rules of Goodenough and Kanamori.²⁰ In molecular solids however, the problem is more complicated. The molecules in solids are held together by other weaker forces such as hydrogen bonds, Van der Waal's interactions and weak ionic interactions. In addition, the magnetic moment is often delocalized within the molecule resulting in complicated superexchange pathways which mediate the magnetic interactions. To date, there are no simple rules which can predict the nature of these interactions, whether ferromagnetic or antiferromagnetic.

Another reason to maintain an interest in antiferromagnetism lies within the scope of this thesis. In molecular materials with dominant antiferromagnetic interactions, it is possible to obtain spontaneous magnetization. One way is by having unequal magnetic moments in each of the antiferromagnetic sublattices. The magnetic properties of these systems, called ferrimagnets, will be introduced in section 1.4.5. Another way is to have the spins in each antiferromagnetic sublattice canted towards or away from one another. Systems of this type are known as canted ferromagnets or weak ferromagnets and will be introduced in section 1.4.6.

1.4.5 Ferrimagnetism

The magnetic properties, in particular the magnetization, of ferrimagnets resemble those of ferromagnets as they can exhibit spontaneous magnetization. In ferrimagnets, the magnetic interactions tend to align the magnetic moments in each sublattice antiparallel to one another, as in antiferromagnets, however the antiparallel sublattices are inequivalent.

Figure 1.10 – Schematic of a two dimensionally ordered ferrimagnetic system. The size of the arrow represents the magnitude of the individual magnetic moments.

Until recently, ferrimagnetism was thought to stem from chemically different species such as different oxidation states of the same ion, elementally different metal ions or atoms (heterometallics), or an interaction between an ion and a free radical. One further ferrimagnetic interaction, shown by Drillon et al, demonstrated that different g tensors (Landé factors) on alternating sites of the same metal ion (homometallic) resulted in ferrimagnetic behaviour.²¹ The g tensors for a given paramagnetic ion can vary based on the coordination sphere about that ion (bond angles, bond lengths, the nature of the inner-sphere ligands, etc.) and because g is an integral part of describing the magnetism of any paramagnetic material, this too must be taken into consideration when examining the magnetic characteristics of any system.

The magnetic characteristics of a ferrimagnetic system are subtle and usually found when a more in-depth analysis of the data is performed. The variable temperature magnetic susceptibility plot usually resembles that of a paramagnetic species however, when a Curie-Weiss plot, χ^{-1} vs. T and a χT vs. T plot of the data is performed, the ferrimagnetic behaviour is elucidated, as seen in figure 1.11. In figure 1.11(a), at temperatures lower than T_c , ferrimagnetic behaviour is seen and at temperatures above T_c , normal paramagnetism is evident. The $\chi_M T$ vs. T plot (figure 1.11(b)) is more revealing. Here, the antiferromagnetic sublattice is clearly visible in the high temperature region and then, at lower temperatures, the plot begins to rise rapidly indicating a net magnetic moment coupling with the applied external magnetic field. Lower dimensional systems usually require such an analysis in order to confirm ferrimagnetic behaviour.

Figure 1.11 – Plots of (a) χ^{-1} vs. T and (b) χT vs. T plots of a ferrimagnetic system.

Clearly, ferrimagnetism offers the possibility of developing spontaneous magnetization in the presence of extended antiferromagnetic interactions. This is quite useful because antiferromagnetic interactions are, as previously stated, more prevalent and easily stabilized than ferromagnetic interactions. This strategy of monopolizing antiferromagnetic interactions for a net gain in magnetization was first introduced by Buchachenko as a route to synthesize organic ferrimagnets.²² Successful strategies to prepare molecular ferrimagnets include the coordination of free radicals, in particular nitronyl nitroxide to transition metal ions²³, charge transfer

salts based on metallocenium donors and organic acceptors²⁴, and bimetallic systems.²⁵ However, by far the most successful route to a ferrimagnetic material was made by focusing on the bimetallic and mixed-valence transition metal bridged cyanide (Prussian Blue analogues) systems which show T_c values from 190 K to 240 K.²⁶

1.4.6 Weak Ferromagnetism (Canted Ferromagnetism)

Finally, there are some substances which display antiferromagnetic properties at high temperatures and below a given transition temperature, display spontaneous magnetization, albeit weak. The magnetic behaviour of such a system is shown in figure 1.12.

Figure 1.12 – (a) Magnetization as a function of applied magnetic field and (b) Magnetization as a function of temperature for a spin-canted system.

It is interesting to notice how the canting of the magnetic moments effect the magnetization and susceptibility curves. Upon examination of the $M(H)$ plot in figure

1.12(a), one notices that above T_N , the weak ferromagnetic substance behaves as a paramagnet. Consequently, at low field, the magnetization will be proportional to the applied magnetic field, H . Below T_N , the magnetization is dependent on the strength of the antiferromagnetic interaction, J , the orientation of the crystal (if single crystal work is being done) and the symmetry. The $M(T)$ plot, shown in figure 1.12(b), resembles that of a ferromagnet although the magnitude of the saturation magnetization (M_s) is considerably smaller.

The origin of the spontaneous moment in these systems (which is 10^{-2} to 10^{-3} times smaller than their nominal value), were in dispute for a long period of time. With $\alpha\text{-Fe}_2\text{O}_3$ being the first compound to exhibit weak ferromagnetism, the anomaly was initially ascribed to the presence of magnetite impurities, to defects of stoichiometry or to crystallographic imperfections. However, single crystal work of this and other materials exhibiting weak ferromagnetism lead researchers to believe that this was a purely intrinsic property of the material. This problem was first studied theoretically by Dzyaloshinskii²⁷ and later chemically by Moriya.²⁸ It was shown that weak ferromagnetism can be an intrinsic property of certain materials. Essentially, weak ferromagnetism is the result of an antisymmetric interaction which tends to align neighbouring spins perpendicular to each other and an isotropic interaction which tends to align them, in the antiferromagnetic case, antiparallel to one another. Thus, it is the antisymmetric interaction that leads to a canting between the spins and to the onset of magnetic ordering. The result is a weak spontaneous magnetization, M_s . The onset of this spontaneous magnetization is seen in three-dimensional (figure 1.13) and

two-dimensional ordered systems but, in no case can it result from one-dimensional ordering.

Figure 1.13 – A two dimensional representation of a spin canted system.

Concentrating on one antiferromagnetic sublattice, shown in figure 1.13, we see how

Figure 1.14 – The angle, α , formed when two neighbouring spins are aligned away from parallel (a) results in a residual magnetic moment (b) thus yielding a weak ferromagnetic ground state.

the sum of the two spins results in a net magnetic moment. In an ordered material, weak magnetization, M_w , should be seen when placed in a weak applied magnetic field. As the field strength is increased, and provided that the antiferromagnetic interaction is not too strong, all the spins in the system should align and the material should reach a saturation magnetization, M_s . The canting angle, represented by α in figure 1.14(a), can be determined by equation (8)²⁹

$$\alpha = \sin^{-1} \left(\frac{M_w}{M_s} \right) \quad (8)$$

The larger the canting angle, the larger the residual magnetic moment, reaching its limit at $\alpha = 90^\circ$.

Weak ferromagnetism is not uncommon in three- and two-dimensional molecular systems, but has never been seen, intramolecularly, in one-dimensional systems. Some well documented examples of extended systems exhibiting weak ferromagnetism are $[4\text{-ClpyH}]_3[\text{FeCl}_4]_2\text{Cl}$ ³⁰, $[(\text{CH}_3)_3\text{NH}]\text{CoCl}_3 \bullet 2\text{H}_2\text{O}$ ³¹, $[(\text{CH}_3)\text{NH}]\text{MnBr}_3 \bullet 2\text{H}_2\text{O}$ ³², $[\text{Co}(\text{NH}_3)_6][\text{CoCl}_4]\text{Cl}$ ³³ and $[\text{Fe}(4\text{-imidazoleacetate})_2] \bullet 2\text{CH}_3\text{OH}$ ³⁴. Alluded to above was the fact that no intramolecularly coupled one-dimensional systems has ever displayed weak ferromagnetism. Many examples have involved one-dimensional systems where interchain antiferromagnetic exchange resulted in a weak ferromagnetic ground state. One of the more interesting and extensively studied examples involves manganese phthalocyanine systems. These systems consist of two types of stacking chains interacting in such a way as to render the local moments canted approximately 90° to one another. ³⁵

1.5 Magnetic Properties of One-Dimensional Cu(II) Systems

Thus far, this introduction has dealt with magnetic phenomena as they apply to chemically ordered systems. However, it has also been stated that chemical order and crystallinity are not necessary conditions to produce a molecular magnet. In fact,

attempts at enhancing interactions between neighbouring magnetic sites have lead to the tendency to produce polymeric or one-dimensional systems.

Copper(II) compounds are conceptually easy magnetic systems to investigate and, at the same time, synthetically frustrating. They are spin $\frac{1}{2}$ systems and thus there is only one magnetic orbital per ion making the electronic and magnetic properties easy to describe. Conversely, copper(II) complexes can assume a wide variety of coordination geometries ranging from tetrahedral to octahedral with many indeterminate or distorted in nature and thus electronic structures are not well defined. Furthermore, the existence of coordinated and semi-coordinated ligands coupled with the flexibility of the coordination geometry, leads to a variety of superexchange pathways.

Chain compounds of copper(II) are very useful in the study of low-dimensional systems for many reasons. The large body of theoretical work that is available^{36,37,38} and easily determined magneto-structural correlations of complicated structures make copper(II) the ideal ion for these studies. In addition, zero field splittings and their resultant anisotropy are compensated for by the low spin of the metal ion which can be represented both quantum mechanically as well as classically as opposed to large spin containing ions which approach classical spins. Some of the more prevalent examples of copper(II) one-dimensional chains will now be introduced in order of their occurrence in nature.

1.5.1 Uniformly Spaced Chains

The simplest case of a magnetic chain compound can be described by an arrangement of Cu(II) ions equally spaced apart.

In this system, the nearest neighbour exchange interaction can be described by one magnetic exchange parameter, J , and the Hamiltonian by

$$H = -2J_{AB} S_A \cdot S_B \quad (9)$$

To determine the type of magnetic interaction in these chain systems, and, in general, the chain systems to follow, one would construct a χT vs. T plot of the magnetic data. In a system with no exchange interactions, the system would obey the Curie law and the χT vs. T plot would be a horizontal straight line. If the interaction were ferromagnetic, high temperature plots would follow the straight line of the Curie paramagnet until a critical temperature. At this point, there would be a divergence of χT towards higher values as the temperature decreased. Conversely, if the interaction were antiferromagnetic in nature, χT would diverge to lower values as the temperature was decreased. These plots must be examined with great care, especially when dealing with systems whose spins are greater than $S = \frac{1}{2}$.

1.5.2 Alternatingly Spaced/Bridged Chains

A somewhat more complicated case than the uniformly spaced chain is the alternatingly spaced chain. Aside from the fact that there are few examples of this type of chain system, their interest lies in understanding the nature of the alternating singlet to triplet energy gap and how it varies with the alternation parameter. The structure of the alternatingly spaced/bridged chain system is shown below.

Here, two distinct magnetic exchange pathways exist where the magnetic exchange constants, J and αJ , alternate along the chain. The Hamiltonian used to describe this system is

$$H = -2J \sum_{i=1}^{(N-1)/2} S_{2i-1} \cdot S_{2i} - 2\alpha J \sum_{i=1}^{(N-1)/2} S_{2i} \cdot S_{2i+1} \quad (10)$$

The assignment of J and αJ to the specific links, whether distance or bridging ligand related, sometimes fallibly, depends on magneto-structural correlations. In addition, the sign of J and αJ can lead to interesting magnetic results and specific labels for each are given. If both J and αJ are negative, the chain is termed an alternating antiferromagnetic chain. Conversely, if they are both positive, the chain is called an alternating ferromagnetic chain. Finally, J and αJ could be opposite in sign, thus resulting in an alternating antiferromagnetic-ferromagnetic chain. If $\alpha = 0$, the system would correspond to one with isolated pairs which may be possible if the value of J , for example, was much larger than that of αJ . Experimentally, the alternating chain and regular chain can be easily distinguished. In the case of an alternating chain, with $J < 0$ and α lying in the range $0 \leq \alpha < 1$, an energy gap exists between the singlet ground state and the next excited state. Consequently, χ tends to approach zero as the temperature approaches absolute zero. The opposite is seen for a regular chain system.

1.5.3 Next-Nearest Neighbour Chains

The next-nearest neighbour chains are schematically shown below and the Hamiltonian for describing the magnetic exchange is

$$H = -2J \sum_{i=1}^{N-1} S_i \cdot S_{i+1} - 2\alpha J \sum_{i=1}^{N-2} S_i \cdot S_{i+2} \quad (11)$$

These types of systems are important as they can sufficiently model the effects of increasing the dimensionality of a system. In addition, systems of this nature could ultimately lead to a better understanding of the magnetic characteristics of interchain interactions. It was this type of system which introduced the concept of spin frustration, represented below.

Assume that the superexchange interaction between M_a and M_c is antiferromagnetic, as indicated by the arrows representing the magnetic moment on each metal ion. Also, the superexchange interaction between M_a and M_b is also antiferromagnetic. The problem that develops is that the superexchange pathway between M_a and M_b and

between M_b and M_c are identical but the spins show that the M_b -X- M_c superexchange pathway is ferromagnetic in nature. This oversimplified illustration of spin frustration is one reason why research in the study of next-nearest neighbour chains is so important.

1.5.4 Spin-Ladder Chains

The spin-ladder chain, shown below, is so called as it resembles a ladder

with unique magnetic exchange interactions present both along the “runners” of the ladder (J) and along the “rungs” of the ladder (αJ). The Hamiltonian describing the magnetic exchange is

$$H = -2J \sum_{i=1}^{N/2} S_{2i-1} \cdot S_{2i} - 2\alpha J \sum_{i=1}^{N-2} S_i \cdot S_{i+2} \quad (12)$$

There are very few examples of spin-ladder chains. Magneto-structural correlations performed on examples that do exist are very complex and often, it is difficult to assign J and αJ unambiguously.

1.5.5 Alternating Next-Nearest Neighbour Chains

The second-last chain in this review, shown below, presents a very rare

and complicated model. To date, only one example of this type of system has been seen, that of copper(II) phthalate monohydrate. Even this compound, with its Hamiltonian describing the nature of the interaction as

$$H = -2J \sum_{i=1}^{N-1} S_i \cdot S_{i+1} - 2\alpha J \sum_{i=1}^{(N/2)-1} S_{2i-1} \cdot S_{2i+1} - 2\beta J \sum_{i=1}^{(N/2)-1} S_{2i} \cdot S_{2i+2} \quad (13)$$

had to set $\beta = 0$, due to the absence of an exchange pathway between these sites.

1.5.6 Pendant Chains

The final example, shown below, has been of interest to many research

groups as they, similar to next-nearest neighbour chains, could give insight into multi-dimensionality analogues of the chain. The interest in these systems, however, has not borne many well characterized examples.

It has been shown that for 1-D systems, structure-function relationships are extremely important when trying to fit magnetic data to established models and chain types. Generation of these magneto-structural correlations would otherwise be a hit-

and-miss approach which could yield an oversimplified result that appears to be correct.

1.6 Theoretical Basis for Ligand Synthesis

Work in our group has predominantly focused on the electronic and magnetic exchange of various metal ions bridged by the *para*-dicyd²⁻ dianionic bridging ligands. The primary mechanism for magnetic coupling here was resonance exchange. In order for resonance exchange to be the dominant mechanism, the appropriate magnetic orbital on the metal ion (the orbital(s) with the unpaired electron in it) must interact with the high lying HOMO or low lying LUMO, of the correct energy and symmetry. This has been shown to be the case with both Ru(III) and Cu(II) systems. It should also be noted that any out-of-plane event incurred by the ligand would reduce the overlap and hence reduce the coupling. This too has been shown by our group by both the 4,4'-dicyanamidobiphenyl²⁻ dianion³⁹, and Me₄-dicyanamdobenzene²⁻ dianion⁴⁰ bridging ligands which exhibit non-planarity reducing *p*-orbital overlap and by steric hindrance inducing out-of-plane twisting of the cyanamide moieties, respectively.

However with the *meta*-dicyd ligands, resonance exchange is predicted to fail based on quantum interference effects. A study done by Richardson and Taube⁴¹ on 1,3-dicyanobenzene and 1,4-dicyanobenzene bridging ligands showed that there was extremely weak metal-metal coupling occurring in the former when compared to the latter. The weakness of the *meta*-isomer interaction can be explained by a cancellation effect. Figure 1.15 shows this effect very well. With the *para*-isomer there is one

Figure 1.15 – Diagram showing the HOMO of *para*-dicyd²⁻ one of the HOMO's of *meta*-dicyd²⁻.

continual π -exchange pathway whereas with the *meta*-isomer, there is a pair of degenerate, mutually orthogonal molecular orbitals which make up the HOMO of this isomer. Therefore, with the *meta*-isomer, the interaction of one metal ion with one of the bridging pathways is appropriate, but the simultaneous presence of the two coupling pathways with different symmetries destroys the overall coupling.

The final spin exchange mechanism that is left to describe is the McConnell spin polarization model. Spin polarization involves the interaction of the ligand HOMO's which are orthogonal to the magnetic orbitals. This effect, which is quantum mechanical in nature, is such that the unpaired spin on the metal ion is induced to align with the spin of the electron on the ligand. There are many examples of this in the literature, but a straightforward example deals with magnetic exchange between two Mo(V) metal centers mediated by a deprotonated 1,3-dihydroxybenzene dianion bridging ligand.⁴²

The resulting magnetic exchange constant, $J = +9.8 \text{ cm}^{-1}$, indicates, as predicted by the McConnell spin polarization model, ferromagnetic behaviour. To further explain this phenomenon, we will examine this mechanism's effect on the *meta*-dicyd²⁻ system.

Again, comparing it to the *para*-isomer, we would expect, based on the previous studies mentioned, the *para*-isomer will show antiferromagnetic behaviour and the *meta*-isomer would yield ferromagnetic behaviour, shown in figures 1.16 and 1.17.

The method employs a simple spin-counting technique where by an odd-number atom bridge results in a pairing of the paramagnetic spins and an even-number atom bridge results in a cancellation of the paramagnetic spins.²

Figure 1.16 – The McConnell spin polarization model predicted magnetic exchange pathway for a *para*-dicyd²⁻ bridged, paramagnetic metal ion dinuclear system.

Figure 1.17 - The McConnell spin polarization model predicted magnetic exchange pathway for a *meta*-dicyd²⁻ bridged, paramagnetic metal ion dinuclear system

This model is not without its limitations. A classic example of the failure of this McConnell model involves μ -azido bridged Cu(II) complexes.⁴³ The π_g MO of the azido bridge plays a dominant role in the antiferromagnetic interaction between the copper ions. A first order approach using the McConnell mechanism would indicate that an end-end bridge of N_3^- would be ferromagnetic directing as seen below

However, with the N_3^- ligand and with other three atom bridged systems as well, the electrons, at any instant, can remain at the ends of the molecular orbital

resulting in an antiferromagnetically coupled system. The absence of significant overlap density caused by a node in the central nitrogen, pushes the two paired electrons towards the extremities of the system. Therefore, when the azido bridges in an end to end fashion, antiferromagnetic behaviour is seen and when it bonds in an end-on fashion, ferromagnetic behaviour results.⁴⁵

Whether the *meta*-dicyd²⁻ bridge mediates the magnetic exchange via the mechanism in figure 1.17 or by the N₃⁻ based model mentioned previously, is difficult to predict theoretically. Based on previous bridging modes of *para*-dicyd (bridges metal ions via the nitrile nitrogen shown in figure 1.16) one would expect that figure 1.17 would be the predicted magnetic behaviour. However, the accuracy of the ligand orbital configurations is limited to the degree of electron repulsion and on the planarity of the bridging ligand itself and, with such a large separation between metal ions, there is little room for imperfection.

Research Aims

There were five major goals of this research:

1. To synthesize and characterize two novel, *meta*-substituted dicyanamidobenzene dianion bridging ligands namely H₂-1,3-dicyanamidobenzene and H₂-1,3-dicyanamidotoluene.

2. To synthesize and characterize novel copper (II) one-dimensional chain systems incorporating the above mentioned bridging ligands. The chain complexes synthesized were of the form

3. To synthesize and characterize a novel 3-D ordered material incorporating metal-cyanamide linkages of the form

4. To synthesize and characterize a novel homoleptic copper(II)-thiocyanato one-dimensional chain of the form

5. To investigate the basis for the magnetic exchange found in all the above mentioned one-dimensional chains and materials.

CHAPTER 2

EXPERIMENTAL

2.1 Starting Materials

2.1.1 Reagents for Ligand Synthesis

Ammonium thiocyanate (97%, ACS Reagent Grade, Aldrich), Benzoyl Chloride (Reagent Grade, 99%, Aldrich), 1,2-phenylenediamine (98%, flakes, Aldrich), 1,3-phenylenediamine (99+%, flakes, Aldrich), Sodium Hydroxide (99.0%, ACS Reagent Grade, Anachemia), Lead(II) Acetate Trihydrate (99+%, Aldrich), Glacial Acetic Acid (99.7%, Anachemia), Tetraphenyl Arsonium Chloride Hydrate (97%, Aldrich), Thallium(I) Acetate (99.99%, Aldrich), Triethylamine (99+%, Alfa Aesar), 2,6-diaminotoluene (97%, Aldrich), Sodium Thiocyanate (98%, Aldrich),

2.1.2 Reagents for Complex Synthesis

Copper Turnings (Fisher Scientific), Copper(II) Methoxide (98%, Alfa Aesar), Trifluoromethanesulfonic Acid (98%, Aldrich), 2,2':6',2''-terpyridine (98%, Aldrich), 2,2'-bipyridine (99+%, Aldrich), Ammonium Hexafluorophosphate (95+%, Aldrich), Tetrabutylammonium Bromide (99%, Aldrich), Tetrabutylammonium Chloride (Eastman Kodak Co.), Tetrabutylammonium Hexafluorophosphate (98%, Aldrich), Sodium Tetraphenylborate (99.5%, Aldrich, Strem Chemical Co., Alfa Aesar), Tetrabutylammonium Tetrafluoroborate (99%, Aldrich).

2.1.3 Compressed Gases

Nitrogen (BOC Gases), Argon (Ultra High Purity, BOC Gases)

2.1.4 Chromatography Resins and Drying Agents

Aluminum Oxide (WA-1, Acid Washed, Grade III and Grade V, Anachemia),
Molecular Sieves (Type 4A and Type 3A, Aldrich)

2.2 Solvents

Ethanol (Anhydrous, Commercial Alcohols Inc.), Methanol (lab grade, Anachemia, distilled under glass before use), Dimethylformamide (99.8%, Anachemia), Dimethyl Sulfoxide (99.9%, Anachemia), Toluene (99.5%, Caledon Labs), Acetone (lab grade, Anachemia, distilled under glass before use), Acetonitrile (99.5%, Caledon Labs), Diethyl Ether (Anhydrous, 99%, Caledon Labs), Water (distilled using a Millipore MILLI-Q 4-bowl Plus {analytical} deionizer).

2.2.1 Solvents for NMR

Tetramethylsilane (99.9%, Aldrich), Acetonitrile-d³ (99.6 atom %D, Aldrich), Dimethylsulfoxide-d⁶ (99.9 atom %D, CDN Isotopes), Methyl Alcohol-d¹ (99.5 atom %D, Aldrich)

2.3 Ligand Synthesis

1,3-H₂-dicyanamidobenzene

Benzoyl chloride (14.0g, 100 mmol) in 100 mL of acetone, was added to a refluxing solution of ammonium thiocyanate (7.6g, 100 mmol) in 100 mL of acetone. A white precipitate of NH₄Cl began to form. The solution was allowed to reflux for 10 minutes and then a solution of 1,3-phenylenediamine (5.4g, 50 mmol) in 100 mL of acetone was added dropwise over a 10 minute period using a pressure-equalizing dropping funnel. The solution was refluxed for a further 15 minutes. At this point, the entire solution was poured into 2000 mL of vigorously stirring distilled water. The resultant yellow-curdy mass was suction filtered and washed with copious amounts of water followed by 30 mL of acetone (caution: the *meta*-substituted thiourea derivative is soluble in acetone unlike its *para*-substituted counterpart). The thiourea derivative (20.0 g, 46 mmol) was dissolved in 250 mL of 2 M NaOH and brought to a boil. Once the thiourea derivative had fully dissolved, the solution was cooled to approximately 65 °C. At this point, a 60 °C solution of lead acetate trihydrate (37.9g, 0.1 mol) in 100 mL of H₂O was added with constant stirring. The stirring was maintained until the solution had turned completely black by the formation of lead sulfide. The solution was filtered, using a large Buchner funnel and the filtrate was collected while the filter flask was immersed in an ice bath. The cooled filtrate was then neutralized by the addition of 29.4 mL of glacial acetic acid forming a white precipitate of 1,3-dicyanamidobenzene (H₂-*meta*-dicyd). The precipitate was washed with copious amounts of distilled water until the smell of acetic acid was minimal. The crude product was recrystallized by dissolving the product in hot 1:1

methanol:water and allowing the solution to cool. Yield 5.61 g, 77.2%. Elemental Analysis based upon $C_8H_6N_4$, F.W. 158.16 g mol⁻¹: Calcd(%) C, 60.75; H, 3.82; N, 35.43. Found(%) C, 58.18; H, 3.74; N, 31.78.

[AsPh₄]₂[*meta*-dicyd]

H₂-*meta*-dicyanamidobenzene (0.2 g, 1.2 mmol) was dissolved in 50 mL of 2M NaOH. To this solution was added a solution of tetraphenylarsonium chloride hydrate (1.11 g, 2.5 mmol) in 100 mL of 2M NaOH. Immediately, a pale yellow precipitate formed, was filtered by suction and washed with 50 mL of distilled water. The crude ligand was recrystallized by diffusing ether into a saturated acetonitrile solution of the ligand. Yield 1.01 g, 87 %. Elemental Analysis based upon [AsPh₄]₂[*meta*-dicyd²⁻] $\cdot$ 2H₂O (as C₅₆H₄₈N₄As₂O₂, F.W. 958.87 g mol⁻¹: Calcd(%) C, 70.15; H, 5.05; N, 5.84. Found(%) C, 70.01; H, 4.89; N, 5.89.

Tl₂(*meta*-dicyd)

H₂-*meta*-dicyanamidobenzene (0.5 g, 3 mmol) was dissolved in 100 mL of a 1:1 acetone/water solution. To this was added thallium(I) acetate (1.65 g, 6.2 mmol) dissolved in 80 mL of a 1:1 acetone/water solution. Triethylamine (1.0 mL, 10 mmol) was added to the stirring solution and immediately, the white precipitate of Tl₂(*meta*-dicyd) formed. This was filtered and washed with 20 mL of distilled water followed by 20 mL of acetone and finally 20 mL of ether. The product was dried overnight. Yield 0.84 g, 47 %. Elemental Analysis based upon [Tl]₂[*meta*-dicyd²⁻] (as C₈H₄N₄Tl₂, F.W.

566.89 g mol⁻¹: Calcd(%) C, 17.01; H, 9.92; N, 0.71. Found(%) C, 17.31; H, 9.91; N, 0.73.

2,6-dicyanamido-H₂-toluene (Me-H₂-*meta*-dicyd)

Benzoyl chloride (12.08g, 86 mmol) in 150 mL of acetone, was added to a refluxing solution of ammonium thiocyanate (6.54g, 86 mmol) in 150 mL of acetone. A white precipitate of NH₄Cl began to form. The solution was allowed to reflux for 10 minutes and then a solution of 1,3-phenylenediamine (5.0g, 40 mmol) in 100 mL of acetone was added dropwise over a 10 minute period using a pressure-equalizing dropping funnel. The solution was refluxed for a further 15 minutes. At this point, the entire solution was poured into 2000 mL of vigorously stirring distilled water. The resultant yellow-curdy mass was suction filtered and washed with copious amounts of water followed by 30 mL of acetone (caution: the *meta*-substituted thiourea derivative is soluble in acetone unlike its *para*-substituted counterpart). The thiourea derivative (20.3g, 45 mmol) was dissolved in 250 mL of 2 M NaOH and brought to a boil. Once the thiourea derivative had fully dissolved, the solution was cooled to approximately 65 °C. At this point, a 60 °C solution of lead acetate trihydrate (34g, 90 mmol) in 100 mL of H₂O was added with constant stirring. The stirring was maintained until the solution had turned completely black by the formation of lead sulfide. The solution was filtered, using a large Buchner funnel and the filtrate was collected while the filter flask was immersed in an ice bath. The cooled filtrate was then neutralized by the addition of 30 mL of glacial acetic acid forming a white precipitate of 2,6-dicyanamidotoluene (H₂-Me-*meta*-dicyd). The precipitate was washed with copious amounts of distilled water until the smell of acetic

acid was minimal. The crude product was recrystallized by dissolving the product in hot 1:1 methanol:water and allowing the solution to cool. Yield 2.6g (34%). Elemental Analysis based upon $C_9H_8N_4$, F.W. $172.19 \text{ g mol}^{-1}$: Calcd(%) C, 62.78; H, 4.68; N, 32.54. Found(%) C, 62.46; H, 4.65; N, 32.36.

- **[AsPh₄][SCN]**

This ligand was made via two routes. The simplest route involved the dissolution of sodium thiocyanate (1 g, 12 mmol) in distilled water. To this was added a solution of tetraphenylarsonium chloride hydrate (5.4 g, 12 mmol) in 100 mL of distilled water. Immediately, a pale yellow precipitate formed, was filtered by suction and washed with copious amounts of water. The crude product was recrystallized by ether diffusion into a saturated acetonitrile solution forming very large rectangular prisms. Yield 4.66g, 88 %

The second method is that similar to the procedure for H_2 -*meta*-dicyd. Benzoyl chloride (14.0g, 100 mmol) in 100 mL of acetone, was added to a refluxing solution of ammonium thiocyanate (7.6g, 100 mmol) in 100 mL of acetone. A white precipitate of NH_4Cl began to form. The solution was allowed to reflux for 10 minutes and then a solution of 1,2-phenylenediamine (5.4g, 50 mmol) in 100 ml of acetone was added dropwise over a 10 minute period using a pressure-equalizing dropping funnel. The solution was refluxed for a further 15 minutes. At this point, the entire solution was poured into 2000 mL of vigorously stirring distilled water. The resultant orange-flocculent mass was suction filtered and washed with copious amounts of water. Yield 3.13g, 58 %. The thiourea derivative (0.5 g, 1.1 mmol) was dissolved in 50 mL of 2 M NaOH and brought to a boil. Once the thiourea derivative had fully dissolved, the

solution was cooled to approximately 65 °C. At this point, a 60 °C solution of lead acetate trihydrate (1.44g, 2.2 mmol) in 20 mL of H₂O was added with constant stirring. The stirring was maintained until the solution had turned completely black by the formation of lead sulfide. The solution was filtered, using a large Buchner funnel and the filtrate was collected while the filter flask was immersed in an ice bath. To the cooled filtrate was added an aqueous solution of AsPh₄Cl•H₂O (1.0 g, 2.3 mmol) which immediately precipitated out a beige solid. The product was filtered and washed with copious amounts of water. The crude product was recrystallized by an ether diffusion into a concentrated acetonitrile solution. Yield 0.21 g, 21.1%.

Elemental Analysis based upon [AsPh₄][SCN⁻] (as C₂₅H₂₀N₁As₁S₁, F.W. 441.43 g mol⁻¹: Calcd(%) C, 68.02; H, 4.57; N, 3.17. Found(%) C, 67.96; H, 4.35; N, 3.23.

2.4 Metal Complex Precursor Synthesis

Cu(CF₃SO₃)₂•4H₂O

This was made in a similar manner to that of Crutchley et al⁴⁶. To a 250 mL beaker containing neat trifluoromethanesulfonic acid (triflic acid, 60 g, 0.4 mol) was added copper turnings (2g, 32 mmol). The solution temperature was maintained at 50-60 °C and a watchglass was placed over the beaker. Slowly the acid began to digest the copper turnings. When the digestion was complete, the addition of copper turnings was repeated up to a total mass of 12.75 g of Cu in approximately 2 g portions. When all the copper had been digested, ether was slowly added to the solution until no further precipitation of the product was noticed. The solution was filtered and the product was

washed with approximately 25 mL of ether and vacuum dried overnight. Yield 81.46, 94 %.

[Cu(trpy)(OH₂)](CF₃SO₃)₂

This complex was prepared by using the method described by Crutchley et al⁴⁶, with a small modification. Cu(CF₃SO₃)₂•4H₂O (0.60 g, 1.4 mmol) was dissolved in 40 mL of ethanol. To this was added 2,2':6',2''-terpyridine (trpy, 0.33 g, 1.4 mmol) and the solution was heated at 50 °C for 1 hour. A blue precipitate formed and was filtered by suction. The precipitate was washed with ether and vacuum dried overnight. Yield 0.51 g, 61 %.

[Cu(bpy)₂(OH₂)](CF₃SO₃)₂

This complex was prepared by using the method described by Crutchley et al⁴⁶. Cu(CF₃SO₃)₂•4H₂O (20 g, 46 mmol) was dissolved in 140 mL of distilled water and brought to a boil. To this solution was added 2,2'-bipyridine (14.4 g, 92 mmol) and the solution went from a blue to a navy blue colour. The solution was boiled for a further 5 minutes then immediately placed in an ice bath for 1 hour. Deep blue crystals were filtered out of the solution, washed with 80 mL of cold water followed by 30 mL of ether and vacuum dried overnight. Yield 18.4 g, 58%.

2.5 Linear Chain Synthesis

$[\text{Cu}(\text{trpy})(\text{OH}_2)]_2[\text{CF}_3\text{SO}_3]_2$ (0.76 g, 1.2 mmol) was dissolved in 150 mL of acetone and filtered using Whatman #1 filter paper. To this solution was added $\text{H}_2\text{-meta-dicyd}$ (0.10 g, 0.6 mmol) dissolved in 15 mL of acetone. After stirring for approximately 5 minutes, 2 mL of 0.625 M NaOH was added and immediately a brown powder precipitated out of solution. The brown precipitate was filtered using suction, washed with 10 mL of acetone followed by 10 mL of ether. The product was recrystallized by ether diffusion into an acetonitrile solution. Yield 0.2 g, 31 %. Elemental Analysis based upon $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{CF}_3\text{SO}_3]_{2n}$ (as $\text{C}_{40}\text{H}_{26}\text{N}_{10}\text{Cu}_2\text{F}_6\text{O}_2\text{S}_2$, F.W. 1047.93 g mol⁻¹: Calcd(%) C, 45.85; H, 2.50; N, 12.13. Found(%) C, 45.65; H, 2.61; N, 12.44.

$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n(\text{CF}_3\text{SO}_3)_{2n}$ (0.28g, 0.27 mmol) was dissolved in 80 mL of acetonitrile and filtered using a Whatman #42 filter paper. To the dark brown solution was added sodium tetraphenylborate (0.19g, 0.56 mmol) which immediately precipitated out the light brown precipitate. The product was filtered by suction and recrystallized by a 1 month evaporation of a concentrated DMSO solution of the final product. Yield 0.19 g, 49%. Elemental Analysis based upon $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\cdot(\text{H}_2\text{O})_n$ (as $\text{C}_{86}\text{H}_{68}\text{N}_{10}\text{B}_2\text{Cu}_2\text{O}_1$, F.W. 1406.26 g mol⁻¹: Calcd(%) C, 73.45; H, 4.87; N, 9.96. Found(%) C, 73.57; H, 4.94; N, 10.10.

$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(2\text{DMF})_n$

This complex was made in a similar fashion as $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(\text{H}_2\text{O})_n$ however, the final product was recrystallized by ether diffusion into a concentrated DMF solution of the complex yielding brown, extensively twinned crystals. Yield 0.23 g, 57 %. Elemental Analysis based upon $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(2\text{DMF})_n$ (as $\text{C}_{92}\text{H}_{80}\text{N}_{12}\text{B}_2\text{Cu}_2\text{O}_2$, F.W. 1534.44 g mol⁻¹: Calcd(%) C, 72.01; H, 5.26; N, 10.95. Found(%) C, 71.68; H, 5.08; N, 10.56.

$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{Br}]_{2n}$

$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n(\text{CF}_3\text{SO}_3)_{2n}$ (0.20g, 0.2 mmol) was dissolved in 80 mL of acetonitrile and filtered using a Whatman #42 filter paper. To the dark brown solution was added tetrabutylammonium bromide (0.19g, 0.6 mmol) which immediately precipitated out the dark red/purple precipitate. The product was filtered by suction, washed with 20 mL of acetone and vacuum dried overnight. Yield 0.13 g, 71 %. Elemental Analysis based upon $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{Br}]_{2n}$ (as $\text{C}_{38}\text{H}_{26}\text{N}_{10}\text{Cu}_2\text{Br}_2$, F.W. 909.59 g mol⁻¹: Calcd(%) C, 50.18; H, 2.88; N, 15.40. Found(%) C, 49.73; H, 2.98; N, 15.07.

$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{Cl}]_{2n}$

$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n(\text{CF}_3\text{SO}_3)_{2n}$ (0.28g, 0.27 mmol) was dissolved in 80 mL of acetonitrile and filtered using a Whatman #42 filter paper. To the dark brown solution was added a 10 mL saturated solution of tetraethylammonium chloride (0.10g, 0.6 mmol) which immediately precipitated out the dark blue powder. The product was

filtered by suction, washed with acetone and vacuum dried overnight. Yield 0.17 g, 77%.

Elemental Analysis based upon $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{Cl}]_{2n}$ (as $\text{C}_{38}\text{H}_{26}\text{N}_{10}\text{Cu}_2\text{Cl}_2$, F.W. 820.69 g mol⁻¹: Calcd(%) C, 55.61; H, 3.19; N, 17.07. Found(%) C, 54.96; H, 3.51; N, 16.51.

$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BF}_4]_{2n}$

$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n(\text{CF}_3\text{SO}_3)_{2n}$ (0.28g, 0.26 mmol) was dissolved in 80 mL of acetonitrile and filtered using a Whatman #42 filter paper. To the dark brown solution was added tetrabutylammonium tetrafluoroborate (0.21 g, 0.65 mmol) which immediately precipitated out the light brown precipitate. The product was filtered by suction, washed with 20 mL of acetone, recrystallized by ether diffusion into a concentrated DMF solution of the product and vacuum dried overnight. Yield 0.16 g, 67%. Elemental Analysis based upon $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BF}_4]_{2n}$ (as $\text{C}_{38}\text{H}_{26}\text{N}_{10}\text{B}_2\text{Cu}_2\text{F}_8$, F.W. 923.39 g mol⁻¹: Calcd(%) C, 49.43; H, 2.84; N, 15.17. Found(%) C, 48.83; H, 2.97; N, 14.54.

$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{PF}_6]_{2n}$

$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n(\text{CF}_3\text{SO}_3)_{2n}$ (0.28g, 0.27 mmol) was dissolved in 80 mL of acetonitrile and filtered using a Whatman #42 filter paper. To the dark brown solution was added tetrabutylammonium hexafluorophosphate (0.23 g, 0.6 mmol) which immediately precipitated out the brown precipitate. The product was filtered by suction, washed with 20 mL of acetone, recrystallized by ether diffusion into a concentrated DMF solution of the product and vacuum dried overnight. Yield 0.12 g, 43%. Elemental

Analysis based upon $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{PF}_6]_{2n}$ (as $\text{C}_{38}\text{H}_{26}\text{N}_{10}\text{Cu}_2\text{P}_2\text{F}_{12}$), F.W. 1039.71 g mol⁻¹: Calcd(%) C, 43.90; H, 2.52; N, 13.47. Found(%) C, 43.70; H, 2.64; N, 13.33.

$[\{\text{Cu}(\text{bpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{CF}_3\text{SO}_3]_{2n}\cdot(2\text{H}_2\text{O})_n$

$[\text{Cu}(\text{bpy})_2(\text{OH}_2)](\text{CF}_3\text{SO}_3)_2$ (1.0 g, 1.4 mmol) was dissolved, with slight heating, in 60 mL of acetone. To this stirring solution was added a solution $\text{H}_2\text{-meta-dicyd}$ (0.114g, 0.7 mmol) dissolved in 15 mL of acetone. The solution was left to stir at room temperature for 30 minutes then TEA (0.15 g, 1.4 mmol) dissolved in 20 mL of acetone was added with stirring. The solution went from a deep blue to a purple colour with the purple colour due to a suspended precipitate. The precipitate was filtered by suction, washed with 50 mL of acetone followed by 20 mL of ether. Yield 690 mgs, 53 %.

Elemental Analysis based upon $[\{\text{Cu}(\text{bpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{CF}_3\text{SO}_3]_{2n}\cdot(2\text{H}_2\text{O})_n$ (as $\text{C}_{30}\text{H}_{24}\text{N}_8\text{Cu}_2\text{F}_6\text{O}_8\text{S}_2$), F.W. 929.78 g mol⁻¹: Calcd(%) C, 38.75; H, 2.60; N, 12.05. Found(%) C, 39.27; H, 2.42; N, 12.47.

$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-Me-meta-dicyd}]_n[\text{BPh}_4]_{2n}\cdot(\text{H}_2\text{O})_n$

To a solution of $\text{Cu}(\text{CF}_3\text{SO}_3)_2\cdot 4\text{H}_2\text{O}$ (1.86g, 43 mmol) dissolved in 50 mL of acetone was added 2,2':6',2''-terpyridine (1.00 g, 43 mmol) in 10 mL of acetone and $\text{H}_2\text{-Me-meta-dicyd}$ (0.37 g, 22 mmol). To the stirring dark blue solution was then added 0.1 mL of triethylamine which immediately turned the solution brown. The solution was allowed to stir for one hour. The brown precipitate was filtered by suction. Yield 2 g, 43 %. The precipitate was then dissolved in 200 mL of acetonitrile and filtered using a

Whatman #42 filter paper. To the dark brown solution was then added sodium tetraphenylborate (0.4g, 0.56 mmol) which immediately precipitated out the light brown precipitate. The product was filtered by suction and recrystallized by a 1 week evaporation of a concentrated DMSO solution of the final product. Yield 0.55 g, 21 %. Elemental Analysis based upon $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-Me-meta-dicyd}]_n[\text{BPh}_4]_{2n}\cdot(\text{H}_2\text{O})_n$ (as $\text{C}_{87}\text{H}_{71}\text{N}_{10}\text{Cu}_2\text{B}_2\text{O}_1$), F.W. $1421.30 \text{ g mol}^{-1}$: Calcd(%) C, 73.52; H, 5.04; N, 9.85. Found(%) C, 73.90; H, 5.24; N, 9.61.

$[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$

To a methanolic solution of $\text{Cu}(\text{CF}_3\text{SO}_3)_2\cdot 4\text{H}_2\text{O}$ (0.3g, 0.7 mmol) was added a methanolic solution of $[\text{AsPh}_4][\text{SCN}]$ (0.64g, 14 mmol). Upon addition of the $[\text{AsPh}_4][\text{SCN}]$ the solution turned pale blue to a dark yellow in colour. The solution was left to evaporate in the dark. After four days in the dark, evaporation of the yellow/brown solution yielded small white crystals of $(\text{AsPh}_4)(\text{CF}_3\text{SO}_3)$ and very large brown rectangular prisms of the product. The dark brown crystals of were manually separated and washed with hot ethanol to remove any residual $(\text{AsPh}_4)(\text{CF}_3\text{SO}_3)$. Yield 0.1 g, 23 %. Elemental Analysis based upon $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$ (as $\text{C}_{27}\text{H}_{20}\text{N}_3\text{Cu}_1\text{As}_1\text{S}_3$), F.W. $621.14 \text{ g mol}^{-1}$: Calcd(%) C, 52.21; H, 3.25; N, 6.76. Found(%) C, 51.47; H, 3.01; N, 6.48.

2.6 Material Synthesis

$\text{Cu}(\text{CF}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.32 g, 0.74 mmol) was dissolved in 40 mL of acetone. To this stirring solution was added H_2 -*meta*-dicyd (0.117 g, 0.74 mmol). Upon addition of the bridging ligand, the solution slightly darkened its blue colour. Next, TEA (0.20 mL, 1.9 mmol) was added to the solution which immediately precipitated a dark blue product. The product was filtered by suction, washed with 20 mL of acetone and vacuum dried overnight. Yield 110 mg, 51%. Elemental Analysis based on $[\text{Cu}_{12}(\text{meta-dicyd})_{11}(\text{C}_3\text{H}_6\text{O})_{12}(\text{CF}_3\text{SO}_3)_2]_n$ as, F.W. 3475.27 g mol⁻¹: Calcd(%) C, 43.55; H, 3.36; N, 17.73. Found(%) C, 43.65; H, 2.73; N, 18.05.

2.7 Physical Measurements

2.7.1 Infrared Spectroscopy

Infrared Spectroscopy was performed on a Bomem Michelson 120 FT-IR as KBr pellets. Data was analyzed using Bomem Grams/386 version 3.04.

2.7.2 Nuclear Magnetic Resonance Spectroscopy

All ¹H and ¹³C-NMR were performed on a Bruker AMX-400 Spectrometer at 300K using ultra-imperial grade PP507 sample tubes (Wilmad) and were referenced to solvent resonances for TMS.

2.7.3 X-ray Crystallography

The X-ray structures of two ligands and two one-dimensional chain complexes were determined by Dr. G.P.A. Yap at the University of Ottawa. Data were collected on a Bruker SMART CCD diffractometer using a multi-run routine which collects two-dimensional data frames with an effective coverage of > 80% of the Ewald sphere. The standard Lorentz polarization correction was applied. All non-hydrogen atoms were refined with anisotropic displacement coefficients excepting those atoms on the anions and solvent molecules which were refined isotropically. All hydrogen atoms were treated as idealized contributions excepting those hydrogen atoms on the water molecules which were ignored by their inclusion in calculations for intrinsic properties. The structures were solved by direct methods, completed by subsequent Fourier syntheses and refined with full-matrix least-squares methods. All scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library.

2.7.4 Mass Spectrometry (MS)

Direct Probe Mass Spectrometry was performed at the Ottawa-Carleton Universities Centre for Mass Spectrometry.

2.7.5 Magnetic Susceptibility Measurements

Variable temperature magnetic susceptibility measurements were performed at the Brockhouse Institute for Materials Research (BIMR) at McMaster University, Hamilton, Ontario, by Professor J.E. Greedan and Raju Nandyala using a Quantum Design Superconducting Quantum Interference Device (SQUID) susceptometer. Measurements

were made on powder samples which were transferred to a type 0 gelatin capsule. The capsule was then embedded into a white drinking straw (some organic dyes can contribute significantly to the experimental susceptibility) and secured to the sample insert rod with a copper wire. The sample was slowly inserted into the susceptometer so as not to allow rapid evolution of He(l), centered within the superconducting detection coil (either manually or by computer control) and allowed to follow a pre-programmed control sequence to collect the raw data.

2.7.6 Elemental Analyses

Elemental analyses were performed by Canadian Microanalytical Services Ltd., Delta, British Columbia, Canada and at the Chemistry Department of the University of Ottawa.

2.7.7 Thermal Gravimetric Analysis

TGA were carried out on a Seiko TB/DTA 320 purged with 200 mL/min of N₂. Degradation temperatures were determined from experiments carried out at 10 °C/min from temperatures corresponding to 5% weight loss. In this technique, a sample is heated as its mass is measured. Thus, the TG signal consists of a weight gain or loss. The thermal stability of materials is commonly probed by TG scans by measuring the temperature at which significant weight loss from degradation begins to occur. The method used to determine the sample's decomposition temperature was to record the temperature corresponding to 5% weight loss, reported as T_d. Comparison of these

temperatures is often used as a means of qualitatively comparing thermal stabilities of different materials.

2.8 Modeling

2.8.1 Molecular Modeling

Molecular modeling was performed using a Silicon Graphics Instruments (SGI) Workstation. The software used was Spartan 5.0 for Unix workstations. Calculation methods included AM1 for all ligand calculations and PM3(tm) semi-empirical method which included basis sets for transition metals. In the case of the one-dimensional chain systems, the fragments were drawn and crystallographically obtained bond lengths and angles were input manually and constrained during geometry minimization.

2.8.2 Magnetic Modeling

All magnetic modeling was performed on an Intel Pentium 200 MMX processor using Jandel Scientific's software package Table Curve version 1.0 for Windows and Sigma Plot version 1.02 for Windows.

CHAPTER 3

THE BRIDGING LIGANDS

3.1 Synthesis

3.1.1 *meta*-dicyd based bridging ligands

The synthesis of the two meta-substituted dicyanamidobenzene dianion ligands was accomplished in a manner similar to their *para*-isomers done in our laboratory for many years as shown in scheme 3.1. The phenylenediamines were reacted with benzoyl thiocyanate (formed by the reaction of ammonium thiocyanate and benzoyl chloride) in acetone under refluxing conditions. The product of this reflux, a benzoyl thiourea derivative, was heated in aqueous base giving a thiourea derivative and desulfurized with Pb(II) leaving a dianionic dicyanamidobenzene in solution. The dianion was precipitated from solution, as the neutral form of the dicyanamidobenzene, by acetic acid. Both H₂-*meta*-dicyd and H₂-Me-*meta*-dicyd were produced in this fashion. The unsubstituted dicyd, H₂-*meta*-dicyd, was converted to two different salt forms of the dianion. The first, a tetraphenylarsonium salt of meta-dicyd²⁻ was formed by the addition of an aqueous solution of tetraphenylarsonium chloride into a caustic solution of H₂-*meta*-dicyd. The second, a thallium(I) salt of *meta*-dicyd²⁻ was formed by combining thallium(I) acetate and H₂-*meta*-dicyd solutions in a 1:1 acetone/water mixture and deprotonating the ligand using triethylamine. All three forms of the ligand resulted in a bridging ligand easily adapted to various reaction conditions and practically all solvents.

Scheme 3.1 – Synthesis of the H₂-*meta*-dicyd substituted bridging ligands.

Caution had to be taken in two areas of the H₂-*meta*-dicyd ligand syntheses. It has been shown that these compounds tend to dimerize specifically during the desulfurization step and thus must be done at temperatures no higher than 60°C. The formation of the dimer can be detected by infrared spectroscopy showing a strong

band at approximately 1676 cm^{-1} due to $\nu(\text{C}=\text{N})$ of the dimer, shown below.

3.1.2 Tetraphenylarsonium thiocyanato bridging ligand

In our attempts to synthesize an ortho-substituted dicyd²⁻ dianion bridging ligand, an interesting twist occurred which lead us to incorporate the unexpected compound, [AsPh₄][SCN], into this molecular magnetic study. It was our hypothesis that, due to steric hinderance and proximity of charged species, SCN⁻ was liberated and consequently precipitated out of solution as a tetraphenylarsonium salt. Shown in scheme 3.2, the ortho-diamine compound reacted with benzoyl thiocyanate in a similar manner to that of the *meta*- and *para*-isomers. Simple characterizations gave conflicting results and not until all tests, specifically a crystal structure, had been performed, did we realize that a thiocyanato salt had been made.

Scheme 3.2 - Synthesis of [AsPh₄][SCN]

3.2 Infrared Spectroscopy

The infrared spectra of the two *meta*-substituted dicyd ligands, the AsPh_4^+ and Tl^+ salts of *meta*-dicyd²⁻ and the thiocyanato ligand are shown in figures 3.1-3.5, respectively. The *meta*-dicyd ligands show the characteristically strong $\nu(\text{N}=\text{C}=\text{N})$ stretches and the thiocyanato ligand the strong $\nu(\text{N}=\text{C}=\text{S})$ stretch in the 2050-2250 cm^{-1} range, varying from their salt forms to the neutral forms of the compounds. The IR frequencies are summarized in table 3.1.

Table 3.1 – Characteristic $\nu(\text{N}=\text{C}=\text{N})$ and $\nu(\text{N}=\text{C}=\text{S})$ stretching frequencies.

Ligand	$\nu(\text{N}=\text{C}=\text{N})^{\text{a}}$ and $\nu(\text{N}=\text{C}=\text{S})^{\text{b}}$ (cm^{-1})
H_2 - <i>meta</i> -dicyd	2230 ^a
H_2 -Me- <i>meta</i> -dicyd	2230 ^a
$[\text{AsPh}_4]_2[\text{meta-dicyd}]$	2088 ^a
$\text{Tl}_2(\text{meta-dicyd})$	2111 ^a
$[\text{AsPh}_4][\text{SCN}]$	2052 ^b

The vibrational energy decrease going from the protonated form the *meta*-dicyd ligand to that of the salt forms (Tl^+ and AsPh_4^+) is due to the change from triple bond character to double bond character, respectively. Other major bands of note seen on the *meta*-dicyd ligands are the weak aromatic C-H stretches in the range of 3000-3100 cm^{-1} and C-H bends in the range of 680-760 cm^{-1} . The large broad bands seen at approximately 3400 cm^{-1} are due to water, most of which is due to the hygroscopic nature of the KBr pellet medium.

Figure 3.1 – IR spectrum of H₂-*meta*-dicyd (KBr disk).

Figure 3.2 – IR spectrum of H₂-Me-*meta*-dicyd (KBr disk).

Figure 3.3 – IR spectrum of [AsPh₄]₂[*meta*-dicyd] (KBr disk).

Figure 3.4 – IR spectrum of [Tl]₂[*meta*-dicyd] (KBr disk).

Figure 3.5 – IR spectrum of $[\text{AsPh}_4][\text{SCN}]$ (KBr disk).

3.3 NMR Spectroscopy

The ^1H -NMR and ^{13}C -NMR spectra of $\text{H}_2\text{-Me-}i\text{meta}$ -dicyd are shown in figures 3.6 and 3.7 and table 3.2 summarizes the chemical shifts for both $\text{H}_2\text{-Me-}i\text{meta}$ -dicyd and $\text{H}_2\text{-}i\text{meta}$ -dicyd. The NMR spectra reflected well the expected symmetry of the bridging ligands. In the case of $\text{H}_2\text{-Me-}i\text{meta}$ -dicyd and referring to the labeling on figure 3.6, the ^1H -NMR spectrum shows a strong singlet at 2.01 ppm (1-position) due to the methyl substituent. The phenyl protons at positions 2 and 3 appear as a doublet and triplet, centered at 6.80 and 7.23 ppm, respectively. At position 4, the unusually strong singlet centered at 9.46 ppm is due to the amide hydrogen. It is unusually strong in the sense that the *para*-substituted H_2 -dicyd ligand usually showed a much

Figure 3.6 – ^1H -NMR spectrum of $\text{H}_2\text{-Me-meta-dicyd}$ in DMSO-d^6 (at 300K). The pentet centered at 2.45 ppm is background from DMSO-d^6 .

less intense peak due to their concentration and solvent dependence.⁴⁷

Table 3.2 – ^1H -NMR chemical shifts of $\text{H}_2\text{-meta-dicyd}$ and $\text{H}_2\text{-Me-meta-dicyd}$.*

Ligands	1-Me ^a and 1-Ph ^b	2-Ph	3-Ph	N-H
$\text{H}_2\text{-meta-dicyd}^b$	6.75 (1,s)	6.76 (2,d)	7.36 (1,t)	7.96 (2,s)
$\text{H}_2\text{-Me-meta-dicyd}^a$	2.01 (3,s)	6.80 (2,d)	7.23 (1,t)	9.46 (2,s)

* Integrations are shown in brackets next to the chemical shift values. The values in ppm are referenced to the internal standard, TMS at 0.00 ppm. $\text{H}_2\text{-meta-dicyd}$ was performed in acetone- d^6 and $\text{H}_2\text{-Me-meta-dicyd}$ was performed in DMSO-d^6 . Abbreviations s=singlet, d=doublet, t=triplet.

^{13}C -NMR further confirmed the geometry and the number of carbon atoms in the two bridging ligands via symmetry arguments. The ^{13}C -NMR of $\text{H}_2\text{-Me-meta-dicyd}$, shown in figure 3.7, clearly shows this and the C atom numbering scheme can

be easily followed. Carbon atoms totaling six, are labeled such that symmetrically equivalent carbons are omitted opposite to the plane of symmetry bisecting carbon's 1,2 and 5. Carbon 1, the methyl carbon, appears at 10.9 ppm. The ring current-deshielded phenyl carbons, 5,4,3 and 2 have chemical shift values of 110.4, 112.5, 112.7 and 127.8 ppm, respectively.⁴⁷ The chemical shift of phenyl carbon 3 is slightly upfield to phenyl carbon 4 due to its proximity to the slightly more electronegative nitrogen atom. Finally, the cyanamide carbon at position 6 shows a greatly deshielded chemical shift of 137.9 ppm. The values for these chemical shifts and for those of the H₂-*meta*-dicyd ligand are shown in table 3.3.

Figure 3.7 – ¹³C-NMR spectrum of H₂-Me-*meta*-dicyd in DMSO-d₆ (at 300K). The septet centered at 39.3 ppm is background from DMSO-d₆.

Table 3.3 – ^{13}C -NMR chemical shifts* of H_2 -*meta*-dicyd and H_2 -Me-*meta*-dicyd.

Ligands	1-CH ₃	2-Ph	3-Ph	4-Ph	5-Ph	6-NCN
H_2 - <i>meta</i> -dicyd	n/a	111.8	132.5	110.7	102.9	141.5
H_2 -Me- <i>meta</i> -dicyd	10.9	127.8	112.7	112.5	110.4	137.9

* The values in ppm are referenced to the solvent chemical shifts. H_2 -*meta*-dicyd was performed in acetone- d_6 and H_2 -Me-*meta*-dicyd was performed in DMSO- d_6 .

3.4 Mass Spectrometry

The mass spectra of both H_2 -*meta*-dicyd and H_2 -Me-*meta*-dicyd were performed on the ligands in the early stages of their synthesis as a quick and easy means to determine the molecular weight, indicated by the m/e peaks, and to verify via fragmentation patterns, that certain phenyl substituents were present. The MS plot for H_2 -Me-*meta*-dicyd is shown in figure 3.8 and the observed fragments, seen from the most intense peaks on the spectrum, are tabulated, for both ligands, in table 3.4.

The parent ion peak for H_2 -Me-*meta*-dicyd was found at 172, corresponding to the molecular weight of this ligand, $172.19 \text{ g mol}^{-1}$. Two anomalies on the spectra should also be discussed. First, the three peaks at 197, 241 and 259 are present on all spectra run at the Ottawa University facility and is due to column material bleed-off. Second, the minor peaks which seem to surround the major fragment peaks are due primarily to isotope effects but also due to small variations in fragment weight caused by random loss of hydrogens. Beginning from the m/e peak, expected fragment masses are subtracted. The mass of the small fragment plus the large fragment always totals that of the parent ion allowing for sporadic hydrogen loss in the process.

Figure 3.8 – The Direct Probe Mass Spectrum of H_2 -Me-*meta*-dicyd.

Table 3.4 – Selected Mass Spectral fragments for H_2 -Me-*meta*-dicyd and H_2 -*meta*-dicyd.

H_2 -Me- <i>meta</i> -dicyd*		H_2 - <i>meta</i> -dicyd*	
172	M^+	158	M^+
156	$M^+ - CH_3$	133	$M^+ - CN$
145	$M^+ - CN$	116	$M^+ - NCNH$
129	$M^+ - NCNH$	105	$M^+ - NCN + N$
91	$M^+ - 2NCNH$	90	$M^+ - NCN + CN$
77	$M^+ - 2NCNH + CH_3$	77	$M^+ - 2NCNH$

* unity variation in the peak assignments are due to concurrent proton loss

3.5 X-Ray Crystallography

3.5.1 [AsPh₄]₂[*meta*-dicyd]

Large, pale-yellow rectangular prisms of [AsPh₄]₂[*meta*-dicyd] were grown by ether diffusion into a saturated acetonitrile solution of the ligand. In this case, as with ligand crystal structures performed on the *para*-substituted dicyd's, the cyanamide moiety is coplanar with the phenyl ring. A ball and stick diagram of this ligand is shown in figure 3.9 and the relevant X-ray crystallographic data and data collection details are summarized in tables 3.5-3.9. There are a couple of main points of interest existing in this structure determination.

A ball and stick diagram of the bridging ligand, not an ORTEP, was unavoidably used to elucidate the structure. Only the As(V) cation has a thermal ellipsoid representing its position in space. This point, represented by a poor R indices value of 0.1264 (unweighted), can be explained by the unit cell itself. The *meta*-dicyd²⁻ dianion, surrounded by tetraphenyl arsonium cations on all sides, actually “rattles” in this AsPh₄⁺ cage, thus causing the poor R indices value.⁴⁸ Another interesting result in this structure is that the cyanamide moieties are in a *syn*-conformation, thus bringing the negatively charged species close to one another. This is unprecedented in dicyd²⁻ chemistry. A factor that possibly contributes to this conformer is the water of crystallization present in the unit cell. Two molecules of water, which are most likely hydrogen bonding to the cyanamide moieties, both improve the goodness of fit and the R indices of the structure when included in the refinement and fit in the elemental analysis.

Figure 3.9 – Ball and stick diagram of $[\text{AsPh}_4]_2[\text{meta-dicyd}]$. Only one of the two AsPh_4^+ cations are shown for clarity.

Table 3.5 – Crystal data and structural refinement information for the X-ray structural determination of $[\text{AsPh}_4]_2[\text{meta-dicyd}^2]$

Empirical formula	$\text{C}_{56} \text{H}_{48} \text{As}_2 \text{N}_4 \text{O}_2$
Formula weight	958.82
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$\text{P2}_1/\text{n}$
Unit cell dimensions	$a = 10.390(1) \text{ Å}$ $\alpha = 90^\circ$ $b = 16.134(2) \text{ Å}$ $\beta = 97.466(1)^\circ$ $c = 13.936(1) \text{ Å}$ $\gamma = 90^\circ$
Volume	$2316.5(4) \text{ Å}^3$
Z	2
Density (calculated)	1.375 Mg/m^3
Absorption coefficient	1.490 mm^{-1}
F(000)	988
Crystal size	0.30 x 0.20 x 0.20 mm
Theta range for data collection	1.94° to 28.86°
Limiting indices	$-13 \leq h \leq 13$, $-18 \leq k \leq 21$, $-18 \leq l \leq 14$
Reflections collected	14700
Independent reflections	5466 [$R(\text{int}) = 0.0712$]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5465 / 11 / 223
Goodness-of-fit on F^2	1.260
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.1225$, $wR2 = 0.2974$
R indices (all data)	$R1 = 0.1532$, $wR2 = 0.3100$
Largest diff. peak and hole	2.227 and -1.008 eÅ^{-3}

Table 3.6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{AsPh}_4]_2[\text{meta-dicyd}^{2-}]$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
As	7557(1)	1035(1)	5671(1)	26(1)
O	9989(18)	95(11)	8900(12)	146(6)
N(1)	15988(23)	-1535(15)	11121(17)	63(6)
N(2)	17214(19)	-640(14)	10328(14)	30(5)
N(3)	12073(26)	75(17)	10017(18)	67(6)
N(4)	13231(21)	1093(13)	9415(15)	37(5)
C(1)	15265(13)	316(8)	9798(10)	37(4)
C(2)	16583(14)	159(7)	9820(11)	62(7)
C(3)	17359(10)	707(8)	9383(11)	87(10)
C(4)	16816(10)	1413(7)	8923(8)	13(3)
C(5)	15498(11)	1571(7)	8901(10)	63(7)
C(6)	14722(9)	1022(9)	9338(11)	55(6)
C(7)	16438(23)	-1199(13)	10784(16)	29(5)
C(8)	12612(26)	409(19)	9809(19)	41(7)
C(11)	5967(7)	2436(4)	5221(7)	74(5)
C(12)	4946(9)	2974(4)	5315(8)	89(6)
C(13)	4061(7)	2787(5)	5950(7)	60(4)
C(14)	4197(7)	2062(7)	6492(6)	93(6)
C(15)	5218(8)	1524(5)	6399(6)	68(4)
C(16)	6103(6)	1711(4)	5763(5)	28(2)
C(21)	7213(7)	-94(3)	7196(4)	40(2)
C(22)	7126(9)	-873(4)	7610(4)	53(3)
C(23)	7212(10)	-1582(3)	7055(5)	69(4)
C(24)	7385(10)	-1512(3)	6086(5)	74(5)
C(25)	7471(9)	-734(4)	5671(4)	49(3)
C(26)	7385(7)	-25(3)	6226(4)	31(2)
C(31)	6614(5)	603(4)	3743(4)	36(2)
C(32)	6714(6)	423(4)	2780(4)	43(3)
C(33)	7894(7)	520(4)	2425(3)	47(3)
C(34)	8975(5)	799(4)	3032(4)	41(3)
C(35)	8875(5)	979(4)	3995(4)	38(2)
C(36)	7695(5)	881(4)	4350(3)	25(2)
C(41)	9410(6)	2336(4)	5939(4)	39(2)
C(42)	10458(6)	2768(3)	6421(5)	45(3)
C(43)	11147(5)	2440(4)	7257(5)	41(3)
C(44)	10788(6)	1680(4)	7611(4)	55(3)
C(45)	9740(6)	1248(3)	7129(5)	41(3)
C(46)	9051(5)	1576(3)	6293(4)	26(2)

Table 3.7. Bond lengths [Å] and angles [°] for [AsPh₄]₂[*meta*-dicyd²⁻].

As-C(16)	1.881(5)	C(7)-N(2)-C(2)	120(2)
As-C(36)	1.881(4)	C(8)-N(4)-C(6)	118(2)
As-C(46)	1.890(4)	C(2)-C(1)-C(6)	120
As-C(26)	1.895(5)	C(1)-C(2)-C(3)	120
N(1)-C(7)	0.89(2)	C(1)-C(2)-N(2)	120.8(12)
N(2)-C(7)	1.41(3)	C(3)-C(2)-N(2)	119.2(12)
N(2)-C(2)	1.57(2)	C(2)-C(3)-C(4)	120
N(3)-C(8)	0.86(2)	C(5)-C(4)-C(3)	120
N(4)-C(8)	1.42(3)	C(6)-C(5)-C(4)	120
N(4)-C(6)	1.57(2)	C(5)-C(6)-C(1)	120
C(1)-C(2)	1.39	C(5)-C(6)-N(4)	128.1(12)
C(1)-C(6)	1.39	C(1)-C(6)-N(4)	111.9(12)
C(2)-C(3)	1.39	N(1)-C(7)-N(2)	175(3)
C(3)-C(4)	1.39	N(3)-C(8)-N(4)	166(4)
C(4)-C(5)	1.39	C(12)-C(11)-C(16)	120
C(5)-C(6)	1.39	C(13)-C(12)-C(11)	120
C(11)-C(12)	1.39	C(14)-C(13)-C(12)	120
C(11)-C(16)	1.39	C(15)-C(14)-C(13)	120
C(12)-C(13)	1.39	C(14)-C(15)-C(16)	120
C(13)-C(14)	1.39	C(15)-C(16)-C(11)	120
C(14)-C(15)	1.39	C(15)-C(16)-As	121.4(4)
C(15)-C(16)	1.39	C(11)-C(16)-As	118.5(4)
C(21)-C(22)	1.39	C(22)-C(21)-C(26)	120
C(21)-C(26)	1.39	C(21)-C(22)-C(23)	120
C(22)-C(23)	1.39	C(24)-C(23)-C(22)	120
C(23)-C(24)	1.39	C(23)-C(24)-C(25)	120
C(24)-C(25)	1.39	C(26)-C(25)-C(24)	120
C(25)-C(26)	1.39	C(25)-C(26)-C(21)	120
C(31)-C(32)	1.39	C(25)-C(26)-As	119.9(3)
C(31)-C(36)	1.39	C(21)-C(26)-As	120.1(3)
C(32)-C(33)	1.39	C(32)-C(31)-C(36)	120
C(33)-C(34)	1.39	C(31)-C(32)-C(33)	120
C(34)-C(35)	1.39	C(34)-C(33)-C(32)	120
C(35)-C(36)	1.39	C(35)-C(34)-C(33)	120
C(41)-C(42)	1.39	C(34)-C(35)-C(36)	120
C(41)-C(46)	1.39	C(35)-C(36)-C(31)	120
C(42)-C(43)	1.39	C(35)-C(36)-As	121.1(3)
C(43)-C(44)	1.39	C(31)-C(36)-As	118.7(3)
C(44)-C(45)	1.39	C(42)-C(41)-C(46)	120
C(45)-C(46)	1.39	C(43)-C(42)-C(41)	120
C(16)-As-C(36)	107.9(3)	C(42)-C(43)-C(44)	120
C(16)-As-C(46)	108.7(3)	C(45)-C(44)-C(43)	120
C(36)-As-C(46)	110.3(3)	C(44)-C(45)-C(46)	120
C(16)-As-C(26)	112.1(3)	C(45)-C(46)-C(41)	120

C(36)-As-C(26)	107.7(3)	C(45)-C(46)-As	120.8(3)
C(46)-As-C(26)	110.2(3)	C(41)-C(46)-As	119.1(3)

Table 3.8 - Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{AsPh}_4]_2[\text{meta-dicyd}^{2-}]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
As	27(1)	26(1)	25(1)	-2(1)	2(1)	0(1)
O	185(17)	129(14)	125(12)	11(10)	21(12)	0(12)
C(11)	61(8)	35(7)	135(14)	16(8)	51(9)	8(6)
C(12)	72(10)	16(6)	184(19)	5(8)	34(11)	9(6)
C(13)	32(6)	74(9)	72(9)	-33(7)	0(6)	19(6)
C(14)	63(9)	165(18)	58(9)	36(10)	32(7)	60(11)
C(15)	50(7)	103(11)	55(7)	37(8)	30(6)	36(7)
C(16)	28(4)	27(5)	28(4)	-7(4)	0(3)	1(4)
C(21)	50(6)	35(5)	36(5)	11(4)	10(5)	8(5)
C(22)	70(8)	53(8)	36(6)	14(5)	6(5)	-4(6)
C(23)	116(12)	32(6)	55(8)	16(6)	-6(8)	-25(7)
C(24)	148(15)	25(6)	41(7)	2(5)	-18(8)	-25(7)
C(25)	80(8)	32(5)	33(5)	-5(5)	3(5)	-12(6)
C(26)	34(5)	28(5)	28(5)	4(4)	-7(4)	1(4)
C(31)	43(6)	28(5)	35(5)	-5(4)	-1(4)	-1(4)
C(32)	65(7)	30(5)	34(5)	2(4)	-2(5)	-1(5)
C(33)	78(8)	25(5)	36(6)	-9(4)	3(5)	6(5)
C(34)	55(7)	26(5)	48(6)	-1(4)	24(5)	10(4)
C(35)	40(5)	39(5)	34(5)	-6(4)	4(4)	9(5)
C(36)	26(4)	16(4)	32(4)	-1(3)	0(4)	3(3)
C(41)	40(5)	44(6)	33(5)	4(4)	1(4)	-7(5)
C(42)	47(6)	35(6)	53(7)	1(5)	1(5)	-14(5)
C(43)	29(5)	26(5)	65(7)	-13(5)	-3(5)	-5(4)
C(44)	44(6)	46(7)	66(8)	-5(6)	-25(6)	6(5)
C(45)	41(6)	20(5)	56(7)	0(4)	-13(5)	6(4)
C(46)	28(4)	24(4)	24(4)	-7(3)	-1(3)	3(3)

Table 3.9 - Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{AsPh}_4]_2[\text{meta-dicyd}^{2-}]$.

	x	Y	z	U(eq)
H(0A)	9873(18)	-390(11)	9111(12)	176
H(0B)	10514(18)	424(11)	9227(12)	176
H(1A)	14740(13)	-54(8)	10094(10)	44
H(3A)	18251(11)	601(12)	9398(16)	104
H(4B)	17341(14)	1784(9)	8628(12)	15
H(5A)	15130(15)	2048(9)	8590(15)	75
H(11A)	6565(7)	2563(4)	4792(7)	88
H(12A)	4854(13)	3465(5)	4948(11)	107
H(13A)	3370(9)	3151(7)	6013(10)	72
H(14A)	3598(11)	1935(9)	6921(9)	112
H(15A)	5310(11)	1033(7)	6765(9)	81
H(21A)	7155(7)	385(3)	7571(4)	48
H(22A)	7009(13)	-920(6)	8265(4)	64
H(23A)	7154(14)	-2108(4)	7335(7)	83
H(24A)	7443(14)	-1991(4)	5710(7)	89
H(25A)	7588(13)	-686(5)	5016(4)	59
H(31A)	5816(5)	537(4)	3983(4)	43
H(32A)	5983(7)	234(6)	2369(5)	52
H(33A)	7962(10)	398(6)	1774(4)	56
H(34A)	9773(6)	865(6)	2792(6)	50
H(35A)	9606(5)	1167(6)	4406(6)	45
H(41A)	8944(6)	2557(4)	5374(4)	47
H(42A)	10701(9)	3281(4)	6182(7)	54
H(43A)	11855(7)	2732(5)	7583(7)	49
H(44A)	11253(9)	1459(6)	8176(6)	65
H(45A)	9497(9)	735(4)	7368(7)	49

3.5.2 $[\text{AsPh}_4][\text{SCN}]$

As eluded to in the experimental section, this ligand was somewhat of a surprise. When consulting with the crystallographer, the three atom anion, was initially assumed to be HNCN^- as such a ligand and bridged complex incorporating this ligand had been accidentally synthesized previously.⁴⁹ A fit was attempted for HNCN^- resulting in a poor goodness of fit but, nonetheless, good R indices. However, noting the asymmetry of the anion, the conclusion was reached that, indeed,

thiocyanate had been attained, and now, both the goodness of fit and the R indices reflected this. The ORTEP plot is shown below in figure 3.9 and both the crystallographic data and data collection details are summarized in tables 3.10-3.14.

Figure 3.10 – ORTEP plot showing the atom labeling scheme and 30% probability ellipsoids for [AsPh₄][SCN]. The hydrogen atoms are omitted for clarity.

Table 3.10 – Crystal data and structural refinement information for the X-ray structural determination of [AsPh₄][SCN].

Empirical formula	C ₂₅ H ₂₀ As ₁ N ₁ S ₁
Formula weight	441.40
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	I-4
Unit cell dimensions	a = 12.015(2) Å alpha = 90° b = 12.015(2) Å beta = 90° c = 7.285(2) Å gamma = 90°
Volume	1051.7(4) Å ³
Z	2
Density (calculated)	1.394 Mg/m ³
Absorption coefficient	1.725 mm ⁻¹
F(000)	452
Crystal size	0.4 x 0.4 x 0.4 mm
Theta range for data collection	2.40° to 28.71°
Limiting indices	-15 ≤ h ≤ 15, 0 ≤ k ≤ 15, 0 ≤ l ≤ 9
Reflections collected	3329
Independent reflections	1233 [R(int) = 0.0561]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.927988 and 0.589755
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1233 / 0 / 73
Goodness-of-fit on F ²	1.060
Final R indices [I > 2sigma(I)]	R1 = 0.0275, wR2 = 0.0732
R indices (all data)	R1 = 0.0286, wR2 = 0.0734
Absolute structure parameter	0.075(17)
Extinction coefficient	0.036(3)
Largest diff. peak and hole	0.278 and -0.259 e•Å ⁻³

Table 3.11. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{AsPh}_4]^2[\text{meta-dicyd}^{2-}]$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
As	0	5000	2500	35(1)
C(1)	-2143(2)	4486(2)	4052(4)	47(1)
C(2)	-2834(3)	3965(3)	5304(5)	59(1)
C(3)	-2416(3)	3190(3)	6502(4)	62(1)
C(4)	-1299(3)	2914(3)	6485(5)	68(1)
C(5)	-593(2)	3445(3)	5269(4)	57(1)
C(6)	-1017(2)	4238(2)	4060(3)	39(1)
N(1)	-5000	5000	7800(50)	112(10)
C(7)	-5000	5000	9360(40)	84(8)
S(1)	-5000	5000	11490(10)	118(5)

Table 3.12 - Bond lengths [$\text{\AA}$] and angles [$^\circ$] for $[\text{AsPh}_4][\text{SCN}]$.

Bond Lengths		Bond Angles	
As-C(6)#1	1.903(2)	C(6)#1-As-C(6)#2	110.89(7)
As-C(6)#2	1.903(2)	C(6)#1-As-C(6)	106.67(14)
As-C(6)	1.903(2)	C(6)#2-As-C(6)	110.89(7)
As-C(6)#3	1.903(2)	C(6)#1-As-C(6)#3	110.89(7)
C(1)-C(2)	1.383(4)	C(6)#2-As-C(6)#3	106.67(14)
C(1)-C(6)	1.385(4)	C(6)-As-C(6)#3	110.89(7)
C(2)-C(3)	1.371(5)	C(2)-C(1)-C(6)	119.0(3)
C(3)-C(4)	1.383(5)	C(3)-C(2)-C(1)	120.5(3)
C(4)-C(5)	1.382(4)	C(2)-C(3)-C(4)	120.8(3)
C(5)-C(6)	1.395(4)	C(3)-C(4)-C(5)	119.4(3)
N(1)-S(1)#4	0.52(4)	C(4)-C(5)-C(6)	119.7(3)
N(1)-C(7)	1.13(5)	C(1)-C(6)-C(5)	120.4(2)
C(7)-S(1)#4	0.62(2)	C(1)-C(6)-As	121.4(2)
C(7)-C(7)#4	0.94(5)	C(5)-C(6)-As	118.13(19)
C(7)-S(1)	1.55(3)	S(1)#4-N(1)-C(7)	0.000(7)
S(1)-C(7)#4	0.62(2)	S(1)#4-C(7)-C(7)#4	180.00(3)
S(1)-S(1)#4	2.171(14)	S(1)#4-C(7)-N(1)	0.000(12)
		C(7)#4-C(7)-N(1)	180.00(2)
		S(1)#4-C(7)-S(1)	180.000(2)
		C(7)#4-C(7)-S(1)	0.000(11)
		N(1)-C(7)-S(1)	180.000(12)
		C(7)#4-S(1)-C(7)	0.00(3)
		C(7)#4-S(1)-S(1)#4	0.00(2)
		C(7)-S(1)-S(1)#4	0.000(6)

Symmetry transformations used to generate equivalent atoms:

#1 $-x, -y+1, z$ #2 $-y+1/2, x+1/2, -z+1/2$
 #3 $y-1/2, -x+1/2, -z+1/2$ #4 $y-1, -x, -z+2$

Table 3.13 - Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{AsPh}_4][\text{SCN}]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
As	34(1)	34(1)	38(1)	0	0	0
C(1)	42(1)	40(1)	59(1)	2(1)	2(1)	1(1)
C(2)	46(2)	60(2)	72(2)	-5(2)	15(1)	-9(1)
C(3)	56(2)	73(2)	57(2)	12(2)	10(1)	-21(2)
C(4)	63(2)	83(2)	58(2)	30(2)	-8(2)	-14(2)
C(5)	41(1)	72(2)	57(2)	18(1)	-6(1)	-4(1)
C(6)	39(1)	39(1)	41(1)	-2(1)	2(1)	-6(1)
N(1)	48(6)	165(14)	120(30)	0	0	4(6)
C(7)	80(9)	85(9)	90(30)	0	0	6(7)
S(1)	134(5)	147(7)	73(9)	0	0	20(4)

Table 3.14 - Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{AsPh}_4][\text{SCN}]$.

	x	y	z	U(eq)
H(1A)	-2431	4996	3216	56
H(2A)	-3587	4141	5333	71
H(3A)	-2890	2846	7336	74
H(4A)	-1025	2377	7285	82
H(5A)	162	3273	5258	68

Chapter 4

Results and Discussion

4.1 One-Dimensional Copper(II)-Cyanamide Chain Systems

4.1.1 Synthesis

Although the synthesis of these one-dimensional systems seem relatively straightforward, the route traveled to get here was not. The bridging ligand, H_2 -*meta*-dicyd and its derivatives were extremely tempermental, good results strongly dependent on the use of purified starting reagents and solvents. The synthesis of all these systems involved starting from elemental copper and working in a methodical manner to synthesize the starting materials such as $Cu(CF_3SO_3)_2 \cdot 4H_2O$, $Cu(trpy)(CF_3SO_3)_2$, etc.

The copper(II) salts were reacted in a 2:1 ratio with the bridging ligands as the initial intention was to synthesize dinuclear systems in order to study the effects of positional isomerism of the *meta*-dicyd²⁻ ligand on metal-metal coupling. However, such a stoichiometry always lead to the formation of one-dimensional copper(II) alternating chains. Using the $[\{ Cu(trpy) \}_2 - \mu\text{-}meta\text{-dicyd}]_n [BPh_4]_{2n} \cdot (H_2O)_n$ chain as an example (Scheme 4.1), a 2:1 molar ratio of saturated acetone solutions of $[Cu(trpy)(OH_2)](CF_3SO_3)_2$ to H_2 -*meta*-dicyd were combined. Deprotonation of the bridging ligand was afforded by the addition of 2 mol equivalents of a very dilute NaOH solution. Immediately, the now shown to be triflate salt of the one-dimensional $[\{ Cu(trpy) \}_2 - \mu\text{-}meta\text{-dicyd}]_n [CF_3SO_3]_{2n}$ chain precipitated out of solution. This was

then dissolved in acetonitrile, metathesized to a BPh₄ salt and recrystallized by a 1 month DMSO evaporation, yielding small brown cubes of the final product.

Scheme 4.1 – Synthesis of the one-dimensional chain $[\{[\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}\}_n[\text{BPh}_4]_{2n}]$

4.1.2 IR Spectroscopy

The infrared spectra for all one-dimensional chain systems are shown in figures 4.1 - 4.10 and key stretching frequencies are tabulated in Table 4.1. All systems show the characteristically strong $\nu(\text{NCN})$ stretch at $\sim 2150 \text{ cm}^{-1}$. Comparing these stretching frequencies to those of other Cu(II)-*para*-dicyd systems,⁵⁰ one sees a great deal of similarity. Also of interest is the fact that upon coordination, the stretching frequency of the NCN moiety shifts from low energy in its dianionic form to higher energies when complexed. This is due to the stabilizing effect coordination has on the charge distribution (polarization) of the ligand. Other peaks clearly seen in all complexes are $\nu(\text{C}=\text{C})$ in the 1450 cm^{-1} range and, of course, varying sized peaks in the 3450 cm^{-1} range due to the presence of water $\nu(\text{OH})$ in the hygroscopic KBr pellet medium. Various stretching frequencies due to counterions will be elucidated in table 4.1.

Figure 4.1 – IR spectrum of $[\{Cu(trpy)\}_2-\mu\text{-meta-dicyd}]_n[CF_3SO_3]_{2n}$ as a KBr disk.

Figure 4.2 – IR spectrum of $[\{Cu(trpy)\}_2-\mu\text{-meta-dicyd}]_n[BPh_4]_{2n} \cdot (H_2O)_n$ as a KBr disk.

Figure 4.3 – IR spectrum of $[\{Cu(trpy)\}_2-\mu\text{-meta-dicyd}]_n[BPh_4]_{2n}\bullet(2DMF)_n$ as a KBr disk.

Figure 4.4 – IR spectrum of $[\{Cu(trpy)\}_2-\mu\text{-meta-dicyd}]_n[BF_4]_{2n}$ as a KBr disk.

Figure 4.5 – IR spectrum of $[\{Cu(trpy)\}_2-\mu\text{-meta-dicyd}]_n[PF_6]_{2n}$ as a KBr disk.

Figure 4.6 – IR spectrum of $[\{Cu(trpy)\}_2-\mu\text{-meta-dicyd}]_n[Br]_{2n}$ as a KBr disk.

Figure 4.7 – IR spectrum of $[\{Cu(trpy)\}_2-\mu\text{-meta-dicyd}]_n[Cl]_{2n}$ as a KBr disk.

Figure 4.8 – IR spectrum of $[\{Cu(trpy)\}_2-\mu\text{-Me-meta-dicyd}]_n[BPh_4]_{2n}\cdot(H_2O)_n$ as a KBr disk.

Figure 4.9 – IR spectrum of $[\{Cu(bpy)_2\}_2-\mu\text{-Me-}i\text{meta-dicyd}]_n[BPh_4]_{2n}$ as a KBr disk.

Figure 4.10 – IR spectrum of $[\{Cu(bpy)\}_2-\mu\text{-}i\text{meta-dicyd}]_n[CF_3SO_3]_{2n}\cdot(H_2O)_n$ as a KBr disk.

Table 4.1 – Characteristic IR Bands in cm^{-1} for the one-dimensional chain systems.

Complex	$\nu(\text{NCN})$	Counter ion
$[\text{Cu}(\text{trpy})\text{-meta-dicyd}]_n[\text{Cl}_2]_n$	2112	n/a
$[\text{Cu}(\text{trpy})\text{-meta-dicyd}]_n[\text{Br}_2]_n$	2142	n/a
$[\text{Cu}(\text{trpy})\text{-meta-dicyd}]_n[\text{PF}_6]_{2n}$	2161	843
$[\text{Cu}(\text{trpy})\text{-meta-dicyd}]_n[\text{BF}_4]_{2n}$	2151	1061
$[\text{Cu}(\text{trpy})\text{-meta-dicyd}]_n[\text{CF}_3\text{SO}_3]_{2n}$	2160	1280
$[\text{Cu}(\text{trpy})\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n} \bullet (\text{H}_2\text{O})_n$	2170	n/a
$[\text{Cu}(\text{trpy})\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n} \bullet (2\text{DMF})_n$	2172	DMF 1666
$[\text{Cu}(\text{trpy})\text{-Me-meta-dicyd}]_n[\text{BPh}_4]_{2n} \bullet (\text{H}_2\text{O})_n$	2122	n/a
$[\text{Cu}(\text{bpy})_2\text{-Me-meta-dicyd}]_n[\text{BPh}_4]_{2n}$	2165	n/a
$[\text{Cu}(\text{bpy})\text{-meta-dicyd}]_n[\text{CF}_3\text{SO}_3]_{2n} \bullet (\text{H}_2\text{O})_n$	2151	1278

4.1.3 X-Ray Crystallography

The growth of X-ray quality crystals of the one-dimensional chains was very time consuming. In fact, only one successful crystal structure was refined, namely $[\text{Cu}(\text{trpy})\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n} \bullet (\text{H}_2\text{O})_n$. Due to solubility problems, the choice of solvents was limited and solvent conditions played a strong role in the quality of the crystals. Initially, DMF was used to recrystallize the complex and, while it gave good results, extensive twinning in all crystals prevented a structure refinement. DMSO was then employed and one sample, which was left in the dark for approximately one month gave small cubic crystals of $[\text{Cu}(\text{trpy})\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n} \bullet (\text{H}_2\text{O})_n$, sufficient for X-ray analysis shown in figure 4.11 and data summarized in tables 4.2 - 4.6.

Figure 4.11 - Ball and stick diagram of the one dimensional chain, $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(\text{H}_2\text{O})_n$

Table 4.2 – Crystal data and structural refinement information for the X-ray structural determination of $[\text{Cu}(\text{trpy})\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n} \cdot (\text{H}_2\text{O})_n$.

Empirical formula	$\text{C}_{74} \text{H}_{56} \text{B}_2 \text{Cu}_2 \text{N}_{10}$
Formula weight	1233.59
Temperature	203(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$\text{P2}_1/\text{c}$
Unit cell dimensions	$a = 24.226(2) \text{ Å}$ $\alpha = 90^\circ$ $b = 17.699(1) \text{ Å}$ $\beta = 106.360(1)^\circ$ $c = 18.202(1) \text{ Å}$ $\gamma = 90^\circ$
Volume	$7488.6(8) \text{ Å}^3$
Z	4
Density (calculated)	1.095 Mg/m^3
Absorption coefficient	0.612 mm^{-1}
F(000)	2552
Crystal size	0.10 x 0.10 x 0.10 mm
Theta range for data collection	1.45° to 20.00°
Limiting indices	$-32 \leq h \leq 31$, $-22 \leq k \leq 13$, $-23 \leq l \leq 24$
Reflections collected	23064
Independent reflections	6974 [$R(\text{int}) = 0.1746$]
Absorption correction	SADABS empirical
Max. and min. transmission	0.927993 and 0.592454
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6967 / 28 / 153
Goodness-of-fit on F^2	1.013
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.2436$, $wR2 = 0.5698$
R indices (all data)	$R1 = 0.3488$, $wR2 = 0.6480$
Largest diff. peak and hole	2.158 and $-0.881 \text{ e} \cdot \text{Å}^{-3}$

Table 4.3 - Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Cu}(\text{trpy})\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n} \cdot (\text{H}_2\text{O})_n$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cu(1)	2808(2)	1694(2)	-261(2)	58(2)
Cu(2)	3035(2)	1647(2)	2475(2)	85(2)
C(1)	2879(8)	3975(9)	467(8)	52(8)
C(2)	2861(8)	4346(6)	1133(10)	49(8)
C(3)	2951(8)	3945(8)	1813(8)	52(8)
C(4)	3059(7)	3173(8)	1828(7)	25(6)
C(5)	3077(7)	2802(6)	1162(8)	29(6)
C(6)	2987(8)	3203(9)	482(7)	48(8)
N(1)	3000(9)	2759(12)	-171(12)	47(6)
N(2)	2894(11)	3425(14)	-1389(15)	66(7)
N(3)	3135(9)	2748(12)	2497(12)	47(6)
N(4)	3005(9)	3412(13)	3665(13)	52(6)
C(7)	2947(13)	3147(18)	-821(19)	61(9)
C(8)	3084(13)	3108(17)	3118(18)	59(9)
C(9)	1611(3)	2475(4)	-666(3)	83(11)
C(10)	1013(3)	2460(4)	-881(3)	131(16)
C(11)	724(3)	1773(5)	-1014(3)	220(31)
C(12)	1033(3)	1101(4)	-932(3)	218(31)
C(13)	1631(3)	1116(4)	-717(3)	112(14)
N(14)	1920(3)	1803(4)	-584(3)	70(8)
C(15)	2038(3)	481(4)	-404(3)	72(10)
C(16)	1875(3)	-271(4)	-389(4)	120(15)
C(17)	2292(3)	-827(4)	-145(4)	155(20)
C(18)	2871(3)	-631(4)	82(4)	66(9)
C(19)	3033(3)	120(4)	67(4)	61(8)
N(20)	2617(3)	676(4)	-176(3)	59(7)
C(21)	3562(3)	447(4)	389(4)	54(8)
C(22)	4065(3)	51(4)	726(4)	71(10)
C(23)	4575(3)	440(4)	1041(4)	66(9)
C(24)	4582(3)	1225(4)	1019(4)	72(10)
C(25)	4079(3)	1621(4)	683(3)	62(9)
N(26)	3568(3)	1232(4)	368(3)	60(7)
C(27)	4395(2)	1731(3)	2947(3)	86(11)
C(28)	4939(2)	1407(4)	3194(4)	94(12)
C(29)	4998(3)	625(4)	3225(4)	85(11)
C(30)	4513(3)	167(3)	3008(4)	101(13)
C(31)	3969(3)	491(3)	2760(3)	80(10)
N(32)	3910(2)	1273(3)	2729(3)	72(8)
C(33)	3348(3)	181(3)	2418(3)	71(10)
C(34)	3264(3)	-589(3)	2284(4)	146(18)
C(35)	2721(3)	-863(3)	1905(4)	111(14)

C(36)	2261(3)	-367(3)	1661(4)	146(19)
C(37)	2344(3)	403(3)	1796(3)	79(10)
N(38)	2888(3)	678(3)	2174(3)	93(9)
C(39)	1894(3)	992(3)	1535(3)	148(19)
C(40)	1330(3)	920(4)	1079(3)	118(15)
C(41)	975(2)	1550(4)	913(3)	163(20)
C(42)	1184(2)	2253(4)	1203(3)	227(31)
C(43)	1748(2)	2326(3)	1660(3)	171(22)
N(44)	2103(2)	1695(3)	1826(3)	64(7)
C(45)	3642(3)	7057(3)	2867(4)	96(12)
C(46)	3533(3)	6449(3)	2364(4)	98(13)
C(47)	3647(3)	5717(3)	2641(4)	115(15)
C(48)	3870(3)	5593(3)	3423(4)	118(15)
C(49)	3979(3)	6200(3)	3927(4)	116(14)
C(50)	3865(3)	6933(3)	3649(4)	89(12)
C(51)	3670(4)	7469(4)	5449(5)	133(17)
C(52)	3792(4)	7162(4)	6180(4)	171(22)
C(53)	4318(3)	6811(4)	6502(4)	78(10)
C(54)	4722(3)	6768(4)	6093(4)	150(19)
C(55)	4601(3)	7075(4)	5362(5)	54(8)
C(56)	4075(3)	7425(4)	5040(5)	120(15)
C(57)	4871(4)	7964(4)	3516(5)	74(10)
C(58)	5356(4)	8339(4)	3442(6)	113(14)
C(59)	5640(4)	8853(4)	3999(6)	126(16)
C(60)	5438(4)	8990(4)	4630(6)	138(18)
C(61)	4953(4)	8615(4)	4704(6)	204(28)
C(62)	4669(4)	8101(4)	4147(5)	136(17)
C(63)	3465(4)	9058(3)	4149(6)	140(18)
C(64)	3007(4)	9564(3)	3949(6)	218(30)
C(65)	2454(4)	9302(3)	3603(6)	174(23)
C(66)	2358(4)	8535(3)	3456(5)	229(32)
C(67)	2815(4)	8030(3)	3656(5)	151(19)
C(68)	3368(4)	8291(3)	4002(5)	149(20)
C(69)	667(4)	3884(5)	7867(5)	185(23)
C(70)	1172(4)	4173(5)	8354(4)	167(21)
C(71)	1172(5)	4472(6)	9060(5)	2000(900)
C(72)	667(5)	4481(6)	9280(5)	146(18)
C(73)	162(5)	4193(6)	8793(5)	116(14)
C(74)	162(4)	3894(6)	8087(5)	295(41)
C(75)	-1065(4)	4839(6)	7472(6)	144(18)
C(76)	-1567(4)	5241(7)	7426(7)	139(17)
C(77)	-2097(4)	4878(7)	7197(7)	229(32)
C(78)	-2125(4)	4114(7)	7013(7)	183(24)
C(79)	-1623(4)	3713(7)	7059(7)	226(30)
C(80)	-1093(4)	4075(6)	7289(6)	587(137)
C(81)	-761(5)	2389(6)	8137(6)	181(24)

C(82)	-820(5)	1628(7)	8290(6)	230(33)
C(83)	-695(5)	1079(6)	7816(6)	201(27)
C(84)	-512(5)	1289(6)	7188(6)	228(31)
C(85)	-452(4)	2050(6)	7034(6)	414(73)
C(86)	-577(4)	2599(6)	7509(6)	150(20)
C(87)	-754(4)	3158(6)	5953(6)	250(36)
C(88)	-813(3)	3265(5)	5178(5)	229(32)
C(89)	-580(3)	3903(5)	4933(5)	331(53)
C(90)	-289(3)	4434(5)	5464(5)	204(27)
C(91)	-230(4)	4328(5)	6239(5)	116(15)
C(92)	-463(4)	3690(5)	6483(5)	254(36)
B(1)	3992(8)	7776(11)	4140(12)	105(16)
B(2)	-460(9)	3562(12)	7430(12)	1805(631)

Table 4.4 - Bond lengths [Å] for [Cu(trpy)-*meta*-dicyd]_n[BPh₄]_{2n}•(H₂O)_n.

Cu(1)-N(20)	1.876(7)	C(40)-C(41)	1.39
Cu(1)-N(1)	1.94(2)	C(41)-C(42)	1.39
Cu(1)-N(26)	2.046(8)	C(42)-C(43)	1.39
Cu(1)-N(14)	2.073(8)	C(43)-N(44)	1.39
Cu(1)-N(4)#1	2.15(2)	C(45)-C(46)	1.39
Cu(2)-N(38)	1.805(6)	C(45)-C(50)	1.39
Cu(2)-N(3)	1.96(2)	C(46)-C(47)	1.39
Cu(2)-N(32)	2.145(8)	C(47)-C(48)	1.39
Cu(2)-N(2)#2	2.19(3)	C(48)-C(49)	1.39
Cu(2)-N(44)	2.235(8)	C(49)-C(50)	1.39
C(1)-C(2)	1.39	C(50)-B(1)	1.72(2)
C(1)-C(6)	1.39	C(51)-C(52)	1.39
C(2)-C(3)	1.39	C(51)-C(56)	1.39
C(3)-C(4)	1.39	C(52)-C(53)	1.39
C(4)-C(5)	1.39	C(53)-C(54)	1.39
C(4)-N(3)	1.40(2)	C(54)-C(55)	1.39
C(5)-C(6)	1.39	C(55)-C(56)	1.39
C(6)-N(1)	1.43(2)	C(56)-B(1)	1.71(2)
N(1)-C(7)	1.34(4)	C(57)-C(58)	1.39
N(2)-C(7)	1.12(3)	C(57)-C(62)	1.39
N(2)-Cu(2)#1	2.19(3)	C(58)-C(59)	1.39
N(3)-C(8)	1.33(3)	C(59)-C(60)	1.39
N(4)-C(8)	1.19(3)	C(60)-C(61)	1.39
N(4)-Cu(1)#2	2.15(2)	C(61)-C(62)	1.39
C(9)-C(10)	1.39	C(62)-B(1)	1.74(2)
C(9)-N(14)	1.39	C(63)-C(68)	1.39
C(10)-C(11)	1.39	C(63)-C(64)	1.39
C(11)-C(12)	1.39	C(64)-C(65)	1.39
C(12)-C(13)	1.39	C(65)-C(66)	1.39

C(13)-N(14)	1.39	C(66)-C(67)	1.39
C(13)-C(15)	1.5	C(67)-C(68)	1.39
C(15)-N(20)	1.39	C(68)-B(1)	1.72(2)
C(15)-C(16)	1.39	C(69)-C(74)	1.39
C(16)-C(17)	1.39	C(69)-C(70)	1.39
C(17)-C(18)	1.39	C(70)-C(71)	1.39
C(18)-C(19)	1.39	C(71)-C(72)	1.39
C(19)-C(21)	1.38	C(72)-C(73)	1.39
C(19)-N(20)	1.39	C(73)-C(74)	1.39
C(21)-C(22)	1.39	C(74)-B(2)	1.74(2)
C(21)-N(26)	1.39	C(75)-C(76)	1.39
C(22)-C(23)	1.39	C(75)-C(80)	1.39
C(23)-C(24)	1.39	C(76)-C(77)	1.39
C(24)-C(25)	1.39	C(77)-C(78)	1.39
C(25)-N(26)	1.39	C(78)-C(79)	1.39
C(27)-N(32)	1.39	C(79)-C(80)	1.39
C(27)-C(28)	1.39	C(80)-B(2)	1.74(2)
C(28)-C(29)	1.39	C(81)-C(82)	1.39
C(29)-C(30)	1.39	C(81)-C(86)	1.39
C(30)-C(31)	1.39	C(82)-C(83)	1.39
C(31)-N(32)	1.39	C(83)-C(84)	1.39
C(31)-C(33)	1.56	C(84)-C(85)	1.39
C(33)-N(38)	1.39	C(85)-C(86)	1.39
C(33)-C(34)	1.39	C(86)-B(2)	1.74(2)
C(34)-C(35)	1.39	C(87)-C(88)	1.39
C(35)-C(36)	1.39	C(87)-C(92)	1.39
C(36)-C(37)	1.39	C(88)-C(89)	1.39
C(37)-N(38)	1.39	C(89)-C(90)	1.39
C(37)-C(39)	1.49	C(90)-C(91)	1.39
C(39)-N(44)	1.39	C(91)-C(92)	1.39
C(39)-C(40)	1.39	C(92)-B(2)	1.74(2)

Symmetry transformations used to generate equivalent atoms:

#1 $x, -y+1/2, z-1/2$ #2 $x, -y+1/2, z+1/2$

Table 4.5 - Bond angles [°] for [Cu(trpy)-*meta*-dicyd]_n[BPh₄]_{2n}•(H₂O)_n.

N(20)-Cu(1)-N(1)	170.3(7)	N(38)-C(37)-C(39)	114.9
N(20)-Cu(1)-N(26)	77.0(3)	C(33)-N(38)-C(37)	120
N(1)-Cu(1)-N(26)	100.6(7)	C(33)-N(38)-Cu(2)	115.6(2)
N(20)-Cu(1)-N(14)	81.5(3)	C(37)-N(38)-Cu(2)	124.1(2)
N(1)-Cu(1)-N(14)	97.9(7)	N(44)-C(39)-C(40)	120
N(26)-Cu(1)-N(14)	153.5(4)	N(44)-C(39)-C(37)	110.5
N(20)-Cu(1)-N(4)#1	96.6(6)	C(40)-C(39)-C(37)	129.5
N(1)-Cu(1)-N(4)#1	93.0(9)	C(41)-C(40)-C(39)	120
N(26)-Cu(1)-N(4)#1	94.5(6)	C(40)-C(41)-C(42)	120
N(14)-Cu(1)-N(4)#1	103.3(6)	C(43)-C(42)-C(41)	120
N(38)-Cu(2)-N(3)	164.1(7)	C(42)-C(43)-N(44)	120
N(38)-Cu(2)-N(32)	82.6(3)	C(39)-N(44)-C(43)	120
N(3)-Cu(2)-N(32)	101.1(7)	C(39)-N(44)-Cu(2)	111.8(2)
N(38)-Cu(2)-N(2)#2	99.3(7)	C(43)-N(44)-Cu(2)	128.1(2)
N(3)-Cu(2)-N(2)#2	95.2(9)	C(46)-C(45)-C(50)	120
N(32)-Cu(2)-N(2)#2	100.7(7)	C(45)-C(46)-C(47)	120
N(38)-Cu(2)-N(44)	78.0(2)	C(46)-C(47)-C(48)	120
N(3)-Cu(2)-N(44)	94.2(7)	C(47)-C(48)-C(49)	120
N(32)-Cu(2)-N(44)	156.3(3)	C(50)-C(49)-C(48)	120
N(2)#2-Cu(2)-N(44)	95.7(7)	C(45)-C(50)-C(49)	120
C(2)-C(1)-C(6)	120	C(45)-C(50)-B(1)	110.8(6)
C(3)-C(2)-C(1)	120	C(49)-C(50)-B(1)	129.1(6)
C(4)-C(3)-C(2)	120	C(52)-C(51)-C(56)	120
C(3)-C(4)-C(5)	120	C(51)-C(52)-C(53)	120
C(3)-C(4)-N(3)	121.5(14)	C(54)-C(53)-C(52)	120
C(5)-C(4)-N(3)	118.4(14)	C(53)-C(54)-C(55)	120
C(4)-C(5)-C(6)	120	C(54)-C(55)-C(56)	120
C(5)-C(6)-C(1)	120	C(55)-C(56)-C(51)	120
C(5)-C(6)-N(1)	115.1(14)	C(55)-C(56)-B(1)	114.3(5)
C(1)-C(6)-N(1)	124.9(14)	C(51)-C(56)-B(1)	125.7(5)
C(7)-N(1)-C(6)	116(2)	C(58)-C(57)-C(62)	120
C(7)-N(1)-Cu(1)	118(2)	C(57)-C(58)-C(59)	120
C(6)-N(1)-Cu(1)	123(2)	C(60)-C(59)-C(58)	120
C(7)-N(2)-Cu(2)#1	147(3)	C(59)-C(60)-C(61)	120
C(8)-N(3)-C(4)	117(2)	C(62)-C(61)-C(60)	120
C(8)-N(3)-Cu(2)	117(2)	C(61)-C(62)-C(57)	120
C(4)-N(3)-Cu(2)	122(2)	C(61)-C(62)-B(1)	119.7(6)
C(8)-N(4)-Cu(1)#2	148(2)	C(57)-C(62)-B(1)	119.1(6)
N(2)-C(7)-N(1)	175(4)	C(68)-C(63)-C(64)	120
N(4)-C(8)-N(3)	176(3)	C(65)-C(64)-C(63)	120
C(10)-C(9)-N(14)	120	C(64)-C(65)-C(66)	120
C(11)-C(10)-C(9)	120	C(67)-C(66)-C(65)	120
C(10)-C(11)-C(12)	120	C(66)-C(67)-C(68)	120
C(13)-C(12)-C(11)	120	C(63)-C(68)-C(67)	120

C(12)-C(13)-N(14)	120	C(63)-C(68)-B(1)	113.4(6)
C(12)-C(13)-C(15)	127.9	C(67)-C(68)-B(1)	125.7(6)
N(14)-C(13)-C(15)	110.2	C(74)-C(69)-C(70)	120
C(13)-N(14)-C(9)	120	C(71)-C(70)-C(69)	120
C(13)-N(14)-Cu(1)	113.5(2)	C(70)-C(71)-C(72)	120
C(9)-N(14)-Cu(1)	126.5(2)	C(73)-C(72)-C(71)	120
N(20)-C(15)-C(16)	120	C(74)-C(73)-C(72)	120
N(20)-C(15)-C(13)	115.3	C(69)-C(74)-C(73)	120
C(16)-C(15)-C(13)	124.6	C(69)-C(74)-B(2)	117.3(7)
C(17)-C(16)-C(15)	120	C(73)-C(74)-B(2)	122.6(7)
C(18)-C(17)-C(16)	120	C(76)-C(75)-C(80)	120
C(19)-C(18)-C(17)	120	C(75)-C(76)-C(77)	120
C(21)-C(19)-C(18)	128.9	C(78)-C(77)-C(76)	120
C(21)-C(19)-N(20)	110.1	C(77)-C(78)-C(79)	120
C(18)-C(19)-N(20)	120	C(80)-C(79)-C(78)	120
C(15)-N(20)-C(19)	120	C(79)-C(80)-C(75)	120
C(15)-N(20)-Cu(1)	117.8(2)	C(79)-C(80)-B(2)	120.3(6)
C(19)-N(20)-Cu(1)	122.1(2)	C(75)-C(80)-B(2)	119.4(6)
C(19)-C(21)-C(22)	124.9	C(82)-C(81)-C(86)	120
C(19)-C(21)-N(26)	115.1	C(81)-C(82)-C(83)	120
C(22)-C(21)-N(26)	120	C(84)-C(83)-C(82)	120
C(23)-C(22)-C(21)	120	C(83)-C(84)-C(85)	120
C(22)-C(23)-C(24)	120	C(84)-C(85)-C(86)	120
C(25)-C(24)-C(23)	120	C(81)-C(86)-C(85)	120
N(26)-C(25)-C(24)	120	C(81)-C(86)-B(2)	115.4(7)
C(25)-N(26)-C(21)	120	C(85)-C(86)-B(2)	124.4(7)
C(25)-N(26)-Cu(1)	126.1(2)	C(88)-C(87)-C(92)	120
C(21)-N(26)-Cu(1)	113.5(2)	C(87)-C(88)-C(89)	120
N(32)-C(27)-C(28)	120	C(90)-C(89)-C(88)	120
C(29)-C(28)-C(27)	120	C(91)-C(90)-C(89)	120
C(28)-C(29)-C(30)	120	C(90)-C(91)-C(92)	120
C(31)-C(30)-C(29)	120	C(87)-C(92)-C(91)	120
N(32)-C(31)-C(30)	120	C(87)-C(92)-B(2)	117.4(6)
N(32)-C(31)-C(33)	105	C(91)-C(92)-B(2)	122.3(6)
C(30)-C(31)-C(33)	134.8	C(56)-B(1)-C(50)	98.0(9)
C(27)-N(32)-C(31)	120	C(56)-B(1)-C(68)	101.1(9)
C(27)-N(32)-Cu(2)	125.9(2)	C(50)-B(1)-C(68)	111.3(9)
C(31)-N(32)-Cu(2)	113.5(2)	C(56)-B(1)-C(62)	105.0(9)
N(38)-C(33)-C(34)	120	C(50)-B(1)-C(62)	108.8(9)
N(38)-C(33)-C(31)	120.1	C(68)-B(1)-C(62)	127.8(11)
C(34)-C(33)-C(31)	119.5	C(92)-B(2)-C(74)	113.5(11)
C(35)-C(34)-C(33)	120	C(92)-B(2)-C(86)	104.8(10)
C(34)-C(35)-C(36)	120	C(74)-B(2)-C(86)	113.9(10)
C(37)-C(36)-C(35)	120	C(92)-B(2)-C(80)	91.6(8)
C(36)-C(37)-N(38)	120	C(74)-B(2)-C(80)	118.8(11)
C(36)-C(37)-C(39)	125	C(86)-B(2)-C(80)	111.4(10)

Symmetry transformations used to generate equivalent atoms in table 4.5:
 #1 $x, -y+1/2, z-1/2$ #2 $x, -y+1/2, z+1/2$

Table 4.6 - Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Cu}(\text{trpy})\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n} \cdot (\text{H}_2\text{O})_n$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Cu(1)	125(4)	34(2)	18(2)	3(2)	27(2)	27(2)
Cu(2)	186(5)	57(3)	23(2)	-21(2)	49(3)	-81(3)

As in the case of the $[\text{AsPh}_4]_2[\text{meta-dicyd}]$ bridging ligand crystal structure, the refinement of this structure was poor, with the unweighted residual (R_f) for the significant reflections being 24.36%. The structure, nonetheless confirms the uniqueness of the connectivity between metal ions mediated by *meta-dicyd*²⁻.

Figure 4.11 shows the many unique features this crystal structure has compared to other *para-dicyd*²⁻ dinuclear complexes. The chain structure of the title compound shows that each copper ion has a highly distorted, square pyramidal geometry (bordering on trigonal bipyramid) with 5 nitrogen based ligands making up the coordination environment. There are two unique copper(II) ions in the structure which alternately propagate through the chain. The most striking feature is that there is a metal ion bound to the amide nitrogen as well as the nitrile nitrogen on each cyanamide moiety. This is the first time this conformation has been seen on any *dicyd*²⁻ ligand, regardless of the positional isomerism of the cyanamide substituents. On all *para-dicyd*²⁻ metal complexes, synthesized in a similar manner, only the nitrile nitrogen is involved in metal bond formation.⁹ Considering that the *para-dicyd*²⁻ is a less sterically hindered ligand, one would expect the opposite to occur. This unique

bridging mode reclassifies this ligand as an alternating one-dimensional chain. Two dominant bridging pathways can be seen; the first, a cyanamide (NCN) pathway separating the Cu(II) ions and the second, through the phenyl ring via the two amide nitrogens. Examining the unit cell of this one-dimensional chain, we can see that the

Figure 4.12 – Unit cell diagram of $[\text{Cu}(\text{trpy})\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n} \cdot (\text{H}_2\text{O})_n$ showing the distance between chain (i) with counter ions present and (ii) counter ions omitted.

chains are well spaced apart with the closest Cu-Cu distance being 13 Å. One can also see how the tetraphenylborate counter anions are located interspatially between each chain, enhancing the interchain separation.

It was initially reported that there were two unique copper ions which alternate throughout the chain. Figures 4.13-4.15 illustrate this quite well and serve to describe the properties these chains exhibit as will be seen in section 4.1.4. All three figures have arbitrary axes placed on them in order to limit the confusion when describing the

crystallographic differences seen. The axes are meant to reflect the square pyramidal geometry of the copper(II) ions with the axial site represented as the z-axis.

Figure 4.13 shows the through phenyl-amide nitrogen pathway and upon closer examination we can see an interesting result. With respect to the angles of this amide Cu-N linkage, a top view of the chain fragment was used (figure 4.14). Two planes were compared to each other, using the Cu(2) coordination sphere as an example. This first plane was created by the bridging ligand and the second plane was created by the inclusion of the copper ion and the pyridyl group “trans” (y-axis) to the amide nitrogen (atoms shaded black). The angle created by these two planes, for Cu(2) is 99.5° and for Cu(1) is 98.1° . This equates to a 9.5° and 8.1° distortion in the square pyramidal geometry bringing the two copper ions closer together - counterintuitive to what one would expect for charged species.

The final distortion in the coordination environment, shown in figure 4.15, involves two planes as well. One plane, using the axes on the diagram, involved the yz plane including the copper(II) ions and the co-planar pyridyl nitrogen. The second plane is formed by the bridging ligand. Here we see a dramatic shift from coplanarity with the angle formed between these planes equal to 20.5° .

Figure 4.13 – Ball and stick diagram showing a fragment of the one-dimensional chain $[\text{Cu}(\text{trpy})\text{-}i\text{meta-dicyd}]_n[\text{BPh}_4]_{2n} \bullet (\text{H}_2\text{O})_n$.

Figure 4.14 – Top view of the one-dimensional chain fragment of $[\text{Cu}(\text{trpy})\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n} \cdot (\text{H}_2\text{O})_n$. Certain atoms are artificially filled in black in order to define a plane (see text).

Figure 4.15 – Side on view of the one-dimensional chain fragment $[\text{Cu}(\text{trpy})\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n} \cdot (\text{H}_2\text{O})_n$.

4.1.4 Molecular Modeling

Molecular modeling was performed on this one-dimensional system in order to identify the HOMO (magnetic orbital) responsible for the magnetic properties of $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(\text{H}_2\text{O})$. We performed a semi-empirical calculation using the PM3(tm) semi-empirical method on the model complex $[\{\text{Cu}(\text{NH}_3)_3(\text{CH}_3)\}_2(\mu\text{-NCN})_2]^{2+}$. The calculation was constrained by the bond angles and lengths derived from the X-ray structure of $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(\text{H}_2\text{O})_n$ and gave the highest occupied molecular orbital HOMO shown in Figure 4.16(a) and (b). The HOMO illustrates the superexchange pathway for antiferromagnetic coupling between the two, slightly distorted, $\text{Cu}(\text{II}) d_x^2-y^2$ orbitals.

Figure 4.16 - Molecular modeling of the $\mu\text{-(NCN)}_2$ pathway of the $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(\text{H}_2\text{O})_n$ complex, using a model complex $[\{\text{Cu}(\text{NH}_3)_3(\text{CH}_3)\}_2\text{-}\mu\text{-(NCN)}_2]^{2+}$ showing both the end-on view (a) and side-view (b).

To better elucidate this orbital and its bridging pathway, figure 4.16, shows both the end-on (a), and side views (b), of this modeling process. As can be seen from figure 4.16(b), a small amount of mixing of the d_z^2 orbital with the $d_{x^2-y^2}$ orbital is evident. As seen in the crystal structure, this is a result of the significantly distorted coordination environment about each of the Cu(II) ions.

4.1.5 Magnetic Measurements

The solid state, temperature dependent magnetic susceptibility of the one-dimensional chains incorporating the *meta*-dicyd²⁻ and the Me-*meta*-dicyd²⁻ bridging ligands was performed on powder samples from 2 to 298 K in a 1000 Gauss (0.1 T) applied field. Figures 4.18-4.25 show the χ_M versus T and χ_M^{-1} vs T plots for all the one-dimensional chains. As shown in the theoretical plot below (figure 4.17), one would expect to see deviations from Curie-Weiss behaviour depending on the nature of the magnetic exchange.

Figure 4.17 – The Curie and the Curie-Weiss laws. The curie constant $C = 0.454 \text{ emu K mol}^{-1}$ ($S = \frac{1}{2}$, $g = 2.2$) has been used for all curves and values of $\theta = +5 \text{ K}$ ($\square$), $\theta = 0 \text{ K}$ ($\triangle$) and $\theta = -5 \text{ K}$ ($\circ$) are plotted.

With respect to the plots of χ versus T , the data (grey data points) for the curves seem to follow the Curie-Weiss law at high temperatures and deviate to Curie law behaviour at lower temperatures. Examining these plots, the curves appear essentially paramagnetic in nature with no discernable T_c or T_N indicating long-range order.

Figure 4.18 – Plot of χ_M vs T (grey data points) and χ_M^{-1} vs. T (white data points) for $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\cdot(\text{H}_2\text{O})_n$. The solid line represents the Curie-Weiss fit for the high temperature regime

Figure 4.19 – Plot of χ_M vs T (grey data points) and χ_M^{-1} vs. T (white data points) for $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{CF}_3\text{SO}_3]_{2n}$. The solid line represents the Curie-Weiss fit for the high temperature regime

Figure 4.20 – Plot of χ_M vs T (grey data points) and χ_M^{-1} vs. T (white data points) for $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BF}_4]_{2n}$. The solid line represents the Curie-Weiss fit for the high temperature regime

Figure 4.21 – Plot of χ_M vs T (grey data points) and χ_M^{-1} vs. T (white data points) for $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{PF}_6]_{2n}$. The solid line represents the Curie-Weiss fit for the high temperature regime

Figure 4.22 – Plot of χ_M vs T (grey data points) and χ_M^{-1} vs. T (white data points) for $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{Br}]_{2n}$. The solid line represents the Curie-Weiss fit for the high temperature regime

Figure 4.23 – Plot of χ_M vs T (grey data points) and χ_M^{-1} vs. T (white data points) for $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{Cl}]_{2n}$. The solid line represents the Curie-Weiss fit for the high temperature regime

Figure 4.24 – Plot of χ_M vs T (grey data points) and χ_M^{-1} vs. T (white data points) for $[\{\text{Cu}(\text{bpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{CF}_3\text{SO}_3]_{2n}\cdot(2\text{H}_2\text{O})_n$. The solid line represents the Curie-Weiss fit for the high temperature regime

Figure 4.25 – Plot of χ_M vs T (grey data points) and χ_M^{-1} vs. T (white data points) for $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-Me-meta-dicyd}]_2[\text{BPh}_4]_{2n}\cdot(\text{H}_2\text{O})_n$. The solid line represents the Curie-Weiss fit for the high temperature regime

An indication of long-range order can be seen when a Curie-Weiss plot of χ^{-1} vs. T is used, represented by the white data points and the right y-axis. The χ^{-1} data is fit, at high temperature ranges in order to avoid any possibility of long-range ordering.

In the fitting process, the temperature-independent paramagnetism term (TIP)⁵¹ was ignored. TIP can usually be seen in a χ^{-1} vs T plot as a distinct curvature in the data.

Since the data used included the high temperature values (~170–298 K) and not a great deal of curvature was present, TIP was excluded from all fitting procedures. All the one-dimensional chains show evidence of antiferromagnetic exchange as the x-intercepts of the fitted, solid line, were all at negative temperature values. These values, known as the Weiss temperatures (θ), are summarized in table 4.7.

Table 4.7 – Sample data and Weiss temperatures for the series of one-dimensional chain systems containing cyanamide linkages.

Complex	$\chi_{\text{diamagnetic}}$ $\times 10^{-6}$ (emu/mol)	θ (K)
$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(\text{H}_2\text{O})_n$	-804	-20 ± 2
$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{CF}_3\text{SO}_3]_{2n}$	-496	-40 ± 1
$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BF}_4]_{2n}$	-468	-53 ± 1
$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{PF}_6]_{2n}$	-514	-91 ± 2
$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{Br}]_{2n}$	-455	-103 ± 1
$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{Cl}]_{2n}$	-432	-65 ± 1
$[\{\text{Cu}(\text{bpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(2\text{H}_2\text{O})_n$	-396	-31 ± 1
$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-Me-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(\text{H}_2\text{O})_n$	-816	-13 ± 1

In order to elucidate the nature of the antiferromagnetic exchange, it is beneficial, at this point, to plot the $\chi_M T$ vs. T data for these systems. As mentioned in the introduction, subtleties in the susceptibility of a given system can be determined employing this type of plot. The $\chi_M T$ vs. T data, along with the spin-only effective magnetic moment (μ_{eff}), calculated using the equation 14,

$$\mu_{eff} = 2.828\sqrt{\chi_M T} \quad (14)$$

are shown in figures 4.26-4.33. Indeed these plots reveal some interesting magnetic behaviour. The $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{X}]_{2n}$ chains with counter ions, X, being BPh_4 , CF_3SO_3 , BF_4 , and PF_6 all show a decrease in $\chi_M T$ down to a specific critical temperature, T_{min} , then a quick and steady rise down to the lowest temperature measured, 2 K. The $[\{\text{Cu}(\text{bpy})\}\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\cdot(2\text{H}_2\text{O})_n$ chain exhibited an identical type of behaviour. The other two $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{X}]_{2n}$ chains where $\text{X} = \text{Br}^-$ and Cl^- and the $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-Me-meta-dicyd}]_n[\text{BPh}_4]_{2n}\cdot(\text{H}_2\text{O})_n$ gave different results. These three both show the same steady decrease in $\chi_M T$ beginning at high temperatures, but where the quick rise in $\chi_M T$ occurred at T_{min} for the previous systems, these continued toward zero. Only the Br^- system showed some evidence of increasing $\chi_M T$, but decreased further upon further cooling. With respect to the room temperature μ_{eff} values, all are in the range of what one might expected for an uncoupled or weakly coupled, Cu(II) ion (1.90 BM). Values for μ_{eff} at 298 K, T_{min} and $\chi_M T$ at T_{min} are summarized in table 4.8.

Figure 4.26 – Plot of $\chi_M T$ and μ_{eff} as a function of temperature for $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\cdot(\text{H}_2\text{O})_n$. μ_{eff} was calculated using the spin-only expression of equation 14.

Figure 4.27 – Plot of $\chi_M T$ and μ_{eff} as a function of temperature for $[\{\text{Cu}(\text{trpy})\}_2-\mu\text{-meta-dicyd}]_n[\text{CF}_3\text{SO}_3]_{2n}$. μ_{eff} was calculated using the spin-only expression of equation 14.

Figure 4.28 – Plot of $\chi_M T$ and μ_{eff} as a function of temperature for $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BF}_4]_{2n}$. μ_{eff} was calculated using the spin-only expression of equation 14.

Figure 4.29 – Plot of $\chi_M T$ and μ_{eff} as a function of temperature for $[\{Cu(trpy)\}_2-\mu\text{-meta-dicyd}]_n[PF_6]_{2n}$. μ_{eff} was calculated using the spin-only expression of equation 14.

Figure 4.30 – Plot of $\chi_M T$ and μ_{eff} as a function of temperature for $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{Br}]_{2n}$. μ_{eff} was calculated using the spin-only expression of equation 14.

Figure 4.31 – Plot of $\chi_M T$ and μ_{eff} as a function of temperature for $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{Cl}]_{2n}$. μ_{eff} was calculated using the spin-only expression of equation 14.

Figure 4.32 – Plot of $\chi_M T$ and μ_{eff} as a function of temperature for $[\{\text{Cu}(\text{bpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{CF}_3\text{SO}_3]_{2n}\cdot(2\text{H}_2\text{O})_n$. μ_{eff} was calculated using the spin-only expression of equation 14.

Figure 4.33 – Plot of $\chi_M T$ and μ_{eff} as a function of temperature for $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-Me-meta-dicyd}]_n[\text{BPh}_4]_{2n}\cdot(\text{H}_2\text{O})_n$. μ_{eff} was calculated using the spin-only expression of equation 14.

Table 4.8 – Room temperature μ_{eff} , T_{min} and $\chi_{\text{M}}T$ at T_{min} for the one-dimensional chain systems incorporating metal-cyanamide linkages.

Complex	μ_{eff} at 298K (BM)	$T_{\text{min}}^{\text{a}}$ (K)	$\chi_{\text{M}}T$ at T_{min} (emu K mol ⁻¹)
$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(\text{H}_2\text{O})_n$	1.87	47	0.386
$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{CF}_3\text{SO}_3]_{2n}$	1.92	48	0.416
$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BF}_4]_{2n}$	1.93	38	0.376
$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{PF}_6]_{2n}$	2.04	35	0.396
$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{Br}]_{2n}$	2.03	10	0.401
$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{Cl}]_{2n}$	1.97	24 ^b	0.360 ^b
$[\{\text{Cu}(\text{bpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(2\text{H}_2\text{O})_n$	1.95	55	0.433
$[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-Me-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(\text{H}_2\text{O})_n$	1.72	n/a	n/a

^a T_{min} is an artificial assignment denoting the minimum value of the well seen in the $\chi_{\text{M}}T$ plots. It is used to reflect the fact that it is not an indication of 3D ferromagnetic ordering.

^b The value of T_{min} and $\chi_{\text{M}}T$ at T_{min} represent a point of inflection where intermolecular antiferromagnetic interactions are taking place.

4.1.5.1 The $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}][\text{BPh}_4]_2$ System

At this point, and in order to avoid repetition and confusion, the nature of the magnetism shown in these $\chi_{\text{M}}T$ plot will be presented for the system for which the crystal structure was obtained and for which the molecular modeling was performed, namely the $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(\text{H}_2\text{O})_n$.

In order to describe the high temperature portion of the $\chi_{\text{M}}T$ vs T curve for the $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(\text{H}_2\text{O})_n$ chain, a theoretical plot of $\chi_{\text{M}}T$ vs T as a function of θ (figure 4.34) will be used. One can see from this figure that as θ

Figure 4.34 – Plot of $\chi_M T$ vs. Temperature as a function of Weiss temperature (θ) and modeled after a system with $S = \frac{1}{2}$, $C = 0.454 \text{ emu K mol}^{-1}$ and $g = 2.2$ using the Curie-Weiss law.

decreases, there is a downward trend in $\chi_M T$. This is identical to what is seen in our systems and therefore, the downward trend observed when cooling from high temperatures to before $T_{\min}$, is due to an antiferromagnetic interaction.

In order to determine the nature of the upturn in $\chi_M T$, a process of elimination was used. Of course, the first hypothesis was based on the crystal structure of $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\cdot(\text{H}_2\text{O})_n$. Two dominant magnetic exchange pathways can be seen; the first, a double cyanamide (NCN) pathway separating the

Cu(II) ions and the second, through the phenyl ring via the two amide nitrogens. The cyanamide pathway has previously been shown to be antiferromagnetic when bridging two pseudo-trigonal bipyramid Cu(II) ions.⁵² The crystal structure in section 4.1.3 shows that our system has a geometry lying in between that of trigonal bipyramid and square pyramidal. Molecular modeling confirms that this intermediate geometry results in a HOMO for the Cu-NCN linkage, responsible for the dominant antiferromagnetic pathway (figure 4.16). However, the amide/phenyl pathway can be predicted by the McConnell spin polarization mechanism, as explained earlier, to be ferromagnetic in nature. Therefore, one would immediately hypothesize that the system would be an alternating ferromagnetic/antiferromagnetic chain. However, susceptibility measurements contradict this conclusion. Clearly, initial investigation of the $\chi_M T$ versus T curve, disproves any homonuclear alternating ferromagnetic/antiferromagnetic chain system as the $\chi_M T$ versus T curve would show a decrease at low temperatures.⁵³

The $\chi_M T$ versus T curve behavior is also consistent with what one would expect to see in a homonuclear 1-D ferrimagnetic chain with alternating Landé factors.²¹ However, attempts to fit the data to known ferrimagnetic models failed as the well created by the minimum in the $\chi_M T$ versus T curve proved difficult to model. As a result, unrealistic values, in particular for g , were obtained.⁵⁴

Further literature searches lead us to conclude that our system was weakly ferromagnetic upon which is superimposed a dominant antiferromagnetic interaction. This type of magnetic behavior stems from an antiferromagnetic antisymmetric

interaction leading to the canting of the Cu(II) spins, in the ground state as illustrated below.

Thus, such an interaction would result in a non-compensating interaction of local

spins propagating along the chain (a) yielding a weak ferromagnetic ground state (b).

This antisymmetric interaction can be easily ascribed to the crystallographic differences outlined in section 4.1.3, in particular to figure 4.14. The “canting” of the Cu-pyridyl planes with respect to the Cu-amide-NCN plane is directly responsible for this antisymmetric interaction.

But what happened to the McConnell spin-polarization predicted ferromagnetic pathway? This, too, can be explained by the crystal structure. In order for there to be a ferromagnetic interaction, the molecular orbital must be orthogonal in nature. Studies have shown the small deviation in angle and poor overlap can result in a loss of ferromagnetism.⁵⁵ Figure 4.15, shown in section 4.1.3, clearly shows both. The *meta*-dicyd²⁻ bridging ligand is bent out of the plane by approximately 20°. Such a large deviation from planarity may account for the failure of the McConnell spin-polarization mechanism, in this instance.

Normally, the canting angle can be quantified when a spin canted material has been identified. However, since isolated 1-D chains are involved, the degree of canting cannot be determined as the saturation magnetization is never reached, even at very high fields (figure 4.35). Furthermore, no remnant or spontaneous magnetization is seen, again, due to the 1-D structure of the compound.

Figure 4.35 – Magnetization as a function of applied magnetic field for $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}][\text{BPh}_4]_2$ at temperatures of 2 K (●), 5 K (■) and 20 K (▲). The solid line represents the Brillouin function for an uncoupled $S = \frac{1}{2}$ system (equation 15) at 2K.

The magnetization as a function of applied magnetic field, $M(H)$, plot shows that at 20 K, the system behaves as a simple paramagnet. As the temperature is lowered further down to 2 K, saturation magnetization (M_s) is never reached. The Brillouin function⁵⁶ represents an uncoupled $S = \frac{1}{2}$ system, at 2 K, which is determined by the equation below.

$$M = Ng\beta S \left[\frac{2S+1}{2S} \coth\left(\frac{2S+1}{2S} y\right) - \frac{1}{2S} \coth\left(\frac{1}{2S} y\right) \right] \quad (15)$$

$$\text{where } y = \frac{g\beta SH}{kT}$$

Here, N is Avogadro's number, g is the Lande constant, β is the Bohr Magneton, S is the spin, H is the applied field and k is Boltzmann's constant. Even at 5.5 T and 2 K the system never reaches saturation. However, the proximity it gets to M_s is attributed to the weak antiferromagnetism of the Cu-NCN pathway. A good approximation used in quantifying this weak antiferromagnetism through J , the magnetic exchange constant, stems from a paper by Thompson⁵⁷ et al which relates J for dinuclear copper complexes, to the room temperature μ_{eff} values as shown in equation 16, below.

$$-2J = kT \ln \frac{3.0003g^2}{\mu_{eff}^2} - 3 \quad (16)$$

This results in a J value for $[\{\text{Cu}(\text{trpy})\}_2-\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n} \cdot (\text{H}_2\text{O})_n$ equal to -14 cm^{-1} .

4.1.5.2 Perturbations on the $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(\text{H}_2\text{O})_n$ Chain

The remaining seven one-dimensional systems incorporating metal-cyanamide linkages, will be examined in terms of the perturbations they impose on the $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(\text{H}_2\text{O})_n$ chain. First, the simplest alteration in the system was to change the inner sphere spectator ligand of trpy to bpy. As can be seen from the χ_{MT} vs. T data for $[\{\text{Cu}(\text{bpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{CF}_3\text{SO}_3]_{2n}\bullet(2\text{H}_2\text{O})_n$, the behaviour is much the same. The decrease in χ_{MT} , as the sample is cooled from high temperatures is identical to the $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(2\text{H}_2\text{O})_n$. Then at a temperature, T_{min} , of 55 K and a χ_{MT} value of $0.433 \text{ emu K mol}^{-1}$, the curve begins to rise sharply, already deemed as the onset of the weak ferromagnetic ground state. Therefore, this particular change in coordination sphere shows no effect on the magnetic properties of these systems. It should also be noted that other attempts at altering the Cu(II) coordination sphere with other ligands failed synthetically.

Another change made to this system was the introduction of the methyl group between the *meta*-substituted cyanamides in the form of $[\{\text{Cu}(\text{trpy})\}_2\text{-}\mu\text{-Me-meta-dicyd}]_n[\text{BPh}_4]_{2n}\bullet(\text{H}_2\text{O})_n$. The intention here was to see if the methyl group would cause a change in the geometry and hence an alteration of the magnetic properties. The cartoon below represents best what is thought to have happened.

As shown previously, the canting was due the antisymmetric interaction due to crystallographic differences. By substituting the methyl group, between the Cu(trpy) moieties, a sufficient geometry change should perturb the observed canting phenomenon. Indeed, in figure 4.33, no evidence of a weakly ferromagnetic ground state was observed, the plot showing that the antiferromagnetic exchange dominates to the lowest temperature measured.

One final perturbation placed on the $[\{\text{Cu}(\text{trpy})\}_2-\mu\text{-meta-dicyd}]_n[\text{BPh}_4]_{2n}\cdot(\text{H}_2\text{O})_n$ system involves the substitution of the BPh_4^- counter anion with other counter anions, namely CF_3SO_3^- , BF_4^- , PF_6^- , Br^- and Cl^- . As seen in the crystal structure, specifically figure 4.12(i), the BPh_4^- counter anion plays an important role in the isolation of the one-dimensional chains – interchain interactions in this case are negligible. Looking at the χ_{MT} vs. T plots (figures 4.26–4.33) one can plainly see that the size of the counter anion has a direct effect on the degree of interchain antiferromagnetic interactions. Like the BPh_4^- counter anion, the relatively large CF_3SO_3^- , BF_4^- and PF_6^- counter anions show no interchain interaction for here the residual spin caused by the spin canting is allowed to interact freely with the applied magnetic field. However, with the Br^- counter anion, the antiferromagnetic interchain

interaction can now be seen. Instead of rising quickly, the $\chi_M T$ curve (figure 4.30) shows a very small rise and then drops quickly as the temperature is lowered. The trend that is seen here, as one progresses from large, bulky anions, to a still large, yet not as bulky counter anion, is that it brings the chains closer together, thus increasing the contribution of interchain interactions. This is made clearer still by the metathesis of this system to a chloride (Cl^-). As can be seen here, the $\chi_M T$ vs. T plot (figure 4.31) shows an even stronger interchain antiferromagnetic interaction with no sign of an increase in $\chi_M T$ at all. In fact it shows the opposite. Where the increase of other systems is seen, a more rapid decrease is observed. Thus, with the smaller Cl^- counter anion, the one-dimensional chains are brought their closest, resulting in a system dominated by intrachain and interchain antiferromagnetic interactions.

4.2 $[\text{Cu}_{12}(\text{meta-dicyd})_{11}(\text{C}_3\text{H}_6\text{O})_{12}(\text{CF}_3\text{SO}_3)_2]_n$ Material

4.2.1 Synthesis

The next logical step after making the one-dimensional chains is to synthesize a material based on their chemical moieties. The obvious starting point was to take advantage of the like charges of both Cu^{2+} and meta-dicyd^{2-} , combine the two and see what happened. Thus, $\text{Cu}(\text{CF}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{H}_2\text{-meta-dicyd}$ were combined, in acetone, in equal molar amounts followed by the addition of 0.1 mL of triethylamine to deprotonate the bridging ligand, resulting in a navy blue powder quantitatively precipitating out of solution. Elemental analysis was difficult to fit but the best result gave the stoichiometry $[\text{Cu}_{12}(\text{meta-dicyd})_{11}(\text{C}_3\text{H}_6\text{O})_{12}(\text{CF}_3\text{SO}_3)_2]_n$. To justify the large amount of acetone added in this material, a Thermogravimetric Analysis (TGA) was performed on the sample (details to this experiment are in section 2.7.7). What was observed was that over a temperature range of 200°C, a 20% loss in the overall weight of the sample was recorded. From the stoichiometry of the material, twelve acetones account for exactly 20 % of the sample's molar mass. Furthermore, the rate of weight loss was slow and steady indicative of compound integrity and solvent loss. This fact, coupled with the IR data below, signifies the abundance of solvent.

4.2.2 IR Spectroscopy

The IR spectrum for $[\text{Cu}_{12}(\text{meta-dicyd})_{11}(\text{C}_3\text{H}_6\text{O})_{12}(\text{CF}_3\text{SO}_3)_2]_n$ is shown in below in figure 4.36

Figure 4.36 – IR spectrum of $[\text{Cu}_{12}(\text{meta-dicyd})_{11}(\text{C}_3\text{H}_6\text{O}_1)_{12}(\text{CF}_3\text{SO}_3)_2]_n$ as a KBr disk.

This is a relatively simple IR spectrum showing the typically strong $\nu(\text{NCN})$ stretch at 2181 cm^{-1} . Other bands of note are the $\nu(\text{S}=\text{O})$ from the triflate anion at 1283 cm^{-1} and 1028 cm^{-1} , the $\nu(\text{C}=\text{C})$ aromatic at 1594 cm^{-1} and 1486 cm^{-1} and finally the broad $\nu(\text{O-H})$ band at 3439 cm^{-1} due to the water absorbed by the KBr pellet medium.

4.2.3 Magnetic Measurements

The temperature dependence of the magnetic susceptibility was studied in the temperature range of 2-280 K and was run in an applied magnetic field of 100 Gauss (0.01 T). The plots for χ_M vs. T and χ^{-1} vs T are shown in figures 4.37 and 4.38, respectively. The χ_M vs T plot shows a system that appears to obey the Curie Law at high temperatures and the Curie-Weiss law at low temperatures, exhibiting long range

order with higher than normal χ_M values. Upon examination of the χ_M^{-1} vs. T plot, we see that the behaviour is similar to a weak ferromagnet or due to ferrimagnetic exchange. Data interpreted from the plot give values for $\theta = -98$ K and $T_C = 8$ K. T_C is the asymptotic value extrapolated from where the curve is sharply decreasing to where it levels out, shown by the inset of figure 4.38, indicating a phase transition. To further investigate this, a plot of $\chi_M T$ vs. T is used and shown in figure 4.39. The room temperature $\chi_M T$ vs. T value is $0.383 \text{ emu K mol}^{-1}$ which corresponds to an effective magnetic moment, $\mu_{\text{eff}} = 1.75 \text{ BM}$, slightly lower than expected for an uncoupled Cu(II) species. As seen on the inset diagram in figure 4.38, the $\chi_M T$ product decreases monotonically from $0.36 \text{ emu K mol}^{-1}$ at 240 K to $0.26 \text{ emu K mol}^{-1}$ at 60 K . This decrease is related to an antiferromagnetic interaction similar to those seen in the one-dimensional systems. Next, a magnetic phase transition from antiferromagnetic to ferromagnetic starts at 44 K , resulting in a $\chi_M T$ maximum of $8.14 \text{ emu K mol}^{-1}$ at 7 K . After this point the $\chi_M T$ values drops continually to 2 K indicating some degree of intermolecular antiferromagnetic interaction.⁵⁸

Figure 4.37 - χ_M vs. T plot for $[\text{Cu}_{12}(\text{meta-dicyd})_{11}(\text{C}_3\text{H}_6\text{O})_{12}(\text{CF}_3\text{SO}_3)_2]_n$ done in a 0.01 T applied magnetic field.

Figure 4.38 - χ_M^{-1} vs. T plot for $[\text{Cu}_{12}(\text{meta-dicyd})_{11}(\text{C}_3\text{H}_6\text{O}_1)_{12}(\text{CF}_3\text{SO}_3)_2]_n$ done in a 0.01 T applied magnetic field.

Figure 4.39 - $\chi_M T$ vs. T plot for $[\text{Cu}_{12}(\text{meta-dicyd})_{11}(\text{C}_3\text{H}_5\text{O}_1)_{12}(\text{CF}_3\text{SO}_3)_2]_n$ done in a 0.01 T applied magnetic field. The inset figure shows the full temperature range of the $\chi_M T$ data.

In order to consider this system an ordered canted ferromagnet, the two criteria which were covered in the introduction (section 1.4.6, figure 1.11) must be met. First, for a magnetization as a function of temperature plot, $M(T)$, the magnetization should reach an M_s value very much less than the actual M_s value for the system of study. Second, when examining a magnetization as a function of applied magnetic field plot, $M(H)$, there should be some evidence of field dependence at temperatures less than T_N .

Figure 4.40 – The magnetization as a function of temperature, $M(T)$, plot for $[\text{Cu}_{12}(\text{meta-dicyd})_{11}(\text{C}_3\text{H}_6\text{O})_{12}(\text{CF}_3\text{SO}_3)_2]_n$ done in an applied field of 0.01 T. The range of the plot is due to the lack of magnetization at $T > 30$ K.

Figure 4.41 – The magnetization as a function of applied magnetic field plot for $[\text{Cu}_{12}(\text{meta-dicyd})_{11}(\text{C}_3\text{H}_6\text{O})_{12}(\text{CF}_3\text{SO}_3)_2]_n$ at 2, 5 and 20 K.

As can be seen from the $M(T)$ plot of figure 4.40, the curve is just what one would expect for a spin canted system. The M_s value at 2.6 K is 0.347 BM which is a value much less than the expected 13.2 BM (where $g = 2.2$ and $S = 6$). The small drop in magnetization seen between 2.6 K and 2 K is, again, due to intermolecular antiferromagnetic exchange.

Magnetization as a function of applied magnetic field measurements, $M(H)$, performed up to 5.5 T, shown in figure 4.41, also support the theoretical plots of section 1.4.6, figure 1.11. The $M(H)$ plot run at 20 K ($T > T_N$) show that in the paramagnetic region of 20 K, the magnetization varies linearly and is not field dependent. However at

5 K and in particular 2 K where $T < T_N$, the field dependence of the magnetization departs from linearity, and becomes field dependent. At the highest applied field used, 5.5 T, and at the lowest temperature measured, 2K, the magnetization never reaches saturation. The magnetization value is 4.23 BM and saturation for a $S = 6$ system with $g = 2.2$ would be 13.2 BM. An important feature to note on the $M(H)$ plot is the fact that at 5 K and 2 K, when the applied field is zero, the sample remains magnetized by the Earth's magnetic field which has a field strength of approximately 1×10^{-5} T. The fact that there is a magnetization at zero applied field means that there is 3-D ordering, albeit due to a weak ferromagnetic ground state. To put the above plot into perspective, the diagram below shows a hysteresis plot of a soft ferromagnetic material.

The plot of figure 4.41 represents the upper-right quadrant of this diagram, although definitely not as dramatic a hysteresis shown here.

Information this material yields, which the one-dimensional chains could not, is the canting angle resulting from the antisymmetric exchange. Referring to equation 8, in section 1.4.6

$$\alpha = \sin^{-1} \left(\frac{M_w}{M_s} \right)$$

The canting angle can be calculated taking the inverse sine of the result obtained by dividing the magnetization of the sample in a weak field by the saturation magnetization achieved when the sample is placed in a strong field. The magnetization we achieve, at zero applied magnetic field, is 0.54 BM and the M_s for this material is equal to 13.2 BM. Thus the resulting canting angle, $\alpha = 2.5^\circ$ which seems reasonable considering the magnitude of $M(T)$ at 2K.

4.3 [AsPh₄][Cu(SCN)₃] One-Dimensional Chain

The use of small molecules to bridge magnetic centers has recently gained much interest because of the discovery of molecular magnetic materials based on metal-cyano bridges²⁶ and this has lead us to re-examine the coordination chemistry of thiocyanates. Metal-thiocyanato chemistry has had a considerable history of investigation⁵⁹ and examples of copper(II) homoleptic systems⁶⁰ have been confined to cationic salts of the form [Cat²⁺][Cu(SCN)₄]²⁻. In this study, we show that under conditions of excess Cu(II) ions, it is possible to synthesize a novel tetraphenylarsonium copper(II) thiocyanato anion salt, having the stoichiometry [AsPh₄][Cu(SCN)₃]. Furthermore, the crystal structure of this system revealed the complex salt to be a rare example of a metal-thiocyanato one-dimensional chain compound, [AsPh₄]_n[Cu(SCN)₃]_n.

4.3.1 Synthesis

The interest and success of small molecule bridges such as the azido (N₃⁻), cyano (CN⁻), cyanato (CNO⁻) and of course, the thiocyanato (SCN⁻) lead us to reinvestigate this type of chemistry, choosing the SCN⁻ bridging ligand. Undoubtedly, the unpredicted synthesis of the [AsPh₄][SCN] had something to do with this as well. This complex salt was synthesized by combining concentrated methanolic solutions of Cu(CF₃SO₃)₂•4H₂O with [AsPh₄][SCN] in a 1:2 molar ratio. After four days in the dark, evaporation of the yellow/brown solution yielded small white crystals of (AsPh₄)(CF₃SO₃) and very large brown rectangular prisms of the title complex, [AsPh₄]_n[Cu(SCN)₃]_n. These crystals were manually separated and washed with hot

ethanol to remove any residual $(\text{AsPh}_4)(\text{CF}_3\text{SO}_3)$. A single crystal was selected for crystallographic analysis.

4.3.2 X-Ray Crystallography

The results of this analysis are shown as an ORTEP diagram in figure 4.42 and tables 4.9–4.14 compile the bond distance and angle data as well as the atomic positional parameters. In order to clearly show the geometrical features of this system, a ball and stick diagram, shown in figure 4.43 will represent the ORTEP of figure 4.42. The ball and stick diagram shows that each Cu(II) ion of $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$ is in a slightly distorted square pyramidal coordination sphere made up of two sulfur donor atoms in axial and equatorial coordination sites and three nitrogen donor atoms, all in the equatorial plane. A linear chain of Cu(II) ions is formed by alternating pairs of equatorial-axial (EA) and equatorial-equatorial (EE) copper-thiocyanato bridges. An equatorial, monodentate, thiocyanato-*N* ligand completes the coordination sphere about each Cu(II) ion. The separation between the uncoordinated sulfur atom of this monodentate thiocyanato ligand and the nearest Cu(II) ion on another chain is 5.63 Å. This interchain spacing and the means by which the chains pack in the unit cell is illustrated both with the AsPh_4^+ cations present (figure 4.44) and removed (figure 4.45). This arrangement of chains suggests that there will be weak, if any, interaction between the chains.

Figure 4.42 – ORTEP plot of $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$ showing the atomic labeling scheme and the 30% thermal ellipsoids.

Figure 4.43 – Ball and stick diagram of $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$ illustrating the copper(II) coordination geometry and the two bridging pathways of this alternating chain compound.

Figure 4.44 – Ball and stick diagram of the unit cell of $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$ showing the chains from the end-on perspective including the AsPh_4^+ cations.

Figure 4.45 – Ball and stick diagram of $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$ showing the chains from the end-on perspective excluding the AsPh_4^+ cations.

Table 4.9 – Crystal data and structural refinement information for the X-ray structural determination of $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$.

Empirical formula	$\text{C}_{27} \text{H}_{20} \text{As}_1 \text{Cu}_1 \text{N}_3 \text{S}_3$
Formula weight	621.10
Temperature	297(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$\text{P2}_1/\text{c}$
Unit cell dimensions	$a = 13.838(3) \text{ Å}$ $\alpha = 90^\circ$ $b = 9.679(2) \text{ Å}$ $\beta = 105.018(4)^\circ$ $c = 21.623(5) \text{ Å}$ $\gamma = 90^\circ$
Volume	$2797.2(11) \text{ Å}^3$
Z	4
Density (calculated)	1.475 Mg/m^3
Absorption coefficient	2.199 mm^{-1}
F(000)	1252
Crystal size	$0.3 \times 0.3 \times 0.08 \text{ mm}$
Theta range for data collection	1.95° to 22.50°
Limiting indices	$-14 \leq h \leq 14, 0 \leq k \leq 10, 0 \leq l \leq 23$
Reflections collected	17682
Independent reflections	3661 [$R(\text{int}) = 0.0490$]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.801520 and 0.480345
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3661 / 0 / 316
Goodness-of-fit on F^2	1.068
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0356, wR2 = 0.0916$
R indices (all data)	$R1 = 0.0482, wR2 = 0.0953$
Largest diff. peak and hole	0.406 and $-0.489 \text{ e} \cdot \text{Å}^{-3}$

Table 4.10 - Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
As	2312(1)	4185(1)	3232(1)	50(1)
Cu	937(1)	7503(1)	5404(1)	68(1)
S(1)	-1836(1)	4552(1)	4740(1)	67(1)
S(2)	-780(1)	11433(1)	5810(1)	90(1)
S(3)	4223(1)	8674(3)	6371(1)	139(1)
N(1)	-323(3)	6536(4)	5142(2)	75(1)
N(2)	296(3)	9070(4)	5719(2)	74(1)
N(3)	2254(4)	8194(5)	5792(2)	103(2)
C(1)	-952(3)	5727(5)	4981(2)	61(1)
C(2)	-145(3)	10055(5)	5752(2)	58(1)
C(3)	3080(4)	8371(5)	6024(2)	74(1)
C(4)	2883(3)	6754(5)	3869(2)	70(1)
C(5)	3296(4)	8059(6)	3945(3)	94(2)
C(6)	3715(4)	8586(6)	3487(4)	103(2)
C(7)	3723(4)	7829(7)	2957(3)	103(2)
C(8)	3314(4)	6522(5)	2869(2)	74(1)
C(9)	2896(3)	5994(4)	3330(2)	56(1)
C(10)	2093(3)	3713(5)	1898(2)	69(1)
C(11)	2331(4)	3121(6)	1384(2)	83(2)
C(12)	3070(4)	2134(6)	1474(2)	80(2)
C(13)	3569(4)	1737(6)	2077(3)	87(1)
C(14)	3336(4)	2330(5)	2605(2)	69(1)
C(15)	2600(3)	3318(4)	2512(2)	50(1)
C(16)	2380(4)	2157(5)	4210(2)	69(1)
C(17)	2841(5)	1412(5)	4745(2)	87(2)
C(18)	3805(6)	1656(7)	5055(3)	100(2)
C(19)	4334(5)	2664(7)	4851(3)	110(2)
C(20)	3885(4)	3433(6)	4303(2)	83(2)
C(21)	2919(3)	3166(4)	3989(2)	55(1)
C(22)	463(4)	5259(5)	3384(2)	69(1)
C(23)	-549(4)	5242(6)	3334(2)	75(1)
C(24)	-1140(4)	4242(7)	3014(3)	92(2)
C(25)	-691(4)	3183(9)	2759(4)	146(3)
C(26)	322(4)	3179(7)	2806(3)	126(3)
C(27)	896(3)	4237(4)	3114(2)	53(1)

Table 4.11 - Bond lengths [Å] for [AsPh₄]_n[Cu(SCN)₃]_n.

As-C(15)	1.899(4)	C(7)-C(8)	1.379(8)
As-C(21)	1.910(4)	C(8)-C(9)	1.374(6)
As-C(27)	1.911(4)	C(10)-C(11)	1.365(6)
As-C(9)	1.917(4)	C(10)-C(15)	1.384(6)
Cu-N(3)	1.919(5)	C(11)-C(12)	1.375(7)
Cu-N(1)	1.930(5)	C(12)-C(13)	1.362(7)
Cu-N(2)	1.966(4)	C(13)-C(14)	1.388(6)
Cu-S(1)#1	2.4090(13)	C(14)-C(15)	1.373(6)
Cu-S(2)#2	2.7762(18)	C(16)-C(17)	1.373(7)
S(1)-C(1)	1.653(5)	C(16)-C(21)	1.386(6)
S(1)-Cu(1)	2.4090(13)	C(17)-C(18)	1.349(8)
S(2)-C(2)	1.621(5)	C(18)-C(19)	1.361(8)
S(2)-Cu#2	2.7762(18)	C(19)-C(20)	1.401(7)
S(3)-C(3)	1.592(6)	C(20)-C(21)	1.359(6)
N(1)-C(1)	1.156(5)	C(22)-C(27)	1.363(6)
N(2)-C(2)	1.143(5)	C(22)-C(23)	1.377(6)
N(3)-C(3)	1.136(6)	C(23)-C(24)	1.338(7)
C(4)-C(5)	1.379(7)	C(24)-C(25)	1.384(8)
C(4)-C(9)	1.384(6)	C(25)-C(26)	1.379(7)
C(5)-C(6)	1.369(8)	C(26)-C(27)	1.359(6)
C(6)-C(7)	1.363(8)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1 #2 -x,-y+2,-z+1

Table 4.12 - Bond angles [°] for [AsPh₄]_n[Cu(SCN)₃]_n.

C(15)-As-C(21)	109.63(17)	C(9)-C(8)-C(7)	118.5(5)
C(15)-As-C(27)	109.16(17)	C(8)-C(9)-C(4)	120.9(4)
C(21)-As-C(27)	109.60(18)	C(8)-C(9)-As	120.3(4)
C(15)-As-C(9)	108.79(18)	C(4)-C(9)-As	118.8(3)
C(21)-As-C(9)	107.34(18)	C(11)-C(10)-C(15)	119.7(5)
C(27)-As-C(9)	112.28(18)	C(10)-C(11)-C(12)	120.2(5)
N(3)-Cu-N(1)	168.85(19)	C(13)-C(12)-C(11)	120.4(5)
N(3)-Cu-N(2)	92.47(19)	C(12)-C(13)-C(14)	120.0(5)
N(1)-Cu-N(2)	91.26(16)	C(15)-C(14)-C(13)	119.3(4)
N(3)-Cu-S(1)#1	83.09(14)	C(14)-C(15)-C(10)	120.3(4)
N(1)-Cu-S(1)#1	91.08(11)	C(14)-C(15)-As	119.5(3)
N(2)-Cu-S(1)#1	167.55(12)	C(10)-C(15)-As	120.1(3)
N(3)-Cu-S(2)#2	96.68(17)	C(17)-C(16)-C(21)	119.1(5)
N(1)-Cu-S(2)#2	93.35(13)	C(18)-C(17)-C(16)	120.7(6)
N(2)-Cu-S(2)#2	96.33(12)	C(17)-C(18)-C(19)	120.7(5)
S(1)#1-Cu-S(2)#2	95.74(5)	C(18)-C(19)-C(20)	119.8(6)
C(1)-S(1)-Cu#1	104.13(14)	C(21)-C(20)-C(19)	119.0(5)
C(2)-S(2)-Cu#2	98.18(16)	C(20)-C(21)-C(16)	120.7(4)
C(1)-N(1)-Cu	165.9(4)	C(20)-C(21)-As	119.2(4)
C(2)-N(2)-Cu	163.7(4)	C(16)-C(21)-As	120.2(3)
C(3)-N(3)-Cu	168.2(5)	C(27)-C(22)-C(23)	120.5(5)
N(1)-C(1)-S(1)	178.6(4)	C(24)-C(23)-C(22)	121.5(5)
N(2)-C(2)-S(2)	178.6(4)	C(23)-C(24)-C(25)	117.7(5)
N(3)-C(3)-S(3)	177.3(5)	C(26)-C(25)-C(24)	121.7(6)
C(5)-C(4)-C(9)	119.5(5)	C(27)-C(26)-C(25)	119.2(5)
C(6)-C(5)-C(4)	119.8(5)	C(26)-C(27)-C(22)	119.4(4)
C(7)-C(6)-C(5)	120.3(6)	C(26)-C(27)-As	119.6(3)
C(6)-C(7)-C(8)	121.1(6)	C(22)-C(27)-As	120.7(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y+1, -z+1 #2 -x, -y+2, -z+1

Table 4.13 - Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
As	50(1)	51(1)	51(1)	-2(1)	14(1)	1(1)
Cu	65(1)	46(1)	88(1)	-7(1)	9(1)	6(1)
S(1)	57(1)	52(1)	93(1)	2(1)	18(1)	5(1)
S(2)	103(1)	69(1)	103(1)	-16(1)	33(1)	20(1)
S(3)	64(1)	214(2)	133(2)	8(2)	13(1)	-9(1)
N(1)	70(3)	44(2)	111(3)	-7(2)	24(2)	9(2)
N(2)	86(3)	51(2)	82(3)	-7(2)	15(2)	8(2)
N(3)	80(3)	69(3)	142(4)	-24(3)	-1(3)	2(3)
C(1)	59(3)	46(3)	80(3)	7(2)	24(2)	23(2)
C(2)	60(3)	54(3)	57(3)	-8(2)	11(2)	-13(2)
C(3)	76(4)	65(3)	81(3)	-2(3)	19(3)	5(3)
C(4)	65(3)	64(3)	82(3)	-9(3)	20(3)	-8(3)
C(5)	74(4)	67(4)	133(5)	-30(4)	13(4)	-7(3)
C(6)	66(4)	54(3)	178(7)	3(4)	10(4)	-9(3)
C(7)	89(4)	82(5)	140(6)	29(4)	34(4)	-14(4)
C(8)	66(3)	67(3)	91(4)	9(3)	24(3)	-6(3)
C(9)	47(3)	53(3)	65(3)	4(2)	9(2)	1(2)
C(10)	67(3)	81(3)	56(3)	2(2)	12(2)	8(3)
C(11)	89(4)	106(4)	53(3)	-2(3)	19(3)	-11(4)
C(12)	97(4)	88(4)	66(3)	-24(3)	42(3)	-25(3)
C(13)	93(4)	90(4)	87(4)	-9(3)	41(3)	21(3)
C(14)	75(3)	77(3)	56(3)	4(2)	19(2)	14(3)
C(15)	51(2)	51(3)	49(2)	1(2)	17(2)	1(2)
C(16)	82(3)	58(3)	69(3)	-4(2)	24(3)	-3(3)
C(17)	140(6)	64(3)	65(3)	8(3)	41(4)	7(4)
C(18)	132(6)	99(5)	67(4)	24(3)	19(4)	31(4)
C(19)	97(5)	141(6)	76(4)	23(4)	-8(3)	12(4)
C(20)	69(3)	110(4)	67(3)	14(3)	9(3)	-3(3)
C(21)	67(3)	53(3)	43(2)	-3(2)	15(2)	4(2)
C(22)	62(3)	62(3)	83(3)	-17(2)	19(3)	-3(2)
C(23)	65(3)	79(3)	87(4)	-7(3)	27(3)	13(3)
C(24)	54(3)	132(5)	91(4)	-23(4)	21(3)	3(4)
C(25)	67(4)	180(7)	193(7)	-115(6)	38(4)	-35(4)
C(26)	67(4)	140(6)	177(6)	-103(5)	43(4)	-25(4)
C(27)	47(2)	55(3)	59(2)	-5(2)	16(2)	0(2)

Table 4.14 - Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$.

	x	y	z	U(eq)
H(4A)	2598	6388	4178	84
H(5A)	3291	8579	4305	113
H(6A)	3995	9466	3538	124
H(7A)	4010	8200	2650	124
H(8A)	3321	6011	2506	89
H(10A)	1592	4378	1837	82
H(11A)	1993	3386	971	99
H(12A)	3229	1736	1122	96
H(13A)	4067	1067	2135	104
H(14A)	3675	2062	3017	83
H(16A)	1715	1987	3998	83
H(17A)	2486	731	4896	104
H(18A)	4110	1129	5412	121
H(19A)	4992	2843	5075	133
H(20A)	4243	4116	4157	100
H(22A)	855	5974	3603	83
H(23A)	-829	5941	3526	90
H(24A)	-1828	4257	2965	110
H(25A)	-1083	2456	2551	175
H(26A)	609	2463	2628	151

4.3.3 IR Spectroscopy

The infrared spectrum of $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$ is shown in figure 4.46 and displays a $\nu(\text{SCN})$ stretching pattern similar to other homoleptic $\text{M}(\text{SCN})_x$ spectra. Three bands at 2153, 2109 and 2077 cm^{-1} correspond to the three SCN ligands, all of which are in different coordination environments. Other bands correspond with accepted frequencies for AsPh_4 phenyl frequencies and SCN asymmetric stretches. The broad peak at 3432 cm^{-1} is due to water present in the KBr disk medium.

Figure 4.46 – IR spectrum of $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$ as a KBr disk.

4.3.4 Molecular Modeling

Molecular modeling was performed on this one-dimensional system in order to confirm that the HOMO (magnetic orbital) was indeed $d_{x^2-y^2}$ as predicted by the geometry of the copper(II) ions. We performed a semi-empirical calculation using the PM3(tm) semi-empirical calculation on the model complex $[\{\text{Cu}(\text{NH}_3)_2(\text{NCS}\{-\text{N}\})\}_2(\mu\text{-NCS})_2]$ where the bridging thiocyanates are EE and the monodentate thiocyanato ligand occupies the axial coordination site. The calculation was constrained by the bond angles and lengths derived from the X-ray structure of $[\text{AsPh}_4][\text{Cu}(\text{SCN})_3]$ and gave the HOMO shown in figure 4.47. The HOMO illustrates the superexchange pathway for antiferromagnetic coupling between the two Cu(II) $d_{x^2-y^2}$ orbitals and is consistent with EPR studies of square pyramidal Cu(II) complexes that show the odd electron to reside in a $d_{x^2-y^2}$ orbital.⁶¹ It is also important to note that there is no contribution to the HOMO from the axial thiocyanato ligand. To emphasize this point, a semi-empirical calculation of the model complex $[\{\text{Cu}(\text{NH}_3)_2(\text{NCS}\{-\text{N}\})\}_2(\mu\text{-NCS})_2]$ where the thiocyanato bridges are EA gave two degenerate HOMO's as shown in Figure 4.48.

Figure 4.47 – HOMO of the model complex $[\{\text{Cu}(\text{NH}_3)_2(\text{NCS})\}_2(\mu\text{-NCS})_2]$ where the bridging thiocyanates are EE and the monodentate thiocyanato ligand occupies the axial coordination site. The semi-empirical calculation was constrained by the bond angles and lengths derived from the X-ray structure shown in section 4.3.2.

Figure 4.48 - HOMO of the model complex $[\{\text{Cu}(\text{NH}_3)_2(\text{NCS})\}_2(\mu\text{-NCS})_2]$ where the bridging thiocyanates are EA and the monodentate thiocyanato ligand occupies the equatorial coordination site. The semi-empirical calculation was constrained by the bond angles and lengths derived from the X-ray structure shown in section 4.3.2.

4.3.5 Magnetic Measurements

The solid state, temperature dependent magnetic susceptibility of $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$ from 2 to 270 K was performed using 40.3 mg of microcrystalline powder sample in a 2000 Gauss (0.2 T) field. The molar magnetic susceptibility plot, shown in figure 4.49, shows a smooth maximum at 80 K that is characteristic of intramolecular antiferromagnetic exchange. At lower temperatures, the drop in susceptibility approaches zero and then begins to increase at approximately 10 K. This increase most likely results from uncoupled Cu(II) ions owing to mononuclear impurities.⁶²

Figure 4.49 – Molar magnetic susceptibility from 5 to 270 K in a 0.2T field for $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$.

The Curie-Weiss plot, which is a plot of inverse molar susceptibility as a function of temperature, is shown in figure 4.50. This plot, quantified by the y-axis on the left, shows a large spike which begins at approximately 35 K and peaks at 12 K. Magnetically, this means a loss in susceptibility while thermodynamically it represents a population of the singlet ground state. The y-axis on the right shows the high temperature region which was fit to the Curie-Weiss law, shown previously in Chapter 1, equation (5). This plot clearly indicates an antiferromagnetic system with the x-intercept, $\theta = -69$ K.

Figure 4.50 – Inverse molar susceptibility plot of $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$ graphed on left and high temperature data fit to the Curie-Weiss law graphed on the right.

The $\chi_M T$ versus Temperature plot, shown in figure 4.51, shows this antiferromagnetism and the loss of susceptibility at low temperature quite well. Coupled with this diagram, plotted on the right y-axis, is the spin-only effective magnetic moment which is calculated using equation 14. The room temperature magnetic moment for this system is 1.67 BM which is considerably lower (normally 1.90 BM for $S = \frac{1}{2}$, $g = 2.2$) than one would expect for an uncoupled spin $\frac{1}{2}$ copper(II) system.

Figure 4.51 - $\chi_M T$ and effective magnetic moments plots as a function of temperature for $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$

Now that the nature of the magnetism for this system has been well established, an attempt at determining the magnitude of the magnetic interaction must be done. As seen in the crystal structure of $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$ in section 4.3.2, this system is actually an alternating one-dimensional chain. The alternating exchange interactions of a linear chain of are illustrated by,

where J is the exchange constant mediated by an EE bridge and J' is the exchange constant mediated by an EA bridge. Table 4.15 summarizes the exchange constants found for the few copper-thiocyanato bridged systems in the literature. The EA copper-thiocyanato bridge appears to promote weakly ferromagnetic or very weakly antiferromagnetic exchange whereas strong antiferromagnetic exchange was observed for the single example of a complex possessing an EE bridge. Under conditions in which the ratio J'/J is very small, it is possible to simplify treatments of alternating antiferromagnetic chains⁶³ or alternating antiferromagnetic-ferromagnetic chains⁶⁴ to the case of magnetically isolated Cu(II) dimers.

Table 4.15 - Geometry, Bridging Modes and Exchange Constants for Copper(II)-Thiocyanato Bridged Systems.

Complex ^a	Geometry ^b	Bridging Mode ^c	J (cm ⁻¹) ^d	Ref
[Cu ₂ (μ-SCN) ₂ (Et ₃ dien) ₂](ClO ₄) ₂	OC	EA	+7.7	65
[Cu ₂ (μ-SCN) ₂ (Me ₅ dien) ₂](ClO ₄) ₂	SPY	EA	+1.6	65
[Cu ₂ (μ-SCN) ₂ (ept) ₂](ClO ₄) ₂	OC	EA	+1.3	65
[Cu{O(CH ₂) ₃ N(Me) ₂ }(NCS)] _n	SPY	EA	neg	60(m)
[Cu{O(CH ₂) ₃ N(Et) ₂ }(NCS)] _n	SPY	EA	neg	60(m)
[Cu{O(CH ₂) ₃ N(n-Bu) ₂ }(NCS)] _n	SPY	EA	neg	60(m)
[Cu(bheg)NCS] _n	OC	EA	neg	60(j)
[Cu(4-bromopyridine) ₂ (NCS) ₂] _n	OC	EA	e	60(l)
[Cu(bpm)(NCS) ₂] _n	OC	EA	-0.6	60(g)
[Cu(bpm)(NCS) ₄] _n	OC	EA	neg	60(g)
[{Cu ₂ (tmen) ₂ NCS(μ-Cu(pba))(μ-SCN)] _n ·(3H ₂ O)] _n	SPY	AA	wf	60(d)
{[Cu(NCS)(μ-NCS)(Hmtpo)(H ₂ O)] ₂] _n	OC	EE/EA	-148	60(b)
[AsPh ₄][Cu(SCN) ₃]	SPY	EE/EA	-90	this work

^a ligand abbreviations, Et₃dien = 1,4,7-triethyldiethylenetriamine, Me₅dien = 1,1,4,7,7-pentamethyldiethylenetriamine, ept = N-(2-aminoethyl)-1,3-propanediamine, bpm = 2,2'-bipyrimidine, bheg = N,N-bis(2-hydroxyethyl)glycinato, tmen = N,N,N',N'-tetramethylethylenediamine, tren = tris(2-aminoethyl)amine, pba = 1,3-propanediylbis(oxamato), Hmtpo = 4H,7H-5-methyl-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine

^b OC-octahedral geometry, SPY-square pyramidal geometry

^c EA-equatorial-axial bridge, EE-equatorial-equatorial bridge, AA-axial-axial bridge

^d $H = -JS_A \bullet S_B$, from magnetic susceptibility measurements, neg-negligible interaction, wf - weakly ferromagnetic.

^e not determined

Our first attempt, shown by the solid line in Figure 4.52 is the best fit of the data using a modified Bleaney-Bowers equation for exchange coupled dimers,^{1,60(b)}

$$\chi = \frac{2Ng^2\beta^2}{kT \left[3 + \exp\left(\frac{-J}{kT}\right) \right]} (1 - \rho) + \frac{Ng^2\beta^2}{2kT} (\rho) \quad (17)$$

for a Hamiltonian of the form $H = -JS_A \bullet S_B$, where J is the singlet-triplet energy gap.

The modification to this expression, seen in the second term, accounts for the presence

of uncoupled species, quantified by ρ . During the modeling process, g , J and ρ were all taken as adjustable parameters resulting in values of $g = 2.1$, $J = -90 \text{ cm}^{-1}$ and $\rho = 3.6 \times 10^{-4}$. The agreement factor, as determined by the TableCurve software package, is a quite acceptable value of $r^2 = 0.998$ and the remainder of the fitting data can be found in Appendix I.

Figure 4.52 – Temperature dependence of molar magnetic susceptibility of $[\text{AsPh}_4]_n[\text{Cu}(\text{SCN})_3]_n$. The solid line represents the best fit using the Bleaney-Bowers dimer model of equation 17.

Indeed, the model above does fit the data well but, remembering that this is an alternating chain, an attempt to fit the data to an alternating chain model could not be ignored. Attempts at finding a suitable model turned up an expression derived by Hatfield et al⁶³ based on an alternating Heisenberg antiferromagnet. The Hamiltonian for the Heisenberg alternating linear chain may be written as

$$H = -2J \sum_{i=1}^{n/2} [S_{2i} \cdot S_{2i-1} + \alpha S_{2i} \cdot S_{2i+1}] \quad (17)$$

where J is the exchange integral between a spin and its right neighbour and αJ is the exchange integral between a spin and its left neighbour, as illustrated by:

At the extremes, when $\alpha = 0$, the model reduces to a dimer model and when $\alpha = 1$, the model reduces to a linear chain model. The expression for the molar magnetic susceptibility of this model is shown below.

$$\chi_M = \frac{Ng^2\beta^2}{kT} \frac{A+Bx+Cx^2}{1+Dx+Ex^2+Fx^3} \quad \text{where } x = \frac{|J|}{kT} \quad (18)$$

Using the Bleaney-Bowers dimer model as a good approximation, the parameters chosen for A-F were based on values determined for a system with $0 \leq \alpha \leq 0.4$ (ie a system which tends towards the dimer limit). These values are:

$$A = 0.25$$

$$B = -0.12587 + 0.22752\alpha$$

$$C = 0.019111 - 0.13307\alpha + 0.50967\alpha^2 - 1.3167\alpha^3 + 1.0081\alpha^4$$

$$D = 0.10772 + 1.4192\alpha$$

$$E = -0.0028521 - 0.42346\alpha + 2.1953\alpha^2 - 0.82412\alpha^3$$

$$F = 0.37754 - 0.067022\alpha + 6.9805\alpha^2 - 21.678\alpha^3 + 15.838\alpha^4$$

The data and the curve of best fit is shown in figure 4.53. During the modeling process, g , $|J|$ and α were all taken as adjustable parameters resulting in values of

$g = 2.1$, $J = -91 \text{ cm}^{-1}$ and $\alpha J = -10 \text{ cm}^{-1}$ ($\alpha = 0.114$). The agreement factor, as determined by the TableCurve software package, is an acceptable value of $r^2 = 0.997$ and the remainder of the fitting data can be found in Appendix I.

Figure 4.53 - Temperature dependence of molar magnetic susceptibility of $[\text{AsPh}_4][\text{Cu}(\text{SCN})_3]$. The solid line represents the best fit using the alternating chain model of equation 18.

CHAPTER 5

CONCLUSIONS AND FUTURE STUDIES

The continuing and broadening interest in molecular magnetic materials with increased dimensionality and higher T_c values will be the driving force in this field of research for some time to come. Increasingly, research groups are generating data on one-dimensional systems which exhibit a wide variety of magnetic exchange mechanisms. The reason for this is clear when examining it from the point of view of materials magnetochemists. The synthesis of materials is more an art than a science and the inability to grow single crystals for study of structure and magnetic properties remains a constant limitation. However, in synthesizing one-dimensional chains, one has more control over the chemistry of the resulting architecture. Furthermore, interconnected chains are the first step towards two- and three-dimensional systems.

Two novel *meta*-substituted dicyanamidobenzene dianion ligands have been successfully synthesized and characterized. Their purposeful design has led to the creation of interesting systems where both the ligand topology and the metal coordination environment result to form a one-dimensional chain structure exhibiting a weak, ferromagnetic ground state, the first example of its kind. The nature of the counter ion has also been altered such that interchain distances, and hence, interchain interactions were tuned resulting in a complete change in magnetic behaviour. The architecture of the original *meta*-dicyd²⁻ bridging ligand was modified in such a way as to alter the structure of the spin canted chains, thereby removing the crystallographic differences accountable for the antisymmetric interaction in the chain. Finally, a small change in the inner

coordination sphere of the Cu(II) ion resulted in little change in the magnetic properties of these chains further proving that the ligand topology is responsible for the antisymmetric interaction.

The next step was the synthesis of a material, incorporating the building blocks of these one dimensional chains, by taking advantage of like charges and allowing the material to self assemble in solution. The result was a 3D antiferromagnetically ordered material with a remnant magnetization at zero applied magnetic field. Interestingly enough, however, the same antisymmetric interaction persisted accounting for the weak ferromagnetism displayed by the one-dimensional chains, again, further indicating the role of the bridging ligand in these canted systems. Furthermore, calculated canting angle was very close to the angles responsible for the antisymmetric exchange of the one-dimensional chains.

Finally, a reinvestigation of thiocyanate chemistry led us to the discovery of the first homoleptic Cu(II) thiocyanato alternating one dimensional chain. The alternating nature of the chain allowed us to examine the role of the equatorial-equatorial (EE) versus equatorial-axial (EA) bridging modes. As predicted by theory and modeling, the EE bridges were responsible for the strong antiferromagnetic exchange seen in this chain.

Future studies involving the *meta*-dicyd²⁻ bridged one-dimensional systems are currently being approached by three avenues. One, is to increase the dimensionality and thus increase the critical temperature of the materials by synthesizing systems based on the 1,3,5-tricyanamidobenzene trianion (tricyd³⁻) ligand:

Work with tricyd³⁻ is currently underway and expectations are that it will form dendritic, sheet-like structures, thus increasing the number of spins per magnetic domain and hopefully increase T_c . The second approach is to vary the paramagnetic metal center and create both homometallic and heterometallic materials, thereby increasing the number of spins per magnetic domain. Finally, a further study examining the effect of spectator ligands on the metal ion and how coordination number affects the magnetic properties of these materials, will be done.

With the extensive research done by our group on *para*-dicyd²⁻ complexes and the effects of metal-metal coupling mediated by this family of ligands, it was rewarding to start a new area of study based on the *meta*-substituted positional isomer. Now, with the ground work laid, other systems can be made to tune further the magnetic properties of systems incorporating this *meta*-dicyd²⁻ and others derived from it.

Appendix I

1. Numerical and error information associated with the curve-fit for the Bleaney-Bowers equation (17) shown in figure 4.52.

r^2 Coef Det	DF Adj r^2	Fit Std Err	F-value
0.9980790	0.9977588	4.449357e-05	4935.9352

Parameter	Value	Std Error	t-value	95% Confidence Limits
g	2.099101	0.009534	220.1532	2.079129 to 2.119072
J	-90.4721	0.711871	-127.090	-91.9632 to -88.9810
ρ	0.000361	0.000399	0.904935	-0.00047 to 0.001198

Area Xmin-Xmax Area Precision
0.4609437 3.69644e-15

Function min X-Value Function max X-Value
1.465692e-05 11.144921 0.0025556 81.138923

1st Deriv min X-Value 1st Deriv max X-Value
-8.97424e-06 126.64017 7.563286e-05 33.376507

2nd Deriv min X-Value 2nd Deriv max X-Value
-2.44325e-06 47.204920 5.519173e-06 20.137897

r^2 Coef Det DF Adj r^2 Fit Std Err
0.9980790 0.9977588 4.449357e-05

Source	Sum of Squares	DF	Mean Square	F
Regr	1.9543122e-05	2	9.771561e-06	4935.94
Error	3.7613877e-08	19	1.9796777e-09	
Total	1.9580736e-05	21		

2. Numerical and error information associated with the curve-fit for the Alternating Antiferromagnetic Chain equation (18) shown in figure 4.53.

r^2 Coef Det	DF Adj r^2	Fit Std Err	F-value
0.9971775	0.9967071	5.393269e-05	3356.3507

Parameter	Value	Std Error	t-value	95% Confidence Limits
J	90.70730	0.429301	105.6451	88.90888 to 92.50570
α	0.113817	0.013100	8.687725	0.086376 to 0.141258
g	2.122132	0.052573	85.66016	2.096026 to 2.147920

Area Xmin-Xmax Area Precision
0.4597669816 7.815205e-13

Function min X-Value Function max X-Value
-6.97882e-05 12.976295906 0.0025606783 80.940491008

1st Deriv min X-Value 1st Deriv max X-Value
-9.1028e-06 125.13311781 7.484312e-05 32.660556640

2nd Deriv min X-Value 2nd Deriv max X-Value
-2.34075e-06 48.092991138 7.21185e-06 8.2445989221

r^2 Coef Det DF Adj r^2 Fit Std Err
0.9971775338 0.9967071227 5.393269e-05

Source	Sum of Squares	DF	Mean Square	F
Regr	1.952547e-05	2	9.762735e-06	3356.35
Error	5.5265966e-08	19	2.908735e-09	
Total	1.9580736e-05	21		

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