Synthesis and Characterization of Novel Multidentate 1,2,3,5-Dithiadiazolyl Radical Ligands with Potential Luminescent and Magnetic Applications

by

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SYNTHESIS AND CHARACTERIZATION OF NOVEL MULTIDENTATE 1,2,3,5-DITHIADIAZOLYL RADICAL LIGANDS WITH POTENTIAL LUMINESCENT AND MAGNETIC APPLICATIONS

Scott B. Mackenzie
University of Guelph, 2015

Novel, multidentate (denticity greater than two) 1,2,3,5-dithiadiazolyl radical ligands have been synthesized and characterized. The 4-(2',2''-bipyrid-6'-yl)-1,2,3,5-dithiadiazolyl (bipyDTDA) radical ligand has been characterized via X-ray crystallography and displays cis-cofacial dimerization in the solid state. BipyDTDA features a tridentate nitrogen coordination pocket and was successfully coordinated to Ln(III) metal centers including Ce(III), Pr(III) and Dy(III). The complexes above are structurally interesting in terms of Ln-Thiazyld compounds as they are isostructural throughout most of the lanthanide series. An additional undimerized complex SbCl\textsubscript{3}(bipyDTDA) has also been synthesized which contains contacts that imply a potential pathway for intermolecular magnetic coupling.

A second DTDA ligand 6,6'-bis-1,2,3,5-dithiadiazolyl-2,2'-bipyridine (bisDTDAbipy) has been prepared and characterized via DART-MS. The EPR spectrum for this diradical species exhibits a five-line pattern consistent with two non-interacting radical centers each with coupling to two equivalent \textsuperscript{14}N nuclei. Coordination of bisDTDAbipy has yet to be achieved.
Acknowledgements

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<td>Δ</td>
<td>heat</td>
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<td>χ</td>
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Theory
1.1 Foreword

The so-called “metal-radical approach” has been used in the design of molecular magnetic materials and employs stable, radical species as spin bearing ligands coordinated to paramagnetic metal centers.\(^1\) The approach can produce magnetic materials with properties similar to those of conventional bulk magnets, such as magnetic hysteresis, but with the possibility that these properties can be produced by just one single molecule (i.e., a single molecule magnet). In the past, radical species (such as verdazyls\(^2\), nitronyl nitroxides\(^3\) and thiazyls\(^4\)) have been utilized as ligands to produce magnetic materials that are tunable through functionalization, as well as soluble and volatile, making them attractive in applications such as data storage and quantum computing. However, the ability to functionalize stable radical species makes them attractive in other fields of materials chemistry. For example, the incorporation of a larger, conjugated aromatic system could bestow luminescent properties to the spin bearing ligands, producing applications within the realm of photochemistry. Open shell analogues of various closed shell systems can be synthesized to impart novel properties to well established molecular materials, expanding their potential application.

This thesis describes the design and synthesis of paramagnetic ligands and their coordination to transition metal and lanthanide ions. Coordination of spin bearing ligands to paramagnetic metal centers could potentially create novel magnetic materials via the metal radical approach, however, this is not the major goal herein. Paramagnetic systems based on well known luminescent species, 2,2′-bipyridine and 2,2′:6′,2″-terpyridine, were designed in an effort to generate novel open shell
luminescent systems. The new spin bearing ligands are capable of coordinating in a tridentate fashion, expanding the known coordination chemistry of the thiazyl radical species. The current chapter discusses background information necessary for the design of luminescent and magnetic materials. Chapter 2 covers background information on thiazyl radical species, the stable radical of choice for these systems, emphasizing the 1,2,3,5-dithiadiazoyl (DTDA) radical moiety. Chapter 3 discusses the design, synthesis and coordination of two novel 2,2'-bipyridine based radical ligands, and Chapter 4 introduces the design and synthesis of an open shell 2,2':6',2''-terpyridine based ligand.

1.2 Luminescence

Following the absorption of a photon by a molecule, an excited state is generated which undergoes relaxation via a photochemical reaction, the emission of light, the production of radiation in the form of heat, or the interaction with another species causing quenching to occur. Of these, the process of interest for the compounds in this thesis is photoluminescence, so the main concern herein is a complex emitting light after it has been electronically excited following the absorption of the photon. This is a form of cold body radiation in which heat is not required to induce an emission. From a traditional standpoint, luminescence was divided into two categories based on the decay time of the luminescence itself. Rapidly decaying luminescence was labeled “fluorescence”, whereas persistent luminescence lasting long after the excitation event was classified as “phosphorescence”. However, classification from a mechanistic standpoint is preferable. The modern definition of fluorescence involves a decay of radiation from
an excited state of the same multiplicity as the ground state (Figure 1.1), making the transition spin-allowed, occurring with a half-life on the order of nanoseconds.\footnote{1}{Footnote text}

Fluorescence is an example of an internal conversion, which consists of a transition from a higher electronic state to a lower state, without a change in multiplicity. Phosphorescence consists of decay from an excited state of a different multiplicity to the ground state (Figure 1.1). The transitions are therefore spin-forbidden and occur at a much slower rate than fluorescent decay. The initial excitation of a phosphorescent molecule is typically a spin-allowed transition, which is then followed by a conversion of the excited state to a state of different multiplicity via an intersystem crossing, made possible by spin-orbit coupling. Spin-orbit coupling within complexes allows for relaxation of the spin selection rule, allowing the luminescent decay to occur slowly, with the phosphorescence of some d-metal complexes lasting longer than a few microseconds.

\textbf{Figure 1.1:} Jablonski diagram demonstrating excitation from the ground state ($S_0$) to excited states ($S_1$ or $S_2$) followed by various luminescent processes - fluorescence, phosphorescence, internal conversion and intersystem crossing.
1.3 Quantification of Luminescence

The quantification of luminescent processes can be defined in terms of the quantum yield. A quantum yield ($\Phi$) is a ratio between the number of moles of photons or molecules produced and the number of moles of photons absorbed.

$$\Phi = \frac{\text{moles of photons emitted}}{\text{moles of photons absorbed}}$$  

Equation 1.1

The quantum yield is equivalent to the emission efficiency of the compound and typically, the most useful quantum yield for a system is the phosphorescence yield, $\Phi_p$, generated from the emission of the lowest spin-forbidden state. It is also possible to describe the quantum yield for a fluorescent process in terms of rate:

$$\Phi = \frac{\text{rate of emission}}{\text{rate of absorption of light}}$$  

Equation 1.2

With a system under steady state conditions, the rate of absorption into the excited state ($S_1$) must equal the total rate of decay by processes such as intersystem crossing, internal conversion, quenching, energy transfer, decomposition and bimolecular reactions in the excited state. Therefore,

$$\Phi = \frac{k_f}{\sum_i k_i^s}$$  

Equation 1.3

where $k_f$ is the rate of fluorescence emission and the summation of $k_i^s$ describes the rate of all relevant deactivation processes. The same is also true for a phosphorescent process, however, it must also be noted that the rate of the formation and decay of the
\( \text{T}_1 \) excited state must be equal:

\[
k_{ST}[S_1] = \sum_j k_j^i [T_1]
\]  
Equation 1.4

where \( k_{ST} \) is the rate of intersystem crossing and \( k_j \) is the rate of deactivation processes excluding fluorescence and intersystem crossing. This can then be rearranged:

\[
\frac{[T_1]}{[S_1]} = \frac{k_{ST}}{\sum_j k_j^i}
\]  
Equation 1.5

By analogy with the fluorescence quantum yield expression, we can state:

\[
\Phi_p = \frac{k_p[T_1]}{\sum_j k_j^i[S_1]}
\]  
Equation 1.6

We can then substitute Equation 1.5 into this expression giving:

\[
\Phi_p = \frac{k_p k_{ST}}{\sum_j k_j^i \sum_j k_j^i}
\]  
Equation 1.7

Ideally, a system would achieve a quantum yield of unity, however, the ideal is rarely achieved. After absorption of the photon occurs, relaxation occurs via competing processes, making the energy of emission less than that of the absorbed energy. By comparing the absorption and emission spectra, the energy difference will be apparent as the wavelength maximum of the emission will be higher or, “red shifted”. The energy difference is referred to as a Stokes shift and is dependent on the fluorophore
itself and the environment it is in (i.e., solvent or molecule to which it is bound). Although less common, an emitted photon can also occur at a higher energy, causing a “blue shift” or upconversion. The energy difference for upconversion is known as an anti-Stokes shift, but will not be discussed further as it is irrelevant to the work presented in this thesis.

1.4 Selection Rules

The absorption of a photon can cause many different transitions, however, since luminescence is a quantum mechanical process, some of these transitions are allowed and some are forbidden, as governed by selection rules. An allowed transition has a nonzero transition dipole moment, which gives a nonzero intensity for the transition. If the dipole moment of the transition is calculated to be zero, the transition is forbidden, unless the assumptions upon which the dipole were calculated become invalid. The spin selection rule is one such restriction and it states that transitions between states of different spin multiplicities are forbidden. This restriction can be clearly stated as $\Delta S=0$ for a spin allowed transition. In other words, for a pair of electrons that have opposite spins, the spins cannot undergo a transition to become parallel. Relaxation of the spin selection rule can be achieved through spin-orbit coupling, and as a result a singlet state can achieve some triplet character and vice versa. However, spin-orbit coupling is fairly weak for light atoms, up to the 3d series. As the atomic number increases, the effect of spin orbit coupling becomes much stronger. As a result, spin forbidden bands begin to play a larger role in the spectra of compounds containing heavier elements. This observation is
classified as the heavy-atom effect. Additionally, transitions that maintain parity are forbidden by what is known as the Laporte rule. In a centrosymmetric molecule, the only allowed transitions consist of an excitation from gerade to ungerade or vice versa. One could also interpret this rule as $\Delta L=\pm 1$ for many cases, since the quantum number ($L$) must change in order for a change of parity to occur. Consequently, s-s, p-p, d-d and f-f transitions are forbidden unless the symmetry of the molecule becomes distorted and it is no longer centrosymmetric. Lowering of symmetry occurs via vibronic coupling. Bond vibrations temporarily distort the centrosymmetric environment, allowing d-d transitions to be observed in metal complexes with $O_h$ symmetry, for example, albeit very weakly (10-50 $\text{mol}^{-1} \text{cm}^{-1}$). In a tetrahedral transition metal complex, d-d transitions are much more intense than in their octahedral counterpart as they are not Laporte forbidden. Sigma bonding between the metal and the ligand allows for easier mixing of the p and d orbitals due to sp$^3$ and sd$^3$ hybridization. As a result, d-d transitions can be observed quite readily. Orbital symmetry can also play a role in electronic transitions. If an aromatic or conjugated organic system is considered, transitions from $\pi-\pi^*$ or $n-\pi^*$ orbitals are generally responsible for the luminescence within these materials. If the orbital overlap between the ground state and the excited state is quite large (i.e., the orbitals occupy a similar region in space), then a transition would be considered allowed. This is the case for the $\pi-\pi^*$ transition as the orbitals are within the same plane. However, investigation of the $n-\pi^*$ reveals the orbitals to be orthogonal to one another. In this case, an electron must travel through a region of space with minimal orbital overlap, making the transition forbidden. As with the previous selection rules, relaxation can still be
achieved by vibronic coupling. The coupling of the electronic and vibrational motion allows for observation of a weak n-$\pi^*$ transition via this breakdown of the Born-Oppenheimer approximation.$^{11}$

1.5 Quenching of Luminescence

Selection rules can hinder individual transitions, however, they do not stop luminescent processes as a whole. Luminescent properties can be completely, or at least significantly, disrupted by means of quenching.$^{12}$ With respect to fluorescence, quenching is defined as any event that decreases the intensity of emission from the sample.$^{13}$ Possible contributions to quenching involve: collisions in the excited state, molecular rearrangements, ground state complex formation and energy transfer.$^{13}$ However, in this thesis the term quenching will refer only to an energy transfer type situation.

It has been established that quenching of luminescence within luminescent species is apparent with the incorporation of radicals substitutents such as the imidazolidine and nitroxyl radicals.$^{14,15}$ Studies conducted by Green et al. proposed this quenching to be a result of contributions from electron exchange induced intersystem crossing, energy transfer and electron transfer.$^{15,16}$ Fluorescence quantum yields and lifetime measurements of compounds containing intramolecular radical interactions were analyzed using nitroxide derivatives to quantify the level of quenching taking place$^{17}$. Paramagnetic radical derivatives have previously demonstrated significantly lower quantum yields compared to diamagnetic counterparts, and fluorescent lifetimes are also shown to be diminished significantly;
ranging from a 4-fold to a several 100-fold decrease.\textsuperscript{17} The incorporation of diamagnetic species is therefore required if luminescence is expected to be maintained.

\textbf{1.6 Charge Transfer Bands}

Just as luminescent processes can be diminished through quenching, they can also be enhanced through charge transfers. Charge transfer bands are responsible for strong, vividly coloured transitions especially within coordination complexes.\textsuperscript{5} Two types of charge transfers exist between a metal and a ligand: MLCT and LMCT.

\textbf{1.6.1 MLCT}

A metal to ligand charge transfer (MLCT) involves the transfer of an electron from an orbital that is predominantly metal-centered to an orbital predominantly ligand-based in character (Figure1.2). MLCT is most commonly seen in complexes with a metal in a low oxidation state containing ligands with low-lying $\pi^*$ acceptor orbitals, since the d orbitals are relatively close in energy to the empty ligand orbitals. MLCT results in oxidation of the metal, so a Ru\textsuperscript{2+} species (for example) would be oxidized to Ru\textsuperscript{3+} within the excited state. It is important to note that metal to ligand charge transfers will vary in energy for a homologous series of compounds (ML\textsubscript{6}). As the coordination number decreases, an increase in energy will be observed, whereas a decrease in energy will be observed for metals with lower oxidation states and an increase in ligand electronegativity.\textsuperscript{18}
Figure 1.2: Depiction of a metal to ligand charge transfer (MLCT) occurring between a ligand and a $d^5$ metal center.

1.6.2 LMCT

Just as electrons can be excited from a metal-type orbital to an empty ligand-type orbital, the reverse situation is also observed. Electrons can be excited from $\sigma$ orbitals belonging to the ligands to the empty or partially empty $d$ orbital $e_g$ set of the metal in $O_h$ symmetry (Figure 1.3).$^{10}$ LMCT transitions can also be observed with Jahn-Teller distorted systems displaying $D_{4h}$ symmetry.$^5$ Furthermore, if the ligand has occupied $\pi$-type orbitals, then LMCT transitions can originate from these to the $t_{2g}$ orbitals. There are four possible transitions in which an electron can be promoted from either the donor $\pi$ or $\sigma$ orbital up to empty or partially filled acceptor $t_{2g}$ or $e_g$ set. Transitions to the $e_g$ set are commonly broad and strong with the $\sigma$-$e_g$ transition typically occurring at high energy, which can be lowered if the metal is in a high oxidation state. For a transition metal in $O_h$ symmetry, the LMCT energy will decrease from left to right across the periodic table. This trend is due to an increase in the effective nuclear charge of the metal, although the trend will not hold true if the acceptor orbital or crystal field energy changes.$^{18}$
Lanthanide Luminescence

Lanthanide species are unique, as their trivalent cations exhibit luminescent properties generated from f-f transitions. The luminescence occurs as very sharp bands with long lifetimes, often more than a millisecond. The enhanced lifetime can be attributed to the fact that the 4f electrons of the lanthanide center are buried within the Xe core of the atom. The 4f electrons are effectively unavailable for bonding and have minimal interaction with their surroundings, making them much less sensitive to quenching from external sources, such as oxygen. The absorption and emission from the trivalent lanthanide cations is typically very weak, as the f-f transitions are Laporte forbidden. However, the weak nature of the f-f absorption and emission can be overcome through the use of sensitizers.

A sensitizer can take the form of an organic ligand, a host lattice or even other metal ions. The main focus in this thesis is the use of organic ligands as sensitizers. The sensitizer acts as an antenna that can efficiently absorb energy, populating a ligand centered excited state. The ligand centered excited state can then transfer...
energy onto the lanthanide metal center, achieving a lanthanide centered excited state, where it can be emitted as the characteristic light of the lanthanide upon relaxation.\textsuperscript{11,19} Efficient antenna ligands are typically aromatic species, giving the $\pi - \pi^*$ and $n - \pi^*$ transitions a large role in the excitation. However, the energy transfer from the antenna cannot be isolated to one transition and thus additional excited states, such as singlet states, intersystem crossing and LMCT bands can play simultaneous roles in transferring energy to the Ln\textsuperscript{3+} center.\textsuperscript{19} The charge transfer process is illustrated in Figure 1.4.

![Jablonski diagram of the antenna effect](image)

\textbf{Figure 1.4:} Jablonski diagram of the antenna effect. The excitation of the ground state ($S_0$) results in an energy transfer to the Ln(III) metal center followed by luminescent emission back to the ground state.
Sensitizing antennae are effective at increasing quantum yields because they increase the efficiency of the initial absorption or excitation. Antennae can also help reduce quenching. The lanthanide centers are especially sensitive to quenching arising from the presence of H$_2$O within the inner or outer coordination sphere. The quenching due to water molecules is a non-radiative decay process originating from high frequency vibrations of O-H bonds, resulting in energy dissipation by vibronic modes. The sensitizing ligands act to occupy coordination sites on the lanthanide center, which effectively hinders the interaction of water molecules with the inner coordination sphere of the lanthanide. However, sources of H$_2$O within luminescent lanthanide applications should be avoided. Water can be replaced with D$_2$O if necessary as a O-D vibration is a much lower frequency oscillation, significantly diminishing the effect of vibrational deactivation. The high sensitivity to H$_2$O can however be used as an advantage as it is possible to make extremely sensitive H$_2$O sensors.

1.8 Magnetism

In its most basic sense, magnetism is the property of a material being attracted to or repelled by a magnetic field. The observed magnetic properties occur due to electronic interactions with the magnetic field. Although nuclei also have magnetic moments that respond to external magnetic fields, the electrons in a molecule having a magnetic moment that is approximately 3 orders of magnitude larger than that of a proton, therefore we can generally ignore the nuclear contribution. A diamagnetic response (repulsion) is apparent for all molecules, arising from a circulation of paired electrons, which are present within the core, bonding, and lone pairs. These paired
electrons are responsible for generating an induced field opposing the applied field. On the other hand, a paramagnetic response (attraction) results from systems containing unpaired electrons and easily overpowers the diamagnetic contribution, as the paramagnetic response is 2-3 orders of magnitude larger. Thus, unpaired electrons are responsible for the dominant characteristic of a magnetic material.\(^{22}\)

### 1.9 Magnetic Coupling

For condensed matter, cooperative interactions between individual atoms, ions or molecules of the system will usually determine the bulk properties.\(^1\) If two systems containing unpaired electrons (e.g., a metal ion and a radical ligand) were to interact with one another, their spins could also interact to produce an increased magnetic response.\(^{1,23-26}\) However, to properly grasp such a concept, it becomes necessary to understand magnetic or exchange coupling, which deals with the interaction of unpaired electron spins in multi-spin systems. Imagine two unpaired electrons in two separate orbitals. The magnetic moments can be aligned either parallel or antiparallel, representing ferromagnetic (FM) and antiferromagnetic (AFM) coupling respectively.\(^5\) For two electrons (i.e., magnetic moments) in two degenerate orbitals, there are four possible microstates grouped as two states, a singlet and a triplet. The difference in energy, or energy gap, between the singlet and triplet states is expressed as the magnetic coupling. When the triplet state is lower in energy, the coupling between the moments is FM, meaning that the moments are aligned in the same direction, combining to give a net spin ground state of S=1. AFM coupling, using the same two-electron system, occurs when the singlet is the ground state (S=0), and the moments cancel each other out. The magnitude, or “strength”, of the
coupling is then the magnitude of the energy gap between the two states.

A simple orbital overlap model can be used to understand and predict the coupling in metal-radical complexes. This is the basis of the metal-radical approach outlined by Caneschi et al. A cartoon representation of the model is shown in Figure 1.5, where a half-filled d-orbital represents the metal and a half-filled p-orbital represents the \( \pi \)-type magnetic orbital of the radical ligand. If the interaction of the metal-based magnetic orbital and the ligand-based magnetic orbital is orthogonal, Hund’s rule of maximum multiplicity is followed and the lowest energy state is a triplet (Figure 1.5). Non-orthogonal overlap of the orbitals therefore gives antiferromagnetic coupling due to the Pauli exclusion principle, which states that two Fermions cannot occupy the same quantum space simultaneously.

\[ E_{S=0} \quad E_{S=1} \]

\[ S=0 \quad S=1 \]

**Figure 1.5:** (Left) Representation of FM coupling showing the triplet ground state and the orthogonal orbitals for the two-electron system; (Right) AFM coupling depicting the singlet ground state and the non-orthogonal orbitals.
Mathematically, this can be represented by the phenomenological spin Hamiltonian:

$$\hat{H} = -J \hat{S}_A \cdot \hat{S}_B$$

where $J$ represents the isotropic interaction parameter or spin coupling constant and $\hat{S}_A$ and $\hat{S}_B$ are the spin operators. Using the example of two electrons in two orbitals, $S_A = S_B = 1/2$. Now, the energy gap between the two possible states, $S_{\text{TOTAL}} = 0$ and $S_{\text{TOTAL}} = 1$, is defined by:

$$J = E(S = 0) - E(S = 1)$$

da triplet ground state ($S=1$) gives rise to a positive $J$ value, indicative of FM coupling, whereas a singlet ground state is associated with a negative $J$ value, defining AFM coupling. The magnitude of $J$ is then a measure of the energy gap, or the “strength” of the magnetic coupling. There also exists a possibility in which there is no interaction. This situation would have an energy gap of zero indicating that no magnetic coupling is occurring between the two systems.¹

Experimentally, it is possible to determine the type of coupling within a system through the analysis of the magnetic susceptibility ($\chi$), which is the ratio of magnetization (M) of a material with respect to an applied magnetic field (H), in the weak field approximation. The $\chi T$ product is proportional to the magnetic moment, so plotting $\chi T$ as a function of temperature generates a graph in which it is easy to see the depopulation of thermally populated spin states as the temperature is lowered. From this data, the relative energy levels of the spin states can be determined,
including the spin ground state.

In the two-electron model (vide supra), for FM coupling, the highest multiplicity state \((S = 1)\) is the ground state. For typical molecular systems, the energy gap between states is small enough that thermal occupation of the higher energy low multiplicity state \((S = 0)\) will be apparent at room temperature. As the temperature decreases, thermal depopulation of higher energy \((S = 0)\) state will occur. The result is an increase in the value of \(\chi_T\). At sufficiently low temperature, the higher lying state is completely depopulated, and the value of \(\chi_T\) then remains constant as a function of further decreasing \(T\). By contrast, a decrease in \(\chi_T\) as the temperature is lowered indicates AFM coupling. The ground state is the smallest spin state \((S = 0)\), and thermal depopulation of higher lying states with higher multiplicity \((S=1)\) explains the observed magnetic properties. In Figure 1.6, a hypothetical plot of each coupling situation is shown. There also exists the situation in which the spin centers are not interacting. In this case, a horizontal line is observed because is no energy difference in the spin arrangements, so no change will occur with temperature.
Figure 1.6: Theoretical $\chi T$ vs. $T$ plot. Ferromagnetic coupling is depicted in red and antiferromagnetic coupling is depicted in blue. The horizontal line demonstrates paramagnetic behavior.

Cooperative interactions between individual molecules of the system can give rise to long-range bulk properties. The magnetic coupling interactions that occur between two centers can sometimes generate macroscopic spin ordering below a critical temperature. Within an ordered system, it becomes favorable for the spins to separate into regions of uniform alignment, called domains. Under the influence of an external magnetic field $H$, a ferromagnetic system’s aligned domains will begin to grow, making the effect from misaligned domains less and less significant until the magnetization ($M$) reaches a saturation point. Removal of the applied field will then
reveal a remnant magnetization, $M_R$, which can only be demagnetized by an applied coercive field ($H_C$) in the opposite direction. The result is a hysteresis loop (Figure 1.7).

![Hysteresis Loop Diagram]

**Figure 1.7:** Example of a hysteresis loop for a ferromagnetic system, $M_R$ is the remnant magnetization, $H_C$ is the coercive field.

In a system that orders as an antiferromagnet, no net magnetic moment will be apparent because the spins will cancel each other out entirely. However, if there is incomplete cancellation due to inequivalent opposing moments, ferrimagnetism is generated and there is still a net magnetization$^{1,27}$ (Figure 1.8).

![Magnetic Ordering Diagram]

**Figure 1.8:** Examples of magnetic ordering.
1.10 Single Molecule Magnets

A single molecule magnet (SMM) is an individual molecule that behaves as its own magnetic domain and thus can exhibit hysteresis of the magnetization (M) as a function of applied field (H) below a blocking temperature (T_B). For a molecule to exhibit SMM behavior, it should contain both a large spin ground state (S) (for a lanthanide species the total (orbital + spin) angular momentum (J) is considered) and an uniaxial magnetoanisotropy (D) in which the “easy axis” is the energetically favorable direction of the magnetic moment in a three dimensional space. In a material with uniaxial magnetoanisotropy, the magnetic moment will be preferentially aligned along an axial direction unless enough energy (e.g., thermal) is supplied to force the moment to align in the “hard plane” (perpendicular to the “easy-axis”). Such a material will resist demagnetization, as energy is required to alter the direction of magnetization. An energy barrier is therefore established in which the product of S^2 and |D| determine the height of the barrier for magnetic relaxation.\(^{28}\)

Thermal relaxation, excitation over the energy barrier, is a common mechanism for magnetic relaxation (Figure 1.9). A larger barrier height means that a higher temperature is required to populate states that result in demagnetization\(^{29}\). However, a higher barrier cannot completely eliminate relaxation as a second process occurs via resonant quantum tunneling. Tunneling may only occur via a suitable perturbation, which can be imagined as a distortion removing axial symmetry, leading to anisotropy in the xy plane. This is classified as transverse anisotropy.\(^{30}\) The larger Ms states (e.g., Ms=±S) will contain a larger transverse anisotropy due to the larger S state, making tunneling processes more apparent. Tunneling may also occur between
pairs of degenerate excited states (e.g., $M_s = \pm (S-1)$). This thermally assisted resonant tunneling mechanism allows magnetic relaxation to occur without the need to go over the “top” of the barrier, creating a shortcut for magnetic relaxation of a molecule.

![Diagram of energy levels and tunneling processes]

**Figure 1.9:** Pictorial representation of the energy barrier of an SMM; examples of resonant quantum tunneling processes that shortcut the energy required to overcome the barrier are indicated.

Experimentally, SMM behavior can be probed by measuring the slow magnetization dynamics of a sample with an oscillating AC magnetic field applied. The sample’s magnetic moment will be aligned by the external magnetic field. As the applied field oscillates (i.e., changes direction, flipping back and forth), an SMM will exhibit a delayed realignment of its magnetic moment in response to the field,
indicating a barrier to relaxation. As the frequency of oscillations is increased, an out-of-phase component of the magnetic susceptibility will become more pronounced. Thus both the frequency dependence and temperature dependence of the in-phase and out-of-phase components of the magnetic susceptibility are measured to characterize the SMM. The slow dynamics are characterized by the out-of-phase component ($\chi''$). If $\chi''$ is non-zero and demonstrates dependence on frequency, then hindered thermal relaxation is present within the system. However, if other possible explanations for this behavior (e.g., long range ordering) are considered plausible, it is common to carry out a doping study to establish that the solid-state sample is in fact demonstrating behavior arising from individual molecules, not multi-molecular domains. This generally requires a diamagnetic analogue to the SMM, into which the SMM will be doped (<10%). The doped system effectively isolates the SMM molecule while leaving the crystal packing unchanged. This allows for intermolecular interactions to be ruled out and the properties ascribed to the single molecule.

An SMM will exhibit resonant quantum tunneling relaxation but an FM ordered system will not. Thus, another method of characterizing an SMM is to apply a weak DC magnetic field while measuring the AC susceptibility. The DC field lifts the degeneracy of many $M_S$ microstates and therefore suppresses the resonant quantum tunneling relaxation mechanism. If an increase in slow dynamics is observed, SMM behavior is confirmed.
1.11 References


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Chapter 2
Thiazyl Chemistry
2.1 SN Chemistry

Heterocyclic compounds are species that contain atoms of at least two different elements within a ring. The most common heterocyclic compounds contain carbon and oxygen, sulfur or nitrogen. In this thesis, the focus rests upon heterocycles containing both sulfur and nitrogen. The paramagnetic SN fragment is the unit of interest in the unique class of compounds known as the thiazyls. The discovery and isolation of the first well known thiazyl compound, sulfur tetranitride (S$_4$N$_4$), dates back to 1835$^2$. The field of thiazyl chemistry gained attention in the 1970s with the discovery of the superconducting and metallic properties$^{3,4}$ of poly(sulfur-nitride) (SN)$_x$. Examining the (SN)$_x$ system further, it becomes clear that the properties of this material arise from $\pi$-delocalization of electrons through each thiazyl unit. Thiazyl linkages possess an inherent propensity for catenation and as a result typically form chains and various cyclic structures that can be neutral species, cations or anions.$^5$ The downside of many sulfur-nitrogen compounds exists in their reactivity. Many thiazyl compounds, for example tetrasulfur tetranitride, are shock sensitive and explosively decompose into their elements very readily. However, just like their isoelectronic counterpart, the nitroxides, thiazyls possess the ability to form stable, isolatable radicals. Although thiazyl radicals are thermally stable, they are air sensitive, suffering oxidation from atmospheric oxygen and prone to hydrolysis which makes them incompatible with aqueous environments. Typically, thiazyl radical species require dry organic solvents or inert atmosphere in the solid state, where they are indefinitely stable as pure compounds.
2.2 Five Membered Ring Radicals

Thiazyl radicals can exist in linear chains and various ring sizes. The most common or well-known structure, however, is the 5-membered ring. The first structurally characterized thiazyl was the 1,2,4,3,5-trithiadiazolyl radical cation $S_3N_2^+$, after which several other isoelectronic 5-membered ring thiazyls have been synthesized.

![Diagram of thiazyl radicals](image)

**Figure 2.1:** Known 5-membered ring thiazyl radicals structurally related to 1,2,4,3,5-trithiadiazolyl radical cation (1) including the 1,2,3,5-dithiadiazolyl radical (2).

For the most part, each 5-membered thiazyl ring system is related to one another by imagining the introduction of a carbon (C-R) group in place of a sulfur cation fragment within $S_3N_2^+$ (Figure 2.1). The 5-membered ring thiazyl radical species are all planar, resonance stabilized, $7\pi$ electron systems with an unpaired electron residing in a $\pi$-antibonding molecular orbital.
This thesis, and much of the work of the Preuss group, concerns the widely studied 1,2,3,5-dithiadiazolyl (DTDA) radical moiety (Figure 2.1). The unpaired electron resides in a singly occupied molecular orbital (SOMO) (Figure 2.2) that places significant $\alpha$-spin density on the sulfur and nitrogen atoms and has a nodal plane bisecting the carbon position C4.

**Figure 2.2:** Right: MO energy level diagram of the 1,2,3,5-dithiadiazolyl (DTDA) moiety; Left: (bottom) SOMO of DTDA; (middle) charge density (negative charge density red, positive charge density green) and total spin density (alpha spin density blue, beta spin density green) of DTDA; (top) total spin density of 4-(benzoxazol-2’-yl)-1,2,3,5-dithiadiazolyl (boaDTDA) demonstrating spin density outside of the DTDA radical moiety due to spin polarization; generated using G03 uB3LYP 6-31G(d, p).
Although the SOMO of the DTDA moiety is nodal at the carbon atom, the node does not imply that there is zero spin density in C4 position of the DTDA. Spin polarization of underlying filled orbitals places an appreciable amount of $\beta$-spin density on the carbon atom, providing a mechanism for sites with non-zero spin density to arise outside the DTDA ring (Figure 2.2). The $\beta$-spin density at the C4 position cannot participate in carbon-carbon $\sigma$ bond formation via pairing of the unpaired electrons of two DTDA rings.

Overlap of $\pi$ SOMOs in adjacent DTDA rings often leads to the formation of $\pi$-stacked [DTDA]$_2$ dimers known as a “pancake bonds”. A typical “pancake bond” exhibits intermolecular distances that are shorter than the sum of the van der Waals radii between the closest contact atoms, however, the contact is longer than a typical single bond interaction. The pancake bonding phenomenon is observed in DTDA radical systems through S…S and S…N contacts. The dimerization of DTDA radical systems through pancake bonding is unlike a typical dimerization in that it is a reversible process. Energetically, the dimerization in these radicals is comparable to hydrogen bonding and in solution exists as a monomer-dimer equilibrium$^2$. It is this equilibrium that plays a key role later on in this thesis. At or below ambient temperature, paramagnetic DTDA radical species tend to form dimers that are measurably diamagnetic, indicating a strong electronic interaction between the radicals, generating an electron pair. Typically, in DTDA radicals, dimerization through the formation of pancake bonds occurs through a number of common modes shown in Figure 2.3.
Figure 2.3: Common dimerization modes of the 1,2,3,5-dithiadiazolyl radical: a) trans-antarafacial, b) trans-cofacial c) cis-cofacial, d) twisted-cofacial.

The most common mode of dimerization for the DTDA radical, with an absence of steric interference, is the cis co-facial dimerization motif which features pancake bonding between the two rings via sulfur-sulfur contacts in a mirror plane arrangement (Figure 2.3). Additional co-facial dimerization modes can be envisioned by rotation of the DTDA heterocycle. A ~90° rotation is characteristic of the twisted co-facial interaction whereas a rotation of ~180° produces the trans co-facial dimerization motif. Maximized SOMO overlap can best explain the common occurrence of the three co-facial dimerization modes, however, there is no simple rule to determine the dimerization a particular compound will adopt. Although it is difficult to predict the exact dimerization motif of a DTDA radical, it is possible to inhibit dimerization to yield undimerized DTDA species. Incorporation of steric bulk, groups that promote electrostatic contacts, as well as electron withdrawing substituents can effectively moderate the dimerization ability of the DTDA moiety. Steric bulk is effective at hindering the geometric requirement for pancake bond formation, reducing π overlap of the adjacent SOMOs, whereas electron withdrawing substituents effectively withdraw electron density from the DTDA moiety, weakening the “pancake bond” interaction.
2.3 Synthesis of the DTDA Radical Moiety

In the past, DTDA radicals were first prepared from their corresponding nitriles utilizing trichlorocyclotrithiazene ($S_3N_3Cl_3$)\textsuperscript{7} a reagent generated from the reaction of $S_2Cl_2$ and NH$_4$Cl followed by treatment with Cl$_2$ gas. This reaction yields a 1,2,3,5-dithiadiazolyl chloride salt, which can then be reduced to the radical species. The crude DTDA chloride salts prepared via this synthetic route are typically impure, contaminated with elemental sulfur, S$_4N_4$, and various sulfur halides. Therefore, a number of synthetic methods have since been developed which include the generation of an amidine species (Scheme 2.1). The amidine can be prepared from the corresponding nitrile, however, synthesis of these species can also be achieved from an organohalide ($R$-$X$; $X$= Br, Cl) via electrophilic attack, utilizing bis(trimethylsilyl)carbodiimide, following lithiation by n-butyllithium. Typically, within the Preuss research group, a persilylated amidine is prepared. This is achieved through treatment of the nitrile with lithium bis(trimethylsilyl)amide etherate, followed by trimethylsilylchloride. Amidines can then be reacted with at least four equivalents of sulfur monochloride to yield a positively charged 1,2,3,5-dithiadiazolium salt with a chloride anion (Scheme 2.1). The 1,2,3,5-dithiadiazolium chloride (commonly referred to as a chloride salt) is later reduced using triphenylantimony or trichloroantimony and then purified by vacuum sublimation. Since sublimation is the preferred method to purify DTDA radical ligands within the Preuss group, the reducing agent utilized in the reduction is selected such that the byproduct can be readily separated from the radical ligand, either by washing or during sublimation. The use of triphenylantimony in the reduction of a chloride salt
produces triphenylantimony dichloride as a by-product, which sublimes at a temperature of ~120 °C (10^{-2} Torr). If the sublimation temperature of the DTDA ligand is below ~110 °C, triphenylantimony is a feasible reducing agent, however, above 110 °C trichloroantimony should be employed as a reducing agent to prevent contamination of the sublimed radical ligand with co-sublimed by-product.

**Scheme 2.1:** *Synthetic routes towards the 1,2,3,5-dithiadiazolyl (DTDA) radical.*

### 2.4 Bistability and Molecular Switching in Thiazyl Radicals

The term bistability has been used to describe the ability of a material to interconvert between two stable forms under the same external conditions, such as temperature and pressure. Although two separate stable states exist, under a specific set of conditions (i.e., temperature) one phase may be less stable and is referred to as a metastable phase. In order for switching to occur, the bistable system must overcome an energy barrier. If substantial reorganization of a lattice is required, or
the energy barrier is too high, interconversion is only possible via the liquid or gas phase. Bistability presents itself as an exciting property in the field of materials chemistry as it allows access to two forms of a compound, each with different electronic and physical properties. In order to develop a truly bistable system, the system must first be able to exist in separate attainable states, or phases. However, a phase change alone does not indicate the presence of bistability within the system. True bistability is only observed if an activation energy barrier ($\Delta E$) exists for interconversion between different phases which is greater than the thermal energy, $kT$ at a given temperature.

Thiazyl radicals can exhibit structural phase transitions in the solid state, resulting from a transformation between regularly spaced $\pi$-stacked diamagnetic $\pi$-dimers to a paramagnetic monomer phase. Lateral movement of a molecular plane via a “plate slip” or tilting of a molecular plane through a “domino cascade” mechanism (Figure 2.4) causes significant distortion, disrupting the $\pi$-stacking of the radicals. Distortion of the molecular planes generates two possible unique paramagnetic metastable phases (Figure 2.4). The two metastable phases will persist until there is sufficient thermal energy to overcome the activation barrier for lattice rearrangement, yielding the distorted $\pi$-stack configuration. This inherent “bistability” results from a small energy difference between open shell paramagnetic monomers or closed shell dimers. By harnessing these characteristics, thiazyl radicals acting as molecular switches may be possible.
Figure 2.4: Phase transition mechanisms for a thiazyl radical species. The lateral “plate slip” movement and a tilting movement of molecular planes causing a “domino cascade”.

2.5 Coordination of 1,2,3,5-Dithiadiazolyl Radical Ligands

Stable neutral spin bearing ligands, such as verdazyl\(^{12}\) radicals and nitronyl nitroxides\(^{13}\), have previously been coordinated to various metal centers. Verdazyl radicals have been coordinated as bidentate ligands to transition metals\(^{14}\) yielding mononuclear complexes. In the case of the nitronyl nitroxides, the ligands have been shown to possess the ability to bridge metal centers,\(^{15}\) form mononuclear complexes\(^{16,17}\) and also exist as polymeric chains.\(^{18}\) The coordination of these species, in all cases, preserves the unpaired electron within the structure, which allows for ferromagnetic or antiferromagnetic exchange coupling between the ligand and metal magnetic moments to take place. The coupling within these complexes allows for the development of molecular materials with interesting magnetic properties.

The coordination of thiazyl radical species has been previously explored. In general, the investigation of thiazyl compounds with metal centers aims to explore either the reactivity of these paramagnetic compounds or to explore these species as potential materials, coordinating them intact to yield enhanced magnetic properties.\(^{2}\)
2.6 S-Coordination of Thiazyl Radicals

The first metal complex of a thiazy l, Fe$_2$(CO)$_6$PhDTDAH, was reported in 1989 by Bannister et al.$^{19}$ The structure of this compound was initially thought to be paramagnetic, with insertion of the iron dimer occurring in the S-S bond of the radical ligand. This structure, which was later proven to be the diamagnetic imine,$^{20}$ was the first transition metal species elucidating the reactivity of thiazyl radicals with softer, low valent metal centers. The thiophilic nature of these metal species causes insertion of the metal into the S-S bond instead of typical coordination to the sulfur atoms. This has been further demonstrated with the phenyl DTDA radical species within complexes utilizing nickel (I), palladium (0) and platinum (0) metal centers (Figure 2.5). Chromium (I) metal complexes do not insert into the S-S bond. Chromium (I) coordinates to the DTDA radical ligand in a $\eta^2$ type fashion (Figure 2.5), maintaining the structure of the DTDA moiety.$^{21}$ The metal center attaches to both sulfur atoms in the ring resulting in a diamagnetic compound displaying endo and exo isomerism.$^{21}$
Figure 2.5: Examples of $S$-coordination of the 1,2,3,5-dithiadiazolyl (DTDA) radical moiety including $\text{Fe}_2(\text{CO})_6\text{PhDTDAH}$ (top left), $\text{Ni}_2\text{Cp}_2\text{PhDTDA}$ (top right), $\text{Cr}(\text{Cp})(\text{CO})_2\text{tolDTDA}$ (bottom left) and $[\text{Pt}(\text{PPh}_3)_2]\text{PhDTDA-Pt-PhDTDA}[\text{Pt}(\text{PPh}_3)_2]$ (bottom right).
2.7 N-Coordination of Thiazyl Radicals

Thiazyl radicals are not limited to sulfur coordination motifs. The first nitrogen coordination complex involving a DTDA radical was synthesized by Preuss et al. in 2004. The Co(hfac)$_2$(pyDTDA) complex features the 2'-pyridyl-1,2,3,5-dithiadiazolyl radical (pyDTDA), designed as a paramagnetic bidentate chelating ligand analogous to 2,2'-bipyridine (Figure 2.6). The synthesis of this complex was conducted as a proof of concept, demonstrating that thiazyl radicals did in fact possess the ability to coordinate via the nitrogen atoms. The DTDA moiety has partial negative charge density on the nitrogen atoms with a partial positive charge density on the sulfur atoms. The partial negative charge density on nitrogen makes this site ideal for coordination to harder metal centers. Due to the fact that the DTDA radical moiety can incorporate a variety of R groups, ligands can be rationally designed with $\sigma$-donating atoms in the ortho position of the R group, generating a chelating pocket with a higher propensity for coordination. Previous DTDA radical ligands have taken advantage of this feature, generating nitrogen chelators utilizing 2-pyrimidyl, various 2-pyridyl ring systems and more recently a benzisothiazole group. Coordination complexes of these ligands can be further tailored to obtain coordination in the nitrogen pocket through the use of electron withdrawing ligands on the metal center, such as 1,1,5,5,5-hexafluoroacetylacetonato (hfac) ligands. Not only do the auxiliary hfac ligands increase the hardness of the metal center, but they also give additional volatility to each system, enabling purification via sublimation.
The coordination of a DTDA radical via the nitrogen donor atoms leaves the DTDA moiety intact, maintaining the ability for pancake bond formation within a metal complex. Although dimerization is possible, many metal complexes of DTDA radicals are undimerized in the solid state. In fact, undimerized complexes are observed almost as often as those that are dimerized and the formation of $\pi$-stacks remains a difficult property to predict. There are many contributing factors that can influence the packing of the DTDA radicals in the solid state, exemplified in transition metal complexes of the type $\text{M(hfac)}_2(\text{pyDTDA})$ (where M=Mn,Fe,Ni,Cu,Co). The only $\text{M(hfac)}_2(\text{pyDTDA})$ complexes that displayed $\pi$-dimer formation were Mn$^{2+}$ and Cu$^{2+}$, which display a more trigonal and Jahn-Teller distorted six coordinate geometry respectively compared to the rigid octahedral structures produced by Fe$^{2+}$, Ni$^{2+}$ and Co$^{2+}$ (Figure 2.7). One hypothesis, based purely on steric hindrance, is that dimerization is permitted by the lack of rigidity of the octahedral coordination sphere so that the bulky hfac ligands are shifted further away from the pyDTDA dimer$^{26}$ allowing for a pancake bond interaction to take place. However, upon examining other examples of DTDA-metal complexes, there are other factors clearly at play. Coordination of Mn$^{2+}$ with a pyDTDA ligand substituted with a cyano group in the 4$'$ position produced Mn(hfac)$_2$(4$'$cyano-pyDTDA)$^{25}$ which is undimerized in the solid state. Unlike Mn(hfac)$_2$(pyDTDA), Mn(hfac)$_2$(4$'$-cyano-}

\[ \text{Figure 2.6: 2,2$'$-bipyridine and the paramagnetic thiazyl analogue 2$'$-pyridyl-1,2,3,5-dithiadiazolyl radical (pyDTDA), both featuring bidentate nitrogen coordination sites.} \]
pyDTDA) contains a CN…S contact within the crystal structure. Additional electrostatic contacts can therefore significantly alter the crystal packing of the molecule, which can lead to an absence of dimerization. Additionally, in the complexes presented (vide supra) it could be argued that the pancake bond involved in the dimerization of the ligands is weakened due to the donation of electron density to the metal center. Typically, the metal complexes are often undimerized whereas the free DTDA ligands are always dimerized in the solid state.

![Figure 2.7: Examples of N-coordinated DTDA radical ligands including undimerized Ni(hfac)$_2$(pyDTDA) (top left), undimerized Ni(hfac)$_2$(boaDTDA) (top middle), a 1D-coordination polymer La(hfac)$_3$(boaDTDA) (top right), dimerized Mn(hfac)$_2$(pyDTDA) (bottom left), a bridging thiazyl ligand complex (Mn(hfac)$_2$(pymDTDA) (bottom middle) and monodentate nitrogen coordination [Mn(hfac)$_2$(cfDTDA)] (bottom right).](image)

For DTDA radicals and their coordination complexes, a monomer-dimer equilibrium typically exists in solution. Thus, it is possible to obtain a solution EPR spectrum for a DTDA species that is dimerized and diamagnetic in the solid state.$^{26}$ As with most monomer-dimer equilibria, at higher temperature, the monomer is
favored, and at lower temperature the equilibrium favors the diamagnetic dimer. The equilibrium can therefore be controlled by external factors such as temperature, suggesting the possibility of a “switchable” system. Furthermore, dimerization can be a reversible process in the solid state, as has been recently observed\textsuperscript{27} in a lanthanide centered DTDA complex.

Since lanthanide ions are capable of coordination numbers up to 10, coordination of two radical species can easily be achieved. Dimerization of the resulting bis-coordinated DTDA lanthanide species can then result in the formation of chains via dimerization, which has been observed in La(hfac)\textsubscript{3}(pyDTDA)\textsubscript{2}\textsuperscript{27}. The resulting dimers or “pancake bonds” demonstrate a demanding geometrical dependence, requiring precise alignment of the planar $\pi$-type orbitals. As a result, external factors such as temperature can cause distortion (or “slippage”) of the geometry resulting in a phase transition in which one of the radical ligand dimers on each of the lanthanide centers is opened, effectively breaking the chain, while pancake bonds still link two metal centers together\textsuperscript{27}. This is the first example of a rupturing of pyDTDA dimers in the solid state. Further alteration of the external conditions (i.e., temperature) of the material can invoke further breaking of the dimers, yielding a monomeric phase (Figure 2.8). This can be reverted back to the polymeric species upon return of the appropriate external conditions. Overall, an increase in temperature produces a re-entrant phase transition of the system. As temperature is increased, the system undergoes a conversion from the initial Phase 1 to a lower symmetry Phase 2 which upon further increase in temperature reverts back to a phase of higher symmetry (Phase 1).\textsuperscript{27} The behavior observed here further
solidifies the possibility for thiazyl radical species to exhibit molecular switching capabilities. Additionally, if the lanthanide metal center is changed or the DTDA ligand is electronically altered via substitution of the pyridyl ring (i.e., 5'-bromo-pyDTDA), the temperature in which this re-entrant phase transition occurs will change, representing an inherent “tunability” of the system.

**Figure 2.8:** The solid state crystal packing of La(hfac)₃(pyDTDA)₂ at various temperatures a) dimerization of all pyDTDA ligands generates supramolecular chains (Phase 1) b) rupturing of one pyDTDA pancake bond per metal center (Phase 2) c) rupturing of all pyDTDA pancake bonds to create La(hfac)₃(pyDTDA)₂ monomer units. Reprinted with permission from Fatila, E. M.; Rouzières, M.; Jennings, M. C.; Lough, A. J.; Clérac, R.; Preuss, K. E. Journal of the American Chemical Society 2013, 135, 9596. Copyright 2015 American Chemical Society.
La(hfac)$_3$(pyDTDA)$_2$ demonstrates the possibility for DTDA radical ligands to produce supramolecular structures. The use of DTDA radical ligands as potential supramolecular synthons is known and has been observed in complexes such as Mn(hfac)$_2$(boaDTDA). Close contacts exist between sulfur and oxygen atoms within the complex, providing a pathway for intermolecular exchange coupling, which could be exploited in the development of larger supramolecular species with magnetic properties.

Expanding design possibilities for DTDA ligands, the Preuss group prepared the 4-(benzoxazol-2'-yl)-1,2,3,5-dithiadiazolyl (boaDTDA) ligand to offer both bidentate $N,N$-coordination and monodentate $N$-coordination. Through the use of lanthanide starting materials, the synthesis of coordination polymers via bidentate and monodentate nitrogen coordination was achieved. Coordination of boaDTDA to a series of Ln$^{3+}$ metal centers in the form of Ln(hfac)$_3$(boaDTDA) (where Ln=La-Eu) resulted in a 1D coordination polymer consisting of Ln(hfac)$_3$(boaDTDA) units bridged through monodentate coordination of the benzoxazole nitrogen opposite the bidentate pocket (Figure 2.7). In La(hfac)$_3$(boaDTDA), the La-N bond distance is indicative of a chemical bond, however, oxygen coordination is less certain given the longer oxygen-lanthanide distances. Analogous structures exist when Ln=Ce-Eu. The larger, flexible coordination sphere of the earlier lanthanide metals allows for more ligands to be coordinated, promoting the bridging of two boaDTDA ligands to form the 1D coordination polymer. However, this is not observed for later, smaller trications.
Although this is only a small glimpse into the coordination of thiazyl radicals, it still remains clear that the chemistry is quite diverse. The choice of the metal center can invoke various coordination motifs including S-S bond insertion or N-coordination. A variation of denticity also exists for these ligands including monodentate, bidentate and bis-bidentate coordination,\textsuperscript{23} which can in turn generate mononuclear, binuclear and polymeric complexes. However, this does not represent the entire realm of thiazyl coordination chemistry. Novel, multidenate (denticity greater than two) thiazyl ligands have since been created and are presented and discussed in later chapters of this thesis.
2.8 References


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Chapter 3
2,2'-Bipyridine Based 1,2,3,5-Dithiadiazolyl Ligands
3.1 Introduction

This chapter focuses on the synthesis, characterization and computational studies of two novel 2,2′-bipyridine-based 1,2,3,5-DTDA ligands. The first, 4-(2′,2″-bipyrid-6′-yl)-1,2,3,5-dithiadiazolyl (bipyDTDA) (Figure 3.1), was designed to coordinate metal centers in a tridentate motif. This paramagnetic terpyridine analogue was designed with the placement of the 1,2,3,5-DTDA moiety in the 6 position of the 2,2′-bipyridine backbone, yielding the intended tridentate nitrogen coordination pocket. The design of bipyDTDA combines the luminescence antenna properties of 2,2′-bipyridine with the potential for monomer-dimer equilibria of the thiazyl. Thus, there is possibility to develop a bi-phase luminescent switch. BipyDTDA can also be used to develop materials with interesting or novel magnetic properties. The unpaired electron of the DTDA moiety can exchange couple with unpaired electrons of coordinated paramagnetic metal centers, potentially leading to magnetically ordered systems. The tridentate coordination environment offers the possibility to produce M(hfac)(bipyDTDA) complexes featuring transition metal centers in a +1 oxidation state, as well as 5-coordinate M(X)_2(bipyDTDA) systems (where X is a halogen such as Cl). The use of a tridentate ligand could also produce neutral species of the type [M(bipyDTDA)_2][X]_2, consisting of a complete DTDA coordination sphere. Heavier transition metal centers in a +3 oxidation state, such as Mo, Os and Ir, could be utilized to produce M(X)_3(bipyDTDA) type species, all of which would be novel coordination motifs expanding the realm of DTDA coordination.

The second new ligand is the diradical, 6,6′-bis-1,2,3,5-dithiadiazolyl-2,2′-bipyridine (bisDTDAbipy) (Figure 3.1), capable of coordination in either a
tetradentate or bis-bidentate fashion. BisDTDAbipy has a DTDA moiety on both the 6 and 6' position of 2,2'-bipyridine. As well as potential luminescent switch functionality, similar to bipyDTDA, bisDTDAbipy also has the potential to bridge different species, providing the possibility for different magnetic interactions at each coordination site, or interactions between different metal centers. The bridging ability of bisDTDAbipy could also be utilized in the production of new supramolecular structures.

![Figure 3.1: Line drawings of (left) 4-(2', 2''-bipyrid-6'-yl)-1,2,3,5-dithiadiazolyl (bipyDTDA) and (right) 6,6'-bis-1,2,3,5-dithiadiazolyl-2,2'-bipyridine (bisDTDAbipy).](image)

### 3.2 2,2'-Bipyridine Luminescence and Design Motivation

Bipyridine (bipy) is a widely studied aromatic compound consisting of two pyridine rings bridged by a carbon-carbon bond. Depending on the location of the carbon bridge, up to six possible isomers can be generated. However, luminescence studies of bipy focus on isomers that are commonly coordinated to metals: the dumbbell-shaped 4,4'-bipyridine bridging ligand and the chelating 2,2'-bipyridine. In this thesis only luminescent properties of the latter will be discussed in detail. Electronically, the σ-bonding orbitals involved in bonding to the metal center are localized on the nitrogen atoms, and the π donor and π* acceptor orbitals are
delocalized around aromatic rings. The majority of the luminescence from metal complexes containing 2,2'-bipyridine ligands then arises through the promotion of electrons from a $\pi$ orbital of the metal to a $\pi^*$ orbital on the ligand, achieving a metal to ligand charge transfer excited state (see Chapter 1). Promotion of an electron from the $\pi$ orbital of the metal to the $\sigma^*$ of the metal, or from the $\pi$ orbital of the ligand to the $\pi^*$ orbital of the ligand, generate additional excited states classified as metal centered (MC) and ligand centered (LC) states respectively. This type of luminescent behavior can be seen in the most widely studied bipy complex to date, tris(2,2'-bipyridine)ruthenium(II).

The crystal structure of Ru(bipy)$_3^{2+}$ was first obtained as a hexafluorophosphate salt exhibiting approximate D$_3$ symmetry and a Ru-N bond length of 205.6pm, which is several pm shorter than some other Ru-N bonds, including Ru-NH$_3$ and Ru-phenanthroline, seen in literature. The short bond length can be explained by a significant degree of back-bonding from Ru(II) to the $\pi^*$ orbitals of the bipy ligands which also gives the complex an enhanced degree of stability compared to similar structures, lasting in solution for several months.

The luminescent behavior of Ru(bipy)$_3^{2+}$ is also influenced by the shortened Ru-N bond within the complex. For transition metal complexes, it is observed that higher energy excited states undergo fast radiationless deactivation and therefore the lowest excited state plays the major role in the luminescent emission. In a d$^6$ octahedral environment, the MC excited state is prone to a strong energy level displacement arising from metal-ligand bond vibration. Lengthening of the ruthenium-nitrogen bond causes the MC state to drop in energy, becoming the lowest
excited state (Figure 3.2) and therefore enabling a fast radiationless decay pathway to the ground state. As a result, luminescence is not observed at room temperature. In contrast, compression of the Ru-N bond raises the energy of the MC state, shifting the radiationless decay pathway to a higher energy state than that of the now lower MLCT. This relationship of the ligand and ligand field strength with the energy ordering of the lower excited states, gives Ru(bipy)$_3^{2+}$ some very interesting and unique luminescent properties.

**Figure 3.2:** Energy level ordering of excited states generated by transition metal complexes in an octahedral environment. Reprinted from Coordination Chemistry Reviews, Vol. 84, A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Ru(II) polypyridine complexes: photophysics, photochemistry, electrochemistry, and chemiluminescence*, Pages 85-277, Copyright 1988, with permission from Elsevier.

The molar absorptivity of Ru(bipy)$_3^{2+}$ was discovered to be 14600 L mol$^{-1}$ cm$^{-1}$ in H$_2$O, which is relatively high. The quantum yield of the formation of the lowest excited state is essentially unity, which demonstrates a high level of efficiency in conversion or population of the excited state mainly responsible for the luminescent behavior. Also, the excited state of Ru(bipy)$_3^{2+}$ emits at approximately 2 eV (λ =
610 nm), characteristic of bright orange light easily observed by the naked eye (Figure 3.3).\textsuperscript{19} It has also been discovered that the excitation of Ru(bipy)$_3^{2+}$ in any of its inherent absorption bands will lead to emission in which the intensity and lifetime are temperature dependent and enhanced luminescence is apparent at low temperatures.\textsuperscript{2}

\[
{^*Ru(bipy)}_3^{2+} \rightarrow Ru(bipy)_3^{2+} + h\nu (\text{ca. } 2eV, 610nm)
\]

**Figure 3.3:** Relaxation of the excited state of Ru(bipy)$_3^{2+}$ causing luminescent emission.

A paramagnetic analogue of Ru(bipy)$_3^{2+}$ containing a DTDA ligand might be envisioned. However, employing the paramagnetic thiazyl analogue of 2,2'-bipy, pyDTDA, is not a practical goal because of the inherent “flip flop” disorder within the crystal structure. The similarity in the size and shape of the DTDA and pyridyl ring creates disorder in the orientation of the ligand,\textsuperscript{20} which is effectively removed by altering the structure of the pyridyl ring. Also, the absence of intermolecular electrostatic contacts in pyDTDA would allow for dimerization to occur and the resulting compound would likely be very insoluble. Instead, attempts were made using 5'-bromo-pyDTDA in an effort to eliminate any “flip-flop” disorder within the complex. The paramagnetic complex would hopefully behave similar to Ru(bipy)$_3^{2+}$ while adding an additional monomer-dimer equilibrium feature. The diamagnetic dimer would enable luminescent emission to occur until the conditions surrounding the system were altered in such a way to produce the paramagnetic monomer unit.
The presence of a radical within the system would ideally quench the luminescence of the complex and therefore afford a bi-phase luminescent switch.

Preliminary synthetic work towards the paramagnetic ruthenium poly-pyridine complex, Ru(5'-bromo-pyDTDA)₃²⁺, proved to be unsuccessful. Coordination attempts between 5-bromo-pyDTDA and a labile [Ru(DMF)₆][OTf]₃ ruthenium starting material indicated either a lack of coordination or overall instability of the complex. As a result, the DTDA substituted 2,2'-bipyridine ligands, 4-(2',2''-bipyrid-6'-yl)-1,2,3,5-dithiadiazolyl and 6,6'-bis-1,2,3,5-dithiadiazolyl-2,2'-bipyridine were designed (Figure 3.1). The increased denticity of the ligands was intended to promote coordination and improve the overall stability of the system via the chelate effect.

3.3 Synthesis of 4-(2', 2''-Bipyrid-6'-yl)-1,2,3,5-Dithiadiazolyl

The synthesis of bipyDTDA was conducted from its corresponding nitrile, 6-cyano-2,2'-bipyridine (bipyCN). However, an efficient synthetic strategy that afforded the desired nitrile in appreciable yields was necessary, as the compound is not commercially available. Initially, synthesis of the compound began from commercially available 2,2'-bipyridine, utilizing mCPBA to create 2,2'-bipyridine N-oxide.²¹,²² The N-oxide could then be reacted with trimethylsilyl cyanide and dimethylcarbamoyl chloride,²¹,²² in a modified Reissert-Henze reaction,²³-²⁵ yielding 6-cyano-2,2'-bipyridine (Scheme 3.1). However, oxidation of bipy with mCPBA resulted in low yielding, highly contaminated product mixtures that make this synthetic route a poor choice. Oxidation of bipy was also attempted with a mixture of 30% hydrogen peroxide and acetic acid, but there was no apparent change in the resulting product. Once enough bipy N-oxide was obtained, cyanation of the N-oxide
suffered from reaction times of more than five days and reaction yields around 30%, compounding the inefficiency of this route.

Scheme 3.1: Proposed synthetic route to produce 6-cyano-2,2'-bipyridine.

An alternative synthetic route towards bipyCN was far more efficient. BipyCN can be synthesized from commercially available 2,6-dibromopyridine. A nitrile precursor, 6-bromo-2-cyano pyridine, is prepared by the treatment of 2,6-dibromopyridine with nBuLi, followed by tert-butyl-isocyanate, to yield a tert-butylamide. The amide can then be dehydrated with POCl₃ in toluene at 110 °C to generate 6-bromo-2-cyano pyridine, which can be purified via sublimation at 65 °C at 10⁻² Torr. Next, 2-bromopyridine is treated with nBuLi at -78 °C to yield a 2-lithiopyridine intermediate, further reacted with trimethyltin chloride to yield 2-(trimethylstannyl)pyridine. A Stille coupling is then conducted by combining the previously synthesized 6-bromo-2-cyano pyridine with 2-(trimethylstannyl)pyridine and a catalytic amount of Pd(PPh₃)₄ in toluene and heating to reflux for two days. The resulting brown powder can then be sublimed at 85°C at 10⁻² Torr to yield bipyCN as a white powder in yields upwards of 80% (Scheme 3.2).
Scheme 3.2: Synthetic route utilized to produce 6-cyano-2,2′-bipyridine (bipyCN).

From bipyCN, synthesis of the radical species followed the standard procedure conducted within the Preuss research group. The nitrile was dissolved in dry toluene before adding a stoichiometric amount of LiN(TMS)₂•Et₂O. Trimethylsilyl chloride was added to the reaction after several hours at room temperature, yielding the amidine, 2,2′-bipyrid-6-yl-N,N,N′-tris(trimethylsilyl)amidine, as an orange tacky solid. The amidine was redissolved in dry acetonitrile and treated with five equivalents of sulfur monochloride under reflux conditions, generating a 1,2,3,5-dithiadiazolium chloride salt that can later be reduced. Typically, triphenyl antimony is utilized as a two-electron reducing agent, generating the desired radical and triphenylantimony dichloride (SbPh₃Cl₂) as a side product. Initially, the chloride salt was reduced with a half molar equivalent of SbPh₃,
which produced yields upwards of 90% crude bipyDTDA (Scheme 3.3). However, purification of bipyDTDA by sublimation proved to be problematic. At 10^{-2} Torr, bipyDTDA co-sublimed with by-product SbPh_3Cl_2. Isolation of the desired radical could only be achieved by extensive washing with dry toluene to remove the by-product. In an effort to make purification easier, antimony trichloride was utilized to reduce the chloride salt. The use of SbCl_3 maintained the same two-electron reduction capability and produced very similar reaction yields while eliminating SbPh_3Cl_2 contamination of the product. However, X-ray crystallography of the crystals produced from the sublimation indicated that bipyDTDA was reduced and simultaneously coordinated to unreacted SbCl_3 and the free ligand was not obtained. Although the coordination of bipyDTDA to SbCl_3 occurs, it is not a disadvantage. By utilizing 1.5 equivalents of SbCl_3, SbCl_3(bipyDTDA) can be prepared and its identity has been confirmed by elemental analysis.

**Scheme 3.3:** Synthetic route to produce 4-(2', 2''-bipyrid-6'-yl)-1,2,3,5-dithiadiazolyl (bipyDTDA).
Scheme 3.4: Synthetic route towards SbCl$_3$(bipyDTDA) via simultaneous reduction and coordination utilizing SbCl$_3$.

3.4 Characterization

3.4.1 Electron Paramagnetic Resonance

An X-band EPR spectrum of bipyDTDA, prepared using SbPh$_3$ as a reducing agent, was obtained at room temperature utilizing a Bruker EMX EPR spectrometer. A suitable sample was loaded into a cell within an inert atmosphere and dissolved in dry CH$_2$Cl$_2$. The spectrum showed a five-line pattern with a relative ratio of intensities of 1:2:3:2:1, consistent with an unpaired electron coupling to two equivalent $^{14}$N atoms (Figure 3.4). The g value was determined to be 2.0133 and $a_\parallel=5.18$ G.
Figure 3.4: Experimental EPR spectrum of bipyDTDA in methylene chloride at ambient temperature.
3.4.2 X-ray Crystallography

3.4.2.1 BipyDTDA Needles

Black needles of bipyDTDA were obtained by static sublimation at 123 °C (10^{-2} Torr) following extensive toluene wash after reduction with SbPh_{3}. A suitable crystal was mounted on a MiTeGen probe with almost no oil and X-ray analysis was conducted using a Cu radiation source at 150 K. The data parameter ratio was fairly low, due in part to using a very small crystal, measuring only 0.25 × 0.04 × 0.04 mm. Typically a crystal of such size would be insufficient for analysis but a high level of symmetry made a solution possible. An acceptable R-value of 4.08% was obtained by modeling disorder of two molecules (50/50) almost on top of each other, in the tetragonal space group P4_2/n. The asymmetric unit contains a single molecule giving a total of eight molecules within the unit cell. The 2,2'-bipyridine portion of the ligand is nearly planar, with a dihedral angle of 4.52° between the two pyridine rings. However, the thiazyl ring is twisted a considerable 18.74° out of the plane of the 2,2'-bipy portion. Dimerization of the radical ligand is cis-cofacial showing S…S contacts of 3.190 and 3.135 Å, well within the sum of the van der Waals radii for two S^2- (3.6 Å) (Figure 3.5). The S…S contact distances are similar to other cis-cofacial dimers of DTDA radical ligands.\textsuperscript{27}
In addition to the contacts involved in dimerization, there are extensive S…S and S…N contacts between non-dimerized molecules (Figure 3.5). The ligand is arranged such that the thiazyl rings of four neighbouring bipyDTDA molecules are facing one another, creating a “propeller-like” shape (Figure 3.6). When extended in three dimensions, the structure creates a large cylindrical column, similar to a winding staircase, containing a network of interactions within the core (Figure 3.7).
**Figure 3.6:** Crystal packing of bipyDTDA from above indicating S...S and S...N close contacts between neighboring molecules in a “propeller-like” arrangement.

**Figure 3.7:** Solid state crystal packing of bipyDTDA from above (left) and from the side (right) of a cylindrical column.
3.4.2.2 *SbCl₃(bipyDTDA)* Prism

Reduction of [bipyDTDA][Cl] using SbCl₃ in an effort to generate bipyDTDA produced black prisms during sublimation at 123 °C (10⁻² Torr). The preliminary crystal structure of the black prisms indicates that the radical ligand is coordinated to unreacted SbCl₃ (Figure 3.8). The raw crystal data were poor, as the crystals were either multicrystals or multitwins, absorbing very strongly with a Cu radiation source at 150 K. Attempts to obtain a publishable structure, using a Mo source, are currently underway. Nevertheless, the data presented herein are sufficient to positively identify the molecular species without any doubt. The structure was solved to R=7.9% in *P*₂₁/ndata, an alternate setting of the monoclinic space group *P*₂₁/c. The present structure solution has some astonishing features. The complex is not dimerized in the solid state, likely due to the metal center withdrawing electron density from the DTDA moiety, making pancake bonding less favorable. This implies that the species remains paramagnetic in the solid state. Furthermore, it appears that an important contact exists between a chlorine atom of SbCl₃ and a neighboring antimony atom. This contact explains the apparent “wonky” geometry about the 6-coordinate antimony center of the complex. In fact, it may be more accurate to consider this a 7-coordinate antimony dimer with two bridging Cl atoms. There are two S⋯N contacts between adjacent DTDA moieties, implying a potential pathway for intermolecular magnetic coupling. A close contact also exists between one of the chlorine atoms of SbCl₃ and both sulfur atoms within the neighboring DTDA ring (Figure 3.9). Better crystallographic data will help elucidate and confirm the tentative structure.
Figure 3.8: Crystal structure fragment of SbCl$_3$(bipyDTDA) indicating Sb...Cl close contacts in a bridging type formation.

Figure 3.9: Solid state crystal packing of SbCl$_3$(bipyDTDA) outlining intermolecular contacts.
3.5 **Computational Studies of bipyDTDA**

The SOMO, spin density, and charge distribution of geometry optimized bipyDTDA were calculated with Gaussian 09 utilizing a uB3LYP method and a 6-31D(d,p) basis set (Figure 3.10). The SOMO is as expected for a DTDA molecule, with coefficients on the nitrogen and sulfur atoms around the DTDA moiety and a node at carbon 4. The majority of the spin density is situated within the DTDA ring, with only a small amount of spin density on bipy atoms. The Mulliken charge distribution calculations confirm the existence of a hard tridentate nitrogen pocket, demonstrating negative charge density similar to previous DTDA radical ligands, supporting the design concept for tridentate coordination.

![bipyDTDA](image)

**Figure 3.10:** a) SOMO of bipyDTDA b) charge density of bipyDTDA with positive charge density green, negative charge density red c) total spin density of bipyDTDA with beta spin density (green) and alpha spin density (blue) calculated using G09 uB3LYP 6-31G(d, p).
3.6 Synthesis of 6,6'-Bis-1,2,3,5-Dithiadiazolyl-2,2'-Bipyridine

The synthetic route towards 6,6'-bis-1,2,3,5-dithiadiazolyl-2,2'-bipyridine (bisDTDAbipy) begins with synthesis of the symmetric 6,6'-dicyano-2,2'-bipyridine, which was generated according to Fife and Hiertzler’s literature procedures. 2,2'-Bipyridine was converted to 2,2'-bipyridine N,N'-dioxide with mCPBA followed by reaction with trimethylsilyl cyanide and benzoyl chloride to obtain 6,6'-dicyano-2,2'-bipyridine.21,22 Unlike the mono-substituted bipyCN, synthesis of the disubstituted 6,6'-dicyano-2, 2'-bipyridine was more straightforward because complete oxidation of both sites eliminates the possibility of product mixtures. Synthesis of the dinitrile was achieved via oxidation of 2,2'-bipyridine with excess mCPBA. The N,N'-dioxide product was then treated with trimethylsilyl cyanide and benzoyl chloride to yield crude 6,6'-dicyano-2,2'-bipyridine, which can be recrystallized in ethanol to obtain white, hair-like needles. From this point, standard Preuss group DTDA synthesis was employed, making appropriate stoichiometric adjustment to obtain the diradical species (Scheme 3.5). The reduction of the radical using trichloro antimony gave approximately 50% crude yield, which is much lower than other radicals previously synthesized.28 The low yield could be attributed to a higher level of impurity in the chloride salt through the use of a large amount of sulfur monochloride, which typically generates significant quantities of sulfur. The diradical species also suffers from extremely low solubility in many solvents, making recrystallization very difficult. Thus far, no recrystallization attempts have been successful. Sublimation of the compound was also attempted, however no pure product was acquired. The additional DTDA moiety of the diradical species could allow for increased π-π
interactions, making the compound much less volatile than previously synthesized radical ligands. Crude radical, confirmed by mass spectrometry, was purified by washing thoroughly with toluene followed by sublimation at 70 °C (10^{-2} Torr) to remove volatile sulfur impurities. However, isolation of pure diradical was not achieved, as the identity of the samples could not be confirmed by elemental analysis at this time.

Scheme 3.5: Synthetic route towards 6,6'-bis-1,2,3,5-dithiadiazolyl-2,2'-bipyridine (bisDTDAbipy).

3.7 Characterization

3.7.1 Electron Paramagnetic Resonance

The X-band EPR spectrum of bisDTDAbipy was obtained at room temperature utilizing a Bruker EMX EPR spectrometer. A suitable sample was loaded into a cell within an inert atmosphere and dissolved in dry CH$_2$Cl$_2$. The spectrum showed a five line pattern with peak intensities of 1:2:3:2:1 (Figure 3.11). The g value
was determined to be 2.0125 and $a_N = 5.14$ G. Although the structure of bisDTDAbipy contains two separate spin centers, a nine-line pattern was not observed. Typically, a nine-line pattern is only observed for systems in which the two spin centers are interacting and $J \geq a$. For bisDTDAbipy, $J$ is expected to be very small as the spin density of the bipyridine moiety, arising from spin polarization of underlying filled orbitals is too small to reasonably expect to see coupling between the two remote DTDA substituents at room temperature. The strongest coupling would be expected for the molecule in a planar geometry, and rotation around single bonds in solution will break the planarity of the molecule. Furthermore, it is unlikely that bisDTDAbipy would be a planar molecule due to the steric contributions of the aryl-H atoms in the molecule. Reduced planarity within the bisDTDAbipy will lead to less communication of the radical moieties via the $\pi$ system of the ligand and a lower $J$ value would be expected. As a result, the EPR spectrum exhibits the five-line pattern characteristic of a monoradical species, indicating that the two DTDA radicals are essentially independent of one another in solution at ambient temperature.
Despite observation of negligible coupling between the two DTDA radicals in the EPR experiment, in general, a biradical system should have either a singlet or a triplet ground state. If the unpaired electrons on each DTDA moiety have the same spin state (i.e., alpha spin density on each radical), then they are said to be in a triplet state whereas opposing spins indicate the singlet ground state. As shown in the spin density calculation for bipyDTDA (Figure 3.10), the alpha and beta spin densities alternate throughout the 2,2'-bipyridine backbone. Placing alpha spin density on the nitrogen atom of one radical moiety and alternating the spin density throughout bipyridine rings indicates that beta spin density should be present on the nitrogen of the second DTDA. Using the model of alternating spin density, it is reasonable to suppose that the bisDTDAbipy molecule has an open-shell singlet ground state, but it
is important to note that the singlet-triplet energy difference is likely to be very small, as indicated by the EPR spectrum.

### 3.7.2 DART Mass Spectrometry

Due to extremely low volatility and solubility of bisDTDAbipy, suitable crystals for X-ray crystallography could not be grown, so characterization of bisDTDAbipy was carried out via Direct Analysis in Real Time (DART) Mass Spectrometry. Ionization of an analyte (M) in DART-MS relies on the formation of a metastable state of helium, He(2^3S), resulting from helium carrier gas passing through a chamber of electrical discharge. Other charged particles generated, such as ions and electrons, are effectively removed by a series of perforated lenses and grids allowing the neutral helium gas and He(2^3S) to pass unaffected. The He(2^3S), with a 19.8 eV energy, can efficiently react with atmospheric H\(_2\)O after it has been isolated, generating ionized water clusters.\(^{29}\) The ionized water clusters undergo proton transfer reactions with the analyte, yielding MH\(^+\) which can be then be detected (Figure 3.12).\(^{30}\)

\[
\begin{align*}
\text{He}(2^3\text{S}) + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}^{**} + \text{He}(1^1\text{S}) + e^- \\
\text{H}_2\text{O}^{**} + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{OH}^* \\
\text{H}_3\text{O}^+ + \text{nH}_2\text{O} & \rightarrow [(\text{H}_2\text{O})\text{nH}]^+ \\
[(\text{H}_2\text{O})\text{nH}]^+ + \text{M} & \rightarrow \text{MH}^+ + \text{nH}_2\text{O}
\end{align*}
\]

**Figure 3.12:** Ionized water cluster formation to generate a protonated analyte signal using DART mass spectrometry.
The 19.8 eV of He(2^3S) is also higher than the ionization energies of many organic molecules, allowing for a standard Penning ionization to occur (Figure 3.13):\textsuperscript{31}

\[
M^* + S \rightarrow S^{**} + M + e^-
\]

**Figure 3.13:** *Penning ionization where M* is an excited gas molecule S is the analyte.*

As a result, it is common for spectra to contain the M+ and MH+ fragmentation patterns of an analyte. For bisDTDAbipy, the mass spectrum indicates the correct m/z of 362.95 for bisDTDAbipyH+ with an accurate isotope pattern (Figure 3.14). An additional peak can be seen at m/z = 361.95 that corresponds to bisDTDAbipy+.

**Figure 3.14:** *Experimental DART mass spectrum of bisDTDAbipy.*
3.8 Metal Complexes of Bipyridine Based DTDA ligands

Examples of metal chelation involving 2,2'-bipyridine and ligands with a 2,2'-bipyridine backbone are plentiful,\textsuperscript{1,27,32} demonstrating a potential to create novel luminescent and magnetic materials.\textsuperscript{33} The coordination of the bipyDTDA ligand to a metal center represents a novel tridentate DTDA coordination mode. The resulting coordination complex contains the conjugation necessary for luminescence, along with the spin bearing DTDA moiety allowing for magnetic interactions with the unpaired electrons of a paramagnetic metal center. To generate the desired luminescent switch functionality, transition metal species, such as Ru\textsuperscript{2+}, would be required. Ru\textsuperscript{2+} chemistry with DTDA ligands is still being developed. However, our groups already has very robust protocols for the use of lanthanide starting materials\textsuperscript{34} and coordination of bipyDTDA to Ln\textsuperscript{3+} was determined to be a good proof of concept, establishing a tridentate coordination motif.

3.9 Metal Starting Materials

The moisture sensitivity of the thiazyl radical moiety makes the use of typical lanthanide hydrate starting materials impossible. An anhydrous alternative, Ln(hfac)\textsubscript{3}(DME), can be synthesized easily and cost-efficiently, replacing the coordinated aqua ligands with the bidentate ether, dimethoxyethane (DME). The hexfluoroacetylacetonato ligands are electron withdrawing, helping to remove electron density from the metal center making it more susceptible to coordination from a hard, nitrogen donating ligand. The hfac group also acts to improve the volatility and solubility of the complex in an effort to simplify purification.
Synthesis of most of the anhydrous lanthanide starting materials begins with the corresponding lanthanide chloride hydrate, treated with Hhfac and Na$_2$CO$_3$ to yield the hydrated Ln(hfac)$_3$(H$_2$O)$_2$ (Scheme 3.6).$^{35}$ Ln(hfac)$_3$(H$_2$O)$_2$ can then be converted to the anhydrous Ln(hfac)$_3$(DME) species utilizing excess DME in hexanes, followed by repeated dissolution in petroleum ether (Scheme 3.6).$^{34}$ Sublimation of the resulting product must be conducted in order to obtain pure complex. In the case of Ce, sublimation is required as a complex containing 1.5 DME units is produced (one ligand bridges metal centers). Lanthanum starting materials are made in the same fashion, except with a nitrate starting material and Gd and Eu species are synthesized from their respective oxides.

![Scheme 3.6: Synthetic scheme for Ln(hfac)$_3$(DME) starting materials with Ln=Ce, Pr, Dy.](image)

**Scheme 3.6: Synthetic scheme for Ln(hfac)$_3$(DME) starting materials with Ln=Ce, Pr, Dy.**

### 3.10 Synthesis of bipyDTDA Complexes

The coordination of bipyDTDA was conducted utilizing material obtained from reductions with SbCl$_3$. Sulfur impurities were effectively removed by sublimation and black crystals of bipyDTDA were grown at 123 °C ($10^{-2}$ Torr). As
mentioned previously, radical ligand reduced via SbCl$_3$ forms primarily SbCl$_3$(bipyDTDA) rather than free bipyDTDA, however the compound was used without further purification and it was determined that the SbCl$_3$ can be displaced by a Ln$^{3+}$ moiety relatively easily. Because the initial coordinations were undertaken before it was known that bipyDTDA is heavily contaminated with SbCl$_3$(bipyDTDA), an intended 1:1 mixture of bipyDTDA/SbCl$_3$(bipyDTDA) and Ln(hfac)$_3$(DME) was combined in dry methylene chloride and stirred at ambient temperature for 4-5 hours, until no more undissolved radical remained (Scheme 3.7).

Although the thiazyl starting material suffers from poor solubility, coordination to the metal center eventually draws the radical into solution. Solvent is then removed under reduced pressure to yield tacky red solids that must be left under an inert atmosphere overnight, until dry, workable red powders are obtained. The crude product can be purified via sublimation on a four-stage dynamic vacuum sublimation furnace. Since a bipyDTDA/SbCl$_3$DTDA mixture was utilized, an excess of Ln(hfac)$_2$(DME) was present, however, the unreacted starting materials can be separated and crystals of Ln(hfac)$_3$(bipyDTDA) can be grown at 123 °C (10$^{-2}$ Torr).

Scheme 3.7: Synthesis of Ln(hfac)$_3$(bipyDTDA) complexes where Ln=La, Ce, Pr, Dy.
3.11 Characterization

Structures of Ln(hfac)$_3$(bipyDTDA) (Figure 3.15), where Ln= Ce, Pr and Dy, have all been determined by single crystal X-ray diffraction utilizing a Mo radiation source at 150 K (Figure 3.15). The complexes are isostructural, crystallizing in a monoclinic space group, $P2_1/c$. The dysprosium complex was solved in $P2_1/n$, however, this is simply an alternate arrangement of the standard space group $P2_1/c$. The structures all contain two molecules of complex in the asymmetric unit and eight molecules in the unit cell.

![Twisted-cofacial dimerization within the crystal structures of Ln(hfac)$_3$(bipyDTDA) where Ln= Ce, Pr, Dy with relevant atom numbering for Table 1.](image)

Figure 3.15: Twisted-cofacial dimerization within the crystal structures of Ln(hfac)$_3$(bipyDTDA) where Ln= Ce, Pr, Dy with relevant atom numbering for Table 1.

The crystal structures indicate that the complexes are dimerized in the solid state in a twisted co-facial mode (Figure 3.15). The contacts present between radical
dimers are all consistent for the three complexes, regardless of the metal center (Table 1) and the closest intermolecular sulfur-sulfur distances range from 2.94-3.01 Å, which is well within the sum of van der Waals radii for two sulfur atoms.

**Table 1**: Relevant bond distances for Ln(hfac)$_3$(bipyDTDA) complexes.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Ce(hfac)$_3$(bipyDTDA) Distance (Å)</th>
<th>Dy(hfac)$_3$(bipyDTDA) Distance (Å)</th>
<th>Pr(hfac)$_3$(bipyDTDA) Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-S53</td>
<td>3.005</td>
<td>3.061</td>
<td>3.072</td>
</tr>
<tr>
<td>S2-S52</td>
<td>2.943</td>
<td>3.011</td>
<td>2.947</td>
</tr>
<tr>
<td>S3-N51</td>
<td>3.081</td>
<td>3.040</td>
<td>3.005</td>
</tr>
<tr>
<td>Ln1-N1</td>
<td>2.627</td>
<td>2.519</td>
<td>2.608</td>
</tr>
<tr>
<td>Ln1-N7</td>
<td>2.694</td>
<td>2.543</td>
<td>2.638</td>
</tr>
<tr>
<td>Ln1-N13</td>
<td>2.626</td>
<td>2.512</td>
<td>2.592</td>
</tr>
</tbody>
</table>

These nine-coordinate lanthanide complexes all demonstrate mono capped square anti prism geometry around the metal center. The Ln-N bond lengths can be seen in Table 1. Ln-N bonds in this series of complexes all change as expected, indicating shorter bond lengths across the lanthanide series. The stronger bonds are consistent with the lanthanide contraction giving a smaller Ln radius and slight increase in electronegativity apparent with the later lanthanide centers.

The torsion angles within complexed bipyDTDA are relatively consistent with the uncoordinated ligand. The 2,2'-bipyridine portion of the ligand remains relatively planar with the thiazyl portion twisting slightly out of plane. The coordination of
bipyDTDA to later lanthanides, such as Dy, causes a slight shift to a more planar state, reducing the torsion angle of the DTDA ring to $\sim 8^\circ$.

La(hfac)$_3$(bipyDTDA) has also been synthesized, however, single crystals suitable for X-ray diffraction analysis could not be obtained. Powder X-ray Diffraction (PXRD) analysis of the compound was compared to the calculated (from the crystal structure) PXRD patterns of the above complexes as well as an experimentally obtained PXRD pattern of Ce(hfac)$_3$(bipyDTDA) (Figure 3.16). The pattern is consistent with all of the previously characterized complexes, which crystallize in $P2_1/c$. The structure of La(hfac)$_3$(bipyDTDA) is confirmed to be isomorphous to the other Ln(hfac)$_3$(bipyDTDA) complexes within the series, if not completely isostructural.

Figure 3.16: Simulated powder X-ray diffraction patterns of Dy(hfac)$_3$(bipyDTDA) and Pr(hfac)$_3$(bipyDTDA) and experimental powder X-ray diffraction patterns of Ce(hfac)$_3$(bipyDTDA) and La(hfac)$_3$(bipyDTDA).
3.12 Conclusions

The desired 2,2'-bipyridine based radical ligands, bipyDTDA and bisDTDAbipy, have both been successfully synthesized. BipyDTDA demonstrates a dimerized, highly symmetric structure in the solid state containing numerous sulfur-nitrogen interactions. Complete purification of the radical has not been achieved, however bipyDTDA has successfully demonstrated novel tridentate coordination of a thiazyl radical species to Sb, La, Ce, Pr and Dy metal centers. The SbCl$_3$(bipyDTDA) complex is of particular interest. A preliminary structure of SbCl$_3$(bipyDTDA) indicates the structure might remain paramagnetic in the solid state, containing unique Cl bridging interactions as well as additional S…N contacts between adjacent DTDA moieties, which could imply a potential pathway for intermolecular magnetic coupling. Magnetic data for the complexes has yet to be collected. Purification of bisDTDAbipy has proven to be difficult. The di-radical 2,2'-bipyridine species has shown to have very poor volatility and solubility which could be a result of increased $\pi-\pi$ interactions via the additional DTDA moiety. Characterization of the di-radical has been conducted via DART Mass Spectrometry. However, successful coordination of the ligand has yet to be achieved.

3.13 Future Work

The current synthetic work has proven that bipyDTDA is an effective paramagnetic tridentate chelator. Although the complexes synthesized were more of a proof of concept, they may yet have value as magnetic materials. The lanthanide complexes previously synthesized will be sent to collaborators for magnetic
measurements. Dy(hfac)$_3$(bipyDTDA) should be investigated as a potential single molecule magnet, and the other complexes examined to determine the magnetic interactions. However, the main goal for these ligands was to create thiazyl complexes with luminescent functionality. Luminescent lanthanide materials could be generated through the coordination to Ln$^{3+}$ metal centers such as terbium and europium. By utilizing additional large antennae ligands around the lanthanide center, phase transitions could be induced through irradiation of the compound. The so called “antenna effect”, seen in the literature for lanthanide containing materials, would cause a conversion of light via an absorption-energy transfer-emission sequence with the antennae ligand as a “light collector”. Energy transfer throughout the complex could be significant enough to “pop open” a dimerized radical pair, generating a paramagnetic phase. Such a process would be dependent on the intensity of the ligand absorption and the efficiency of a ligand to metal energy transfer, requiring specific tailoring of the molecule.

Attempts to isolate free bipyDTDA ligand should be continued. Since SbCl$_3$(bipyDTDA) can be made via the reduction of bipyDTDA with 1.5 equivalents of SbCl$_3$, the complex can be isolated and bipyDTDA could later be displaced from the antimony metal center. Heating SbCl$_3$(bipyDTDA) in a large excess of a coordinating species such as pyridine or monoglyme, could potentially precipitate bipyDTDA, which could be effectively isolated via filtration. The use of free bipyDTDA ligand would allow for the synthesis of various transition metal complexes, without the presence of a competing antimony metal center.
The reduction of bipyDTDA via SbCl$_3$ has demonstrated that transition metal coordination is possible, however, attempts to recreate a similar system through the coordination of bipyDTDA to CoCl$_2$ or RuCl$_3$ have been inconclusive. Poor solubility and volatility of these materials has created difficulty in purification and attempts to produce a single crystal should be continued. Additionally, the chlorine substituents around the transition metal centers could be replaced by auxiliary ligand such as bis(trimethylsilyl)amide, N(SiMe$_3$)$_2$. The N(SiMe$_3$)$_2$ groups would act to increase the solubility and volatility of the complex which could make purification easier.

As touched upon earlier, Ru(II) complexes containing polypyridine ligands, such as 2,2'-bipyridine, typically exhibit significant luminescent properties. With the coordination of bipyDTDA to a ruthenium (II) metal center, it is hoped that much of the luminescent ability of the bipyridine still remains, while adding an additional paramagnetic DTDA moiety. The DTDA ring should exhibit a monomer-dimer equilibrium in solution, which can be shifted by temperature, to produce a paramagnetic state that would quench luminescence. This would afford a bi-phase luminescent switch. It is important to note that ruthenium (III) metal centers could potentially cause redox behavior between the ligand and metal, so any future attempts to synthesize such a complex should be conducted utilizing Ru (II). Synthesis of a paramagnetic compound similar to Ru(bipy)$_3$ such as [Ru(bipyDTDA)$_2$](OTf)$_2$ should be conducted to determine if any substantial luminescent behavior exists within bipyDTDA. Coordination of bipyDTDA to [Ru(DMF)$_6$](OTf)$_2$ would be an appropriate starting point as the synthesis of [Ru(DMF)$_6$](OTf)$_2$ is available in literature. The DMF ligands should be considerably labile, allowing for tridentate
nitrogen chelation to occur rather rapidly (Scheme 3.8). Once synthesized, the material should undergo variable temperature UV-VIS and fluorescence measurements. The change in temperature would effectively alter the monomer-dimer equilibrium of the thiazyl radical, allowing for paramagnetic quenching to be observed.

Scheme 3.8: Synthetic scheme to [Ru(DMF)$_6$][(OTf)$_3$].

Solubility problems with bisDTDAbipy make further synthetic work difficult. The incorporation of additional organic substituents to the 2,2'-bipyridine backbone, such as methyl groups, should be considered. The electron donating ability of methyl groups should assist in coordination to the metal center as well as increase the solubility of the ligand, allowing for a higher probability of metal-ligand chelation. Synthesis of the substituted 2,2'-bipyridine can start from commercially available, 2-amino-4-methylpyridine, at a reasonable cost. The amine is added to a 47% solution of HBr with Br$_2$ and then treated with NaNO$_2$ (aq) at 0 °C, similar to a Sandmeyer reaction.$^{40}$ The product of this reaction, 2-bromo-4-methylpyridine, can then be coupled together via Raney Nickel to yield 4,4'-dimethyl-2,2'-bipyridine.$^{41}$ The
biradical can be further synthesized following the same steps previously discussed for the synthesis of bisDTDAbipy (Scheme 3.9).

**Scheme 3.9:** Proposed synthetic scheme yielding methyl substituted bisDTDAbipy.
3.14 Experimental

General Procedures and Starting Materials: All reagents used were obtained commercially from Sigma Aldrich, Alfa Aesar and Acros Organics and were used as received. LiN(SiMe$_3$)$_2$•Et$_2$O$^{42}$ and all Ln(hfac)$_3$(DME)$^{34}$ starting materials were prepared following literature procedure. Reactions were performed under argon atmosphere using standard Schlenk techniques and for such reactions, anhydrous solvents were obtained from an SP-1 Stand Alone Solvent Purification System from LC Technology Solutions Inc., utilizing molecular sieves (3 Å). $^1$H and $^{13}$C NMR chemical shifts are reported in ppm relative to trimethylsilane and solvent (CDCl$_3$=7.24 ppm, d$_6$-DMSO=2.49 ppm). Infrared spectra were obtained as a KBr pellet or plate utilizing a Nicolet 4700 FT-IR spectrometer at 4 cm$^{-1}$ resolution. Elemental analyses were performed by MHW Labs, Phoenix, AZ, USA. Crystal data was collected by Dr. Dmitriy Soldatov on a SuperNova Dual source diffractometer with Atlas CCD detector. Crystal structures were solved by Dr. Dmitriy Soldatov, with the exception of bipyDTDA solved by Dr. Michael Jennings. Mass Spectrometry was performed by Matthew Forbes at the University of Toronto. Sublimations were carried out on a three stage and four stage variable temperature tube furnace.

6-Bromo-N-tert-butyl-picolinamide. A solution of 2,6-dibromopyridine (5.9020 g, 24.915 mmol) in 160 mL of anhydrous toluene was cooled to -40 °C and 2.0 M n-butyllithium (13.0 mL, 26.2 mmol) was introduced dropwise over 15 min. The dark brown solution was allowed to stir for an additional 2 hours at this temperature before tert-butylisocyanate (3.0 mL, 26 mmol) was added drop wise. The solution was kept
at -40 °C for an hour before slowly warming to -10 °C. When the mixture had reached temperature, it was poured into 100 mL of saturated NH₄Cl solution to quench the reaction. The biphasic solution was vigorously stirred for 30 minutes until the toluene layer changed from dark brown to orange. Upon completion, the toluene layer was isolated and the aqueous layer was washed twice with 25 mL of toluene. The organic extracts were combined and the solvent was removed in vacuo, affording 6-bromo-N-tert-butyl-picolinamide as an orange oil, which was used without further purification. Crude yield assumed to be quantitative. ¹HNMR (600 MHz, CDCl₃), δ (ppm): 8.11 (1H, d, J=7.6 Hz) 7.70 (1H, s) 7.67 (1H, t, J=7.7 Hz) 7.56 (1H, d, J=7.9 Hz) 1.47 (9H, s). IR (NaCl, neat): 3387 (s), 3085 (w), 2968 (s), 2931(m), 1681 (s), 1581(m), 1556(ms), 1520(ms), 1479(m), 1427(ms), 1394(ms), 1365(ms), 1303(m), 1254(m), 1228(ms), 1153(m), 1123(ms), 1072(m), 989(m), 925(m), 891(m), 821(m), 777(ms), 761(ms), 728(ms), 701(w), 645(m), 586(w) cm⁻¹.

6-Bromo-2-cyanopyridine. 6-Bromo-N-tert-butyl-picolinamide (6.41 g, 24.9 mmol) was dissolved in 60 mL of dry toluene producing an orange solution. POCl₃ (20.0 mL, 215 mmol) was added to the solution dropwise and the mixture was refluxed for 15 hours under argon with vigorous stirring. The dark brown solution obtained was cooled to ambient temperature and the solvent was removed in vacuo affording a brown solid. The product was purified by sublimation at 65 °C (10⁻² Torr) to yield a white solid. Product yield (2.2797 g, 36%). ¹HNMR (600 MHz, CDCl₃), δ (ppm): 7.80 (1H, t, J=7.9Hz) 7.63 (1H, d, J=7.5 Hz) 7.56 (1H, d, J=8.2 Hz). IR (KBr): 3116(w), 3068(w), 3050(m), 2240(m), 2011(w), 1831(w), 1710(w), 1569(s),
2-(Trimethylstannyl)pyridine. 2-Bromopyridine (1.0 mL, 10 mmol) was dissolved in 100 mL of dry diethyl ether. The reaction mixture was cooled to -78 °C before 2.0 M n-butyllithium (5.38 mL, 10.8 mmol) was introduced dropwise. The resulting dark red solution was stirred at temperature for 2 hours, then a 1.0 M trimethyltin chloride solution in THF (10.77 mL, 10.77 mmol) was introduced dropwise. The reaction was kept at -78 °C for an additional 3 hours and then allowed to slowly warm to room temperature overnight. Diethyl ether was removed from the yellow opaque solution in vacuo and the resulting solid was redissolved in 100 mL of dry hexane. The yellow solution was filtered under argon and the hexane was removed under reduced pressure affording a yellow-orange oil. Product was used without any further purification. Crude yield assumed to be quantitative.

6-Cyano-2,2′-bipyridine. 6-Bromo-2-cyanopyridine (1.2108 g, 6.6160 mmol) was introduced to a dry 250 mL side arm round bottom flask containing 2-(trimethylstannyl)pyridine (2.5 g, 10 mmol). Tetrakis(triphenylphosphphino) palladium (0) (0.3888 g, 0.3364 mmol) was also introduced and the reagents were dissolved in 80 mL of dry toluene. The reaction was refluxed for 2 days before cooling to room temperature and adding 100 mL of 2 M NaOH. The resulting brown biphasic solution was stirred for 30 minutes until the layers were separated. The aqueous layer was washed twice with 20 mL of toluene and the extracts were
combined. Solvent was removed in vacuo to afford a brown solid which was purified by sublimation at 85 °C (10⁻² Torr). Product yield (0.9648 g, 80%). ¹HNMR (600 MHz, CDCl₃), δ (ppm): 8.67 (1H, d, J=2.8 Hz) 8.65 (1H, d, J=8.1 Hz) 8.45 (1H, d, J=8.0 Hz) 7.93 (1H, t, J= 7.9Hz) 7.84 (1H, t, J=7.8 Hz) 7.68 (1H, d, J=6.7 Hz) 7.36 (1H, t, J= 0.48Hz). IR (KBr): 3066(w), 2233(w), 1583(m), 1553(m), 1475(w), 1450(w), 1426(m), 1294(w), 1267(w), 1194(w), 1147(w), 1093(w), 1076(w), 1045(w), 988(m), 896(w), 828(m), 774(s), 740(m), 711(w), 644(m), 620(w), 576(w) cm⁻¹.

2,2'-Bipyrid-6-yl-N,N,N'-tris(trimethylsilyl)amidine. 6-Cyano-2,2'-bipyridine (1.4753 g, 8.1423 mmol) was dissolved in 100 mL of anhydrous toluene under inert atmosphere. LiN(SiMe₃)₂•Et₂O (2.0835 g, 8.6291 mmol) was added and the yellow-orange solution was stirred for 5 hours. Chlorotrimethylsilane (1.1 mL, 8.7 mmol) was introduced dropwise and the resulting yellow-orange solution was stirred for 12 hours at ambient temperature. The product was filtered under inert atmosphere and the solvent was removed in vacuo to afford a yellow-orange tacky solid that was used without any further purification. Crude yield assumed to be quantitative. ¹HNMR (600 MHz, CDCl₃), δ (ppm): 8.66 (1H, d, J=4.7 Hz) 8.45 (1H, d, J=4.0 Hz) 8.39 (1H, d, J=7.2 Hz) 7.80 (1H, t, J= 6.1 Hz) 7.76 (1H, t, J=7.8 Hz) 7.29 (2H, m) 0.21 (27H, m). IR (KBr): 3056(w), 2952(m), 2898(w), 1648(ms), 1578(m), 1571(m), 1473(w), 1426(m), 1407(w), 1312(w), 1251(m), 1161(m), 1145(m), 1078(w), 1044(w), 1010(m), 991(w), 886(w), 836(s), 791(w), 774(m) 753(w), 685(w), 626(w), 574(w), 501(w) cm⁻¹.
[bipyDTDA][Cl]. 2,2'-Bipyrid-6-yl-N,N,N'-tris(trimethylsilyl)amidine (3.3772 g., 8.1423 mmol) was dissolved in 100 mL of anhydrous acetonitrile under inert atmosphere. Excess sulfur monochloride (3.3 mL, 41 mmol) was added slowly affording an orange slurry that was stirred for 12 hours at ambient temperature. The resultant orange solid was filtered and dried in vacuo. The crude product was used without further purification. Product yield (2.3591 g, 89%) IR (KBr): 3053(br), 1609(w), 1585(w), 1528(m), 1457(m), 1420(w), 1383(m), 1292(w), 1265(w), 1176(w), 1114(w), 995(w), 958(w), 886(w), 848(w), 823(w), 782(m), 746(m), 708(w), 678(w), 631(w), 619(w), 545(w), 471(w) cm\(^{-1}\).

bipyDTDA.

**Reaction A:** Solid triphenylantimony (0.6373 g, 1.805 mmol) was added to an orange slurry of [bipyDTDA][Cl] (1.0717 g, 3.6356 mmol) in 25 mL of dry acetonitrile. The resulting purple slurry was stirred at ambient temperature for 1 hour before being filtered and dried in vacuo. The purple solid was purified via sublimation at 123 °C (10\(^{-2}\) Torr) to obtain purple crystalline solid. The resulting product has not been obtained as pure substance, confirmed by elemental analysis, due to co-sublimation with triphenylantimony dichloride, and as a result, no yield is reported. Crystals suitable for X-ray crystallography were obtained via static sublimation of toluene washed purple crystalline material at 123 °C (10\(^{-2}\) Torr) to yield purple needles. IR (KBr): 3141 (br), 3050(br), 1686(w), 1593(m), 1577(m), 1476(w), 1454(m), 1419(m), 1376(m), 1313(w), 1263(w), 1181(w), 1152(w), 1088(w), 1006(w), 811(w), 780(m), 745(w), 689(w), 649(w), 623(w), 455(w) cm\(^{-1}\). EPR (CH\(_2\)Cl\(_2\), 25 °C) five line pattern.
consistent with coupling to two equivalent $^{14}$N nuclei; $g= 2.0133, a_N= 5.18$ G. Anal. Calcd for $C_{11}H_7N_4S_2$: C, 50.95; H, 2.72; N, 21.60 %. Found: C, 39.13; H, 3.80; N, 15.58 %.

**Reaction B:** [BipyDTDA][Cl] (2.0739 g, 7.0354 mmol) and SbCl$_3$ (0.8177 g, 3.585 mmol) were added to an oven-dried round bottom flask and slurried in 70 mL of anhydrous acetonitrile. A color change from orange to dark purple was observed and the mixture was allowed to stir at ambient temperature for 1 hour. The resulting reddish purple solid was filtered and dried *in vacuo*. The red purple solid was purified via sublimation at 123 °C ($10^{-2}$ Torr) to obtain black purple crystals. Black purple prisms suitable for X-ray crystallography were obtained. The resulting product has not yet been confirmed by elemental analysis due the formation of SbCl$_3$(bipyDTDA) in varying quantities and as a result no yield is reported. Black purple crystals obtained via sublimation were used within subsequent coordination reactions. IR (KBr): 3073(w), 1592(m), 1574(w), 1561(w), 1492(w), 1457(m), 1407(w) 1373(m), 1301(m), 1271(w), 1250(w), 1188(w), 1160(w), 1095(w), 1087(w), 1020(m), 1003(m), 940(w), 901(w), 815(m), 790(m), 760(w), 745(w), 737(w), 683(m), 676(m), 648(w), 641(m), 524(w), 497(w), 466(w), 437(m) cm$^{-1}$. Anal. Calcd for $C_{11}H_7N_4S_2$: C, 50.95; H, 2.30; N, 21.61 %. Found: C, 35.77; H, 2.30; N, 13.80 %.

SbCl$_3$(bipyDTDA). [BipyDTDA][Cl] (1.0175 g, 3.4517 mmol) and SbCl$_3$ (1.2718 g, 5.5751 mmol) were added to an oven dried round bottom flask and slurried in 70 mL of anhydrous acetonitrile. The resulting purple slurry was stirred at room temperature for 2 hours until the reddish purple solid was filtered and dried *in vacuo*. The product
was purified via sublimation at 123 °C (10\(^{-2}\) Torr) to obtain black purple crystals. Product yield (0.0503 g, 3%). IR (KBr): 3073(w), 1592(m), 1574(w), 1561(w), 1492(w), 1457(m), 1407(w) 1373(m), 1301(m), 1271(w), 1250(w), 1188(w), 1160(w), 1095(w), 1087(w), 1020(m), 1003(m), 940(w), 901(w), 815(m), 790(m), 760(w), 745(w), 737(w), 683(m), 676(m), 648(w), 641(m), 524(w), 497(w), 466(w), 437(m) cm\(^{-1}\). Anal Calcd for SbC\(_{11}\)H\(_3\)Cl\(_3\)N\(_4\)S\(_2\): C, 27.10; H, 1.45; N, 11.49%. Found: C, 27.44; H, 1.56; N, 11.63%.

**2,2'-Bipyridine N,N'-dioxide.** 2,2'-Bipyridine (5.0464 g, 32.311 mmol) was dissolved in 20 mL of chloroform and added to a solution of mCPBA (11.2453 g, 65.164 mmol) in 100 mL of chloroform cooled in an ice bath. The mixture was allowed to slowly warm up to ambient temperature and was stirred for two days. The organic layer was washed with 3 \(\times\) 50 mL of saturated NaCO\(_3\)(aq) solution and dried over MgSO\(_4\). The organic layer was isolated the solvent was removed *in vacuo* to obtain the product as a white solid. Product yield (3.4658 g, 57%) \(^1\)HNMR (400 MHz, DMSO), \(\delta\) (ppm): 8.35 (2H, m) 7.64 (2H, m) 7.52 (2H, m) 7.42 (2H, m).

**6,6'-Dicyano-2,2'-bipyridine.** 2,2'-Bipyridine \(N, N'\)-dioxide (2.3915 g, 12.709 mmol) was dissolved in 100 mL of anhydrous DCM under inert atmosphere. The resulting clear solution was cooled to \(-40 \degree C\) prior to the addition of trimethylsilyl cyanide (10.5 mL, 83.9 mmol). Benzoyl chloride (5.9 mL, 50 mmol) was introduced very slowly dropwise while maintaining a temperature of \(-40 \degree C\). The pale brown solution was allowed to warm up to ambient temperature slowly and the mixture was stirred
for 2 days. Saturated Na₂CO₃(aq) was introduced and the biphasic solution was stirred for 30 min. The organic layer was isolated and the aqueous solution was extracted with 3 × 25 mL of DCM. The solvent was removed in vacuo and the product was recrystallized from acetonitrile to afford white needles. Product yield (1.0425 g, 40%). ¹H NMR (600 MHz, CDCl₃), δ (ppm): 8.71 (2H, d, J=6.6 Hz) 8.00 (2H, t, J=7.4 Hz) 7.76 (2H, d, J=6.7 Hz). IR (KBr): 3079(w), 2236(m), 1577(ms), 1557(w), 1508(w), 1499(w), 1491(w), 1434(s), 1208(w), 1157(m), 1101(w), 1081(m), 990(m), 803(s), 735(w), 637(w), 592(w), 563(w) cm⁻¹.

6,6'-Bispersilyatedamidine-2,2'-bipyridine. 6,6'-Dicyano-2,2'-bipyridine (1.0168 g, 4.9311 mmol) was dissolved in 80 mL of anhydrous THF. LiN(SiMe₃)₂•Et₂O (2.5036 g, 10.369 mmol) was added, creating a dark red solution that was stirred for 5 hours at room temperature. Chlorotrimethylsilane (1.3 mL, 10 mmol) was added dropwise and the solution became orange after 12 hours at ambient temperature. The solvent was removed in vacuo and 40 mL of dry acetonitrile was introduced. The resulting solution was filtered under inert atmosphere and the solvent was removed in vacuo to yield an orange-brown solid, which was used without further purification. Crude yield assumed to be quantitative. ¹H NMR (600 MHz, CDCl₃), δ (ppm): 8.49 (m) 7.87 (m) 7.32 (m) 0.21 (m). IR (KBr): 2955(m), 2898(w), 1702(w), 1654(m), 1637(w), 1572(w), 1431(w), 1380(w), 1301(w), 1254(m), 1151(m), 1078(w), 1007(m), 842(s), 760(m), 719(w), 677(w), 631(w), 620(w) 434(w) cm⁻¹.
[bisDTDAbipy]Cl₂. 6,6'-Bispensilyatedamidine-2,2'-bipyridine (2.7854 g, 4.1357 mmol) was dissolved in 80 mL of anhydrous acetonitrile. Excess sulfur monochloride (3.3 mL, 41 mmol) was introduced dropwise creating a brown slurry that was stirred at room temperature for 18 hours. The resulting orange solid was filtered and dried in vacuo and used for subsequent reaction without further purification. Product yield (1.4824 g, 86%). IR (KBr): 3057(br), 1686(m), 1655(w), 1648(w), 1638(w), 1618(w), 1578(m), 1561(w), 1509(w), 1434(w), 1399(w), 1380(w), 1274(w), 1171(w), 1082(w), 991(w), 896(w), 840(w), 812(m), 747(w), 634(w) cm⁻¹.

bisDTDAbipy. [BisDTDAbipy][Cl]₂ (1.4824 g, 3.4205 mmol) and SbCl₃ (0.8036 g, 3.5227 mmol) were loaded into an oven dried round bottom flask and slurried in 40 mL of anhydrous acetonitrile. A color change from orange to dark purple was observed and the mixture was allowed to stir at ambient temperature for 1 hour. The resulting purple solid was filtered and dried in vacuo. Product yield (0.5746 g, 46%). IR (KBr): 3052(br), 1610(w), 1585(w), 1527(w), 1458(w), 1420(w), 1382(m), 1292(w), 1265(w), 1176(w), 1114(w), 995(w), 958(w), 886(w), 848(w), 823(w), 782(m), 747(m), 709(w), 631(w), 619(w), 545(w), 471(w) cm⁻¹. EPR (CH₂Cl₂, 25 °C) five line pattern consistent two non-interacting radical centers each with coupling to two equivalent ¹⁴N nuclei; g = 2.0125, a_N = 5.14 G. MS (High Resolution DART Ionization; 350 °C), parent ion assigned as m/z 363.0 (M=C₁₂H₆N₆S₄) 65%.

La(hfac)₃(bipyDTDA). BipyDTDA (0.1052 g) prepared via reaction B (unknown mixture ratio) and La(hfac)₃(DME) (0.3449 g, 0.4057 mmol) were placed in an oven
dried round bottom flask and dissolved in 30 mL of anhydrous methylene chloride. The resulting red solution was stirred at ambient temperature for 5 hours until the solvent was removed \textit{in vacuo} to afford a red solid. The product was purified via dynamic sublimation at 123 °C (10^{-2} \text{ Torr}) to afford a red crystalline material. Product yield (0.0714 g). IR (KBr): 1650(s), 1601(w), 1577(m), 1530(m), 1489(m), 1427(w), 1382(w), 1254(s), 1211(ms), 1145(s), 1097(m), 1012(w), 948(w), 850(w), 800(m), 783(m), 740(w), 693(w), 659(m), 631(w), 583(m), 528(w), 456(w) cm^{-1}. Anal calcd for LaC_{26}H_{10}F_{18}N_{4}O_{6}S_{2}: C, 30.36; H, 0.99; N, 5.50%. Found: C, 30.86; H, 1.16; N, 5.39%.

\textbf{Ce(hfac)}_{3}(\text{bipyDTDA}). \text{BipyDTDA} (0.1322 g) prepared via reaction B (unknown mixture ratio) and Ce(hfac)_{3}(DME) (0.4209 g, 0.4945 mmol) were placed in an oven dried round bottom flask and dissolved in 30 mL of anhydrous methylene chloride. The resulting red solution was stirred at ambient temperature for 5 hours until the solvent was removed \textit{in vacuo} to afford a red solid. The product was purified via dynamic sublimation at 123 °C (10^{-2} \text{ Torr}) to afford a red crystalline material. Product yield (0.0933 g). Suitable crystals for X-ray crystallography were grown by static sublimation at 123 °C (10^{-2} \text{ Torr}). IR (KBr): 1649(m), 1602(w), 1578(w), 1529(w), 1488(m), 1428(w), 1383(w), 1254(ms), 1208(m), 1143(s), 1097(w), 1013(w), 949(w), 852(w), 800(m), 783(w), 740(w), 692(w), 678(w), 659(m), 631(w), 583(w), 527(w), 458(w) cm^{-1}. Anal calcd for CeC_{26}H_{10}F_{18}N_{4}O_{6}S_{2}: C, 30.60; H, 0.99; N, 5.49%. Found: C, 30.80; H, 1.10; N, 5.29%.
Pr(hfac)$_3$(bipyDTDA). BipyDTDA (0.1115 g) prepared via reaction B (unknown mixture ratio) and Pr(hfac)$_3$(DME) (0.3678 g, 0.4316 mmol) were placed in an oven dried round bottom flask and dissolved in 30 mL of anhydrous methylene chloride. The resulting red solution was stirred at ambient temperature for 5 hours until the solvent was removed in vacuo to afford a red solid. The product was purified via dynamic sublimation at 123 °C (10$^{-2}$ Torr) to afford a red crystalline material. Product yield (0.1261 g). Suitable crystals for X-ray crystallography were grown by static sublimation at 123 °C (10$^{-2}$ Torr). IR (KBr): 1649 (s), 1602(w), 1578(w), 1556(w), 1489(m), 1429(w), 1383(w), 1348(w), 1254(s), 1207(m), 1143(s), 1098(m), 1013(w), 852(w), 800(m), 783(w), 771(w), 749(w), 740(w), 692(w), 659(m), 584(m), 527(w), 459(w) cm$^{-1}$. Anal Calcd for PrC$_{26}$H$_{10}$F$_{18}$N$_4$O$_6$S$_2$: C, 30.57; H, 0.99; N, 5.49%. Found: C, 30.80; H, 1.08; N, 5.29%.

Dy(hfac)$_3$(bipyDTDA). BipyDTDA (0.1277 g) prepared via reaction B (unknown mixture ratio) and Dy(hfac)$_3$(DME) (0.4235 g, 0.4847 mmol) were placed in an oven dried round bottom flask and dissolved in 30 mL of anhydrous methylene chloride. The resulting red solution was stirred at ambient temperature for 5 hours until the solvent was removed in vacuo to afford a red solid. The product was purified via dynamic sublimation at 123 °C (10$^{-2}$ Torr) to afford a red crystalline material. Product yield (0.0818 g). Suitable crystals for X-ray crystallography were grown by static sublimation at 123 °C (10$^{-2}$ Torr). IR (KBr): 1654(s), 1604(w), 1555(w), 1492(m), 1431(w), 1390(w), 1347(w), 1255(s), 1208(m), 1142(s), 1101(w), 1015(w), 951(w), 856(w), 800(m), 783(w), 741(w), 692(w), 661(m), 632(w), 586(m), 527(w) cm$^{-1}$. 
3.15 References

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Chapter 4
Terpyridine Based 1,2,3,5-Dithiadiazolyl Ligand
4.1 Introduction

This chapter describes the design and synthesis of a novel terpyridine 1,2,3,5-dithiadiazolyl ligand. The design of 4’-(1,2,3,5-dithiadiazolyl)-2,2’:6’,2”-terpyridine (terpyDTDA) (Figure 4.1) places the DTDA moiety at the 4’ position of the terpyridine backbone, well removed from the tridentate coordination pocket. The ligand was designed to act as a luminescent material, capable of coordination to transition metals and lanthanide centers without a direct interaction between the thiazyl radical and the metal. The DTDA moiety is then free to engage in dimer formation, and, through π-π stacking, can direct the formation of chains that would be capable of electron transport. Furthermore, the monomer-dimer equilibrium characteristic of thiazyl radicals would enable the DTDA moiety to act as a molecular switch for properties inherent to the terpyridine backbone (e.g., luminescence). The conjugated, aromatic terpyridine backbone would allow for luminescence to occur regardless of the DTDA substituent. Before examining the attempts to synthesize terpyDTDA, further discussion of the luminescence of metal complexes of terpyridine ligands is warranted.

Figure 4.1: Structure of 4’-(1,2,3,5-dithiadiazolyl)-2,2’:6’,2”-terpyridine (terpyDTDA).
4.2 2,2′: 6′, 2″-Terpyridine Chemistry

2,2′:6′,2″-Terpyridine is a tri-nitrogen containing aromatic heterocycle first isolated by Morgan and Burstall in the 1930’s. The initial synthesis involved steel autoclaves loaded with pyridine and FeCl₃ at 340 °C (50 atm), yielding various nitrogen-containing heterocycles. The products of this reaction included the intended dipyridyls as well as tripyridyl systems previously unknown. Of the tripyridyl systems obtained, the highly crystalline 2,2′:6′,2″-terpyridine (terpy) was identified as the abundant isomer, which was later found to exhibit tridentate N-coordination with various transition metals. Over the past 70 years, expansion of terpyridine-based chemistry has demonstrated the effectiveness of this organic species towards the formation of unique metal complexes. Complexes involving terpy ligands demonstrate a high level of stability with potential applications in the field of photophysical, redox and supramolecular chemistry. The stability of such materials is owed to a strong metal-ligand back donation between the d-π* orbitals as well as the chelate effect due to its tridentate coordination motif. However, the stability of the overall complex is also related to the metal ion as well as the number of terpyridine ligands within the coordination sphere. More stable bis-terpyridine coordination is typically observed with metals in a low oxidation state, exhibiting pseudo-octahedral geometry. This behavior is demonstrated by the Ru(II) complex, [Ru(terpy)₂]²⁺ and its d⁶-iridium analogue.

The crystal structure of [Ru(terpy)₂]²⁺ has been previously obtained as the bis(hexafluorophoshate) di-acetonitrile solvate salt. The d⁶ complex crystallizes in the P4₁ space group with a pseudo octahedral geometry as expected. Like Ru(bipy)₃²⁺,
[Ru(terpy)$_2$]$^{2+}$ exhibits photophysical properties, albeit they are not as impressive. The luminescent behavior of Ru[(terpy)$_2$]$^{2+}$ arises from MLCT, which is significantly hindered at temperatures above 77 K. Energy level ordering of the MLCT and MC excited states (see Chapter 3) explains the hindered luminescence at higher temperature. The MLCT excited state goes through a non-radiative decay pathway via the lower MC excited state at higher temperature, however, at low temperature this path becomes less efficient, allowing luminescence to be observed. Although the luminescence of [Ru(terpy)$_2$]$^{2+}$ is temperature dependent, the ligand can be tuned through the introduction of a wide variety of substituents in the 4'-position (well removed from the coordination site of the ligand), enabling enhanced luminescence at room temperature. Maestri et al. have demonstrated increased intensity and red shifting within the visible MLCT band of 4'-substituted terpyridine ligands compared to the parent complex [Ru(terpy)$_2$]$^{2+}$, regardless of the electron donating or electron accepting nature of the substituent. When it comes to luminescence, most of the complexes investigated displayed increased quantum yields as well as longer excited state lifetimes than that of the parent complex. However, this was not observed for strong electron donating substituents, such as the 4'-ethoxy-terpyridine, which displays no luminescent behavior. An explanation for the result lies in the stabilization of the HOMO and LUMO orbitals. Electron acceptor substituents stabilize the LUMO $\pi^*$ ligand orbital more than the HOMO $\pi$ ($t_{2g}$) set on the metal, whereas electron donating substituents destabilize the HOMO $\pi$ ($t_{2g}$) more than the LUMO $\pi^*$ ligand orbital. As a result, when an electron is removed from the metal, the excited state oxidation of Ru$^{2+}$ to Ru$^{3+}$ generates a strong interaction with
the electron donating substituted terpyridine ligand, hindering the excited state responsible for the luminescence.\textsuperscript{16} Although this discussion is focused primarily on the Ru\textsuperscript{2+} based coordination complexes of terpy, the concept is in no way limited to ruthenium. Previous literature has demonstrated the use of terpyridine ligands in the synthesis of luminescent iridium (III)\textsuperscript{17} and osmium (II) centered\textsuperscript{18} species which display increased luminescence at room temperature, compared to their ruthenium counterpart. However, luminescent ruthenium (II) based terpyridine species are the target species in this thesis, attempting to generate a “proof of concept” luminescent thiazyzyl material.

2,2':6',2''-Terpyridine has shown considerable merit in the field of supramolecular chemistry, as the ligand can be specifically designed to offer structural control of the resulting system. A number of different molecular architectures are achievable, which include “Grid and Rack” type structures,\textsuperscript{19} cycles,\textsuperscript{20} rotaxanes,\textsuperscript{21} catenanes\textsuperscript{22} and oligomer species.\textsuperscript{23} Each respective architecture is worthy of lengthy discussion, however, this thesis focuses on the use of terpy in the synthesis of oligomers, or the formation of molecular chains.

The smallest possible oligomer chain is referred to as a “dyad”, in which two metal centers are connected together via a linkage between coordinated moieties. There are many types of linkages between coordinated terpyridine ligands, including a 4' linked bis-terpyridine ligand\textsuperscript{24} as well as terpyridine ligands linked via ethyl,\textsuperscript{25} alkyne,\textsuperscript{26} phenyl,\textsuperscript{27} thiophene\textsuperscript{28} and 2,2'-bipyridine groups (Figure 4.2).\textsuperscript{26} Some linkages, such as those listed here, offer rigid structures, keeping the molecule in a “rod-like” or linear formation. For the most part, if the linkage connecting two metal
centers is continuous and unsaturated, then excitation of one unit within the dyad can induce energy transfer to the neighbouring metal center. This is exemplified in dyad complexes of Ru(II) utilizing an alkyne linked bis-tridentate terpyridine ligand.\textsuperscript{29} Incorporation of the linked terpyridine ligand increases the triplet state lifetime 3000 times compared to that of [Ru(terpy)\textsubscript{2}]\textsuperscript{2+}. As a result, significant luminescence is observed at room temperature due to a lower triplet state energy. The increased luminescence can be explained by electron delocalization over an extended \(\pi^*\)-orbital across most of the bis-terpyridine ligand as well as a lowered triplet state energy decoupling the MLCT and MC excited state, lying at higher energy.

**Figure 4.2:** Examples of linkages: (top) alkyne; (center) phenylene; (bottom) bipy.
The increased luminescence in dyads of Ru(II) is limited to ligands with extended planar linkages. The use of p-phenylene terpyridine linkages alters the planarity of the ligand, removing complete conjugation in the system and thus diminishing the luminescence compared to the alkynyl linked counterpart.\(^{24}\) Replacement of one of the two Ru(II) metal centers with Os(II) maintains this higher triplet lifetime while generating photo-induced, ultra-fast, quantitative triplet energy transfer along the molecular axis.\(^{29}\) Such a process suggests a potential application as a molecular wire, providing electron transport throughout the oligomeric system. Similar energy transfer processes are observed in analogous Ru(II)-Fe(II) and Ru(II)-Zn(II)\(^{30}\) systems as well as Ru(II)-Rh(III),\(^{31}\) Ru(II)-Co(III)\(^{32}\) dyads consisting of a phenylene linked bis-terpyridine ligand. Thus, there is a notable potential for developing molecular circuitry that can be tested or designed with the incorporation of a variety of transition metal centers. Furthermore, tailored ligands can be designed in order to achieve enhanced luminescence or “switchable” functionality. The incorporation of acceptor substituents in the 4' position of a terpyridine ligand can alter the luminescence observed. Enhancement of the luminescence produced via the linked bis-terpyridine ligand can be further improved by substitution at the terminal terpyridine ligand in the 4'-position.\(^{3}\) By tailoring the linkage between the two metal centers, additional switchability can be achieved. Hissler et al. reported control of the luminescent properties of a dyad system through a 2,2'-bipyridine linkage.\(^{33}\) Coordination of the bipyridine ligand with various transition metals can enhance or quench the luminescence of the system based on the strength of binding. Cations such as Ba\(^{2+}\), Cd\(^{2+}\) and Zn\(^{2+}\) possess a moderate propensity to coordinate to the bidentate
2,2'-bipyridine nitrogen pocket. Coordination of moderately associated cations cause an increase in the luminescent intensity and lifetime which can be effectively reversed by the introduction of ethylenediamine, causing a competition for coordination of the introduced cationic species. Conversely, Ag\(^+\) and Hg\(^+\) cations are strongly coordinated to 2,2'-bipyridine. Enhanced association of the cationic species in the bidentate nitrogen pocket effectively quenches luminescence through a light induced electron transfer and reduction of the bipy chelated cation. Overall, the tunability of the terpyridine substituents provides excellent control for the design of unique molecular materials capable of enhanced, switchable, luminescence and luminescent mediated electron transport on a molecular scale.

If a terminal ligand is avoided, the dyad can be extended to produce chains of varying lengths otherwise known as “polyad” structures. Incorporation of the terpyridine based substituents to polyad materials can extend the di-nuclear photoinduced electron transport over a long range through specifically designed molecular wires. Sakamoto et al have demonstrated that such a system is in fact possible. Fe(II) and Co(II) centered bis(terpyridine) oligomer wires were synthesized and successfully mounted on a gold electrode via sulfide anchors on a silicone based molecular tripod scaffold. The oligomer wire presented featured a ferrocene terminated terpyridine ligand and rapid long-range intrawire electron transport was observed via the redox reaction between the gold electrode and the terminating ferrocene moiety. A similar thiazyl based terpyridine system can be imagined. A 4'-DTDA substituted terpyridine would enable the formation oligomer wires through \(\pi\)-\(\pi\) stacking of the radical moiety. The inherent monomer-dimer equilibrium of the
thiazyl ligand would allow for “switchability” of the material, producing non-luminescent radical monomer units, until a time in which the conditions of the system are altered to produce dimers that link the terpyridine units together. The linked terpyridine ligands would provide enhanced luminescence of the system and allow for electron transport through the coordinated thiazyl chain.

4.3 Synthesis of 4'-(1,2,3,5-Dithiadiazolyl)-2,2':6',2''-Terpyridine (terpyDTDA)

The attempted synthesis of 4'-(1,2,3,5-dithiadiazolyl)-2,2':6',2''-terpyridine (terpyDTDA) begins with the corresponding nitrile, 4'-cyano-2,2':6',2''-terpyridine (terpyCN). Commerically available 4'-cyano-2,2':6',2''-terpyridine is not financially feasible for conversion to the DTDA moiety and a synthetic strategy yielding large amount of terpyCN was necessary. An initial one-pot synthesis by Potts et al.\textsuperscript{34} (Scheme 4.1) involved the use of readily available 2-acetylpyridine and carbon disulfide to create 3,3-bis(methylthio)-1-(2-pyridinyl)-2-propen-1-one, followed by subsequent Kröhnke condensation with glacial acetic acid and NH\textsubscript{4}OAc to yield methylsulfanylt erpyridine.\textsuperscript{35} Oxidation of the methylsulfanyl group via mCPBA yields 4'-methanesulfonyl-(2,2';6',2'')-terpyridine which can be converted to the desired terpyCN through nucleophilic substitution with KCN.\textsuperscript{35} Attempts to replicate this procedure proved successful up until the step to generate terpyCN. Conversion to the nitrile from the sulfone did not go to completion as the sulfone lacked sufficient nucleophilic substitution by CN\textsuperscript{−}, generating yields of only 5%. Poor solubility of KCN was observed in dry DMF and therefore small amounts of H\textsubscript{2}O were introduced, varying from a few drops to 1 mL, to help solubilize the nucleophile. Little to no improvement was observed in reaction yields of terpyCN and as a result KCN was
replaced with NEt₄CN in an effort to increase the concentration of the nucleophile in dry DMF solution, while eliminating competition from H₂O. Once again, poor conversion of 4'-methanesulfonyl-(2,2';6',2')-terpyridine was observed. Poor reaction yields were attributed to poor solubility of the cyanide nucleophiles in DMF solvent, which was subsequently changed to DMSO in a final effort to produce terpyCN via the nucleophilic substitution of the sulfone. The reaction in DMSO yielded no conversion to the desired nitrile and a new synthetic route was deemed necessary.

Scheme 4.1: Initially proposed synthetic route towards 4'-cyano-2,2':6',2"-terpyridine (terpyCN).

A second route towards terpyCN (Scheme 4.2) was attempted, beginning with the reaction of ethylpyridine-2-carboxylate and the dianion of acetone to yield a 1,3,5-trione.³⁶ Closure of the 1,5-diketone using NH₄OAc in ethanol generated 2,6-bis(2'-pyridyl)-4-pyridone, which can be converted to 4'-chloro-terpyridine through chlorination with PCl₅ and POCl₃.³⁶ Veauthier et al. reported palladium-catalyzed cyanation of the chloro substituent in a 98% yield.³⁷ The reaction utilizes Pd(OAc)₂
catalyst with KCN, dpppe (1,5-bis(diphenylphosphino)pentane) and TMEDA (tetramethylethlenediamine) in refluxing mesitylene for 16 hours. However, attempts to reproduce the reported findings proved futile. The TMEDA introduced to the reaction is effectively boiled off at mesitylene reflux temperature and the Pd(OAc)$_2$ catalyst is converted to inactive palladium black$^{38}$ or suffers deactivation with CN$^-$$^{39}$ resulting in recovery of the 4'-chloroterpyridine starting material. Although the cyanation was unsuccessful, production of the pyridone starting material was relatively cheap, easy and provided yields up to 80%. Conversion to the 4'-chloro-substituted terpy compound proceeded in yields of about 30% and provided an aryl halide capable of catalyst insertion for future attempts to synthesis terpyCN.

![Scheme 4.2: Second attempted synthetic route toward 4'-cyano-2,2':6',2'-terpyridine (terpyCN).](image)

In the Preuss group, nitrile starting materials are commonly synthesized via POCl$_3$ dehydration of an amide starting material. In a further effort to synthesize
terpyCN in good yield, the synthesis of a 4'-amide terpyridine molecule was targeted (Scheme 4.3). 2-Acetylpyridine and furfural were combined under basic conditions to produce a 1,5-diketone, which achieved ring closure with NH₄OH in a one pot synthesis, generating a 4'-furyl terpyridine.⁴⁰ Oxidation of the furan group with KMnO₄ followed by NaOH workup achieved a stable sodium carboxylate salt⁴¹ which can be converted to the carboxylic acid with HCl if desired. Refluxing the carboxylic acid in SOCl₂ generates an acyl chloride, allowing the use of ammonia gas to yield the 4' amide substituted terpyridine in yields around 10%. Conversion of the amide group to the nitrile via POCl₃ was successful in producing small amounts of terpyCN, however, poor solubility of the terpyridine carboxylic acid in thionyl chloride made this route impractical.

Scheme 4.3: Synthetic route toward terpyCN through the production of an amide substituted terpyridine compound.

Numerous catalytic routes towards terpyCN exist in literature, starting from a halide substituted terpyridine like the chloro-substituted species prepared from a
pyridone precursor (Scheme 4.2). Also, utilizing the halide, the nitrile starting material can be bypassed to create a silylated amidine directly. As a result, attention was focused on reactions utilizing these starting materials. Lithiation of the halide group allows for electrophilic attack via bis(trimethylsilyl)carbodiimide which is followed by a subsequent reaction with SiMe$_3$Cl to generate the silylated amidine. Attempts to lithiate the terpyridine ring were conducted with 4'-bromo terpyridine, as the bromine acts as a better leaving group than chlorine. To synthesize the bromo-substituted starting material, the pyridone described previously was reacted with Br$_2$/PBr$_3$ and P$_2$O$_5$ to generate POBr$_3$ in situ. Bromination of the pyridone starting material produced 4'-bromo terpyridine in ~60-65% yields. However, lithiation of the bromo starting material proved problematic. The lithium salt generated is extremely insoluble in dry organic solvent at the reaction temperature of -40 °C and does not undergo subsequent reaction. Attempts to run the reaction at increased temperatures provided the same result and the synthetic route was abandoned.

Having achieved greater yields in converting the pyridone to the bromo substituted terpyridine, as opposed to the chloro substituent, the 4'-bromo terpyridine was utilized in attempts at palladium catalyzed cyanation. Preparation of terpyCN with a Pd$^0$ catalyst was cited by Gary S. Hanan demonstrating intriguing results.$^{42}$ The catalytic method was first conducted by Jin and Confalone$^{39}$ and involved the use of 4'-chloroterpyridine with Pd$_2$(dba)$_3$ catalyst, dppf [$1,1'$-bis(diphenylphosphino)ferrocene], a catalytic amount of Zn powder and Zn(CN)$_2$ as the cyanide source to generate the nitrile in a 95% yield. The dppf is used to enhance the activity of the palladium complex, while the Zn(CN)$_2$ and Zn powder act to
decrease deactivation of the Pd\(^0\) catalyst by CN\(^-\).\(^3^9\) Attempts to reproduce the findings were successful. 4'-Bromoterpyridine was treated with the required starting materials in DMA solvent and terpyCN was produced in a 91% yield at 120 °C in 5 hours (Scheme 4.4).

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{CN} \\
\text{Et} & \quad \text{Et}
\end{align*}
\]

\[
\begin{align*}
\text{NaH, DME}\quad\text{0.5 eq} & \quad \text{O} \\
\text{EtOH} & \quad \text{NH}_4\text{OAc}
\end{align*}
\]

\[
\begin{align*}
25\% & \quad 80\% \\
\text{91\%} & \quad 65\%
\end{align*}
\]

Scheme 4.4: Successful palladium catalyzed synthesis utilized to produce terpyCN in high yield.

From terpyCN, conversion of the nitrile to the silylated amidine was attempted via standard Preuss lab techniques (see Chapter 2). The nitrile was dissolved in dry toluene before adding a stoichiometric amount of LiN(SiMe\(_3\))\(_2\)•Et\(_2\)O. However, upon introduction of the etherate species, a solid precipitate, similar to that obtained via lithiation with nBuLi, was produced, suggesting lithiation of a different site within the terpyridine molecule. To circumvent this reaction, a protonated amidine HCl salt was generated from freshly prepared NaOMe followed by treatment with NH\(_4\)Cl. Further treatment of the amidine HCl with five equivalents of sulfur monochloride to produce the Cl salt was unsuccessful (Scheme 4.5). The resulting
terpyridine species produced via the introduction of S₂Cl₂ was highly insoluble in dry organic solvent and ring closure was not observed under any conditions, including heating in neat S₂Cl₂. Reduction attempts of the resulting product with SbPh₃ never produced a five-line EPR signal, suggesting that even trace amounts of ring-closed material were never made.

Scheme 4.5: Proposed synthetic scheme to produce terpyDTDA from terpyCN.

A final effort towards terpyDTDA synthesis was made, reacting terpyCN and S₃N₃Cl₃, following a similar approach to the original DTDA preparation outlined by Alange and Banister.⁴³ S₃N₃Cl₃ is prepared from the reaction of sulfur monochloride, NH₄Cl and elemental sulfur to yield S₃N₃Cl₂, which is subsequently treated with chlorine gas to yield S₃N₃Cl₃ as yellow-orange crystals. TerpyCN was reacted with S₃N₃Cl₃ at ~50 °C in DCE overnight (Scheme 4.6), achieving no formation of the desired Cl salt. The result was confirmed by reduction of the product using SbPh₃,
producing no visible five-line EPR signal.

\[ \text{Scheme 4.6: Attempted synthesis towards terpyDTDA bypassing the production of an amidine intermediate.} \]

4.4 Computational Studies of terpyDTDA

Although attempts to synthesize terpyDTDA were unsuccessful, computational studies of the ligand were conducted and are reported here (Figure 4.3). The SOMO, spin density and charge distribution of terpyDTDA were calculated with Gaussian 09 utilizing a geometry optimized uB3LYP calculation and a 6-31G(d,p) basis set. A small amount of spin density is present outside of the DTDA moiety, primarily on the central pyridyl ring of the terpyridine structure. The SOMO is isolated on the DTDA moiety with a node bisecting the C4 atom, and the nitrogen atoms in the tridentate coordination pocket of terpy have significant partial negative charge density, indicative of a “hard” binding site.
4.5 Conclusions

The desired terpyDTDA radical ligand was not successfully synthesized. After trials following several unproductive routes, the terpyCN was finally produced in high yields. Conversion to the DTDA Cl⁻ salt, however, was not observed. Several synthetic routes toward terpyDTDA were attempted, but the ligand precursors suffer from very poor solubility in organic solvents. Electron paramagnetic resonance
confirmed the findings of the synthetic work, demonstrating no five-line pattern indicative of the thiazyl radical functionality.

4.6 Future Work

The current synthetic work has demonstrated the inherent solubility problems with larger aryl structures. Therefore, future work towards a terpyridine based thiazyl radical ligand should be focused on the improvement of the solubility of the molecule. Recent synthetic work by Laramée-Milette et al. has demonstrated that terpyridine ligands substituted with di-tert-butyl groups in the 4- and 4''- positions can dramatically increase the solubility of the compounds in many organic solvents with the exception of hexane. However, substitution of the peripheral terpyridine rings with t-butyl groups can only be conducted with aryl or heteroaryl 4'-substituents based on the required ketone starting material, 2-acetylpyridine. As a result, terpyDTDA must be extended to produce 4'-aryl DTDA substituent (Figure 4.4).

![Figure 4.4: Line drawing of a proposed 4'-aryl DTDA terpyridine ligand with 4,4'' tert-butyl substituents capable of increasing solubility.](image)
The tert-butyl substituted terpyridine backbone is relatively easy to prepare and can be conducted in a one-pot synthesis. 2-Acetylpyridine is placed in 10% H$_2$SO$_4$ solution with AgNO$_3$ and pivalic acid and heated to 70 °C prior to the addition of aqueous ammonium persulfate$^{45}$ to yield 4-tert-butyl-2-acetylpyridine. 4-tert-Butyl-2-acetylpyridine can then be reacted with 4-formylbenzonitrile in EtOH with KOH and NH$_4$OH to yield the desired nitrile starting material (Scheme 4.7).

\[
\text{Scheme 4.7: Proposed synthetic route towards a nitrile starting material capable of producing a 4’-aryl DTDA terpyridine ligand with 4,4’ tert-butyl substituents.}
\]

If solubility of the terpyridine backbone is substantially improved, it is expected that ring closure of the DTDA Cl$^-$ salt should be achievable as the amidine HCl salt was synthesized. In the event that the ligand is successfully synthesized, coordination of the DTDA radical can be conducted using the [Ru(DMF)$_6$][(OTf)$_3$]$_x$ starting material discussed in Chapter 3. UV-VIS and fluorescence measurements of the system should be conducted to determine if any luminescence is observed within the complex in both its paramagnetic and diamagnetic state. Finally, polymerization of the system to produce long-range molecular wires should be investigated. If successful, electron transport will hopefully be observed through the \(\pi-\pi\) stacking of the DTDA radical dimers.
4.7 References


(21) Sauvage, J.-P. *Chemical Communications* **2005**, *1507*.


Appendix A
Compound Data Sheets
**Compound Name:** 2,2'-bipyrid-6-yl-N,N,N'-tris(trimethylsilyl)amidine  

**MW:** 414.77 g/mol  

**Appearance:** Yellow-orange tacky solid  

**Lit. and/or notebook # and page:** SM-3-70  

**First made on date:** June 17/14  

**Made by:** Scott Mackenzie  

**Experimental Data:**  

$^1$HNMR (600 MHz, CDCl$_3$), $\delta$ (ppm): 8.66 (1H, d, J=4.7 Hz) 8.45 (1H, d, J=4.0 Hz) 8.39 (1H, d, J=7.2 Hz) 7.80 (1H, t, J= 6.1 Hz) 7.76 (1H, t, J=7.8 Hz) 7.29 (2H, m) 0.21 (27H, m).  

**IR (KBr):** 3056(w), 2952(m), 2898(w), 1648(ms), 1578(m), 1571(m), 1473(w), 1426(m), 1407(w), 1312(w), 1251(m), 1161(m), 1145(m), 1078(w), 1044(w), 1010(m), 991(w), 886(w), 836(s), 791(w), 774(m) 753(w), 685(w), 626(w), 574(w), 501(w) cm$^{-1}$. 
**Compound Name:** 4-(2', 2''-bipyrid-6'-yl)-1,2,3,5-dithiadiazoliumchloride [bipyDTDA]Cl

**MW:** 294.77 g/mol

**Appearance:** Orange powder

**Lit and/or notebook # and page:** SM-3-72

**First made on date:** June 18/14

**Made by:** Scott Mackenzie

**Experimental data:**

**IR (KBr):** 3053(br), 1609(w), 1585(w), 1528(m), 1457(m), 1420(w), 1383(m), 1292(w), 1265(w), 1176(w), 1114(w), 995(w), 958(w), 886(w), 848(w), 823(w), 782(m), 746(m), 708(w), 678(w), 631(w), 619(w), 545(w), 471(w) cm\(^{-1}\).
**Compound Name:** 4-((2′, 2″-bipyrid-6″-yl)-1,2,3,5-dithiadiazolyl (bipyDTDA)

**MW:** 259.33 g/mol

**Appearance:** purple powder

**Lit. and/or notebook # and page:** SM-3-74

**First made on date:** June 19/14

**Made by:** Scott Mackenzie

**Experimental data:**

**IR (KBr):** 3141 (br), 3050(br), 1686(w), 1577(m), 1476(w), 1454(m), 1419(m), 1376(m), 1313(w), 1263(w), 1181(w), 1152(w), 1088(w), 1006(w), 811(w), 780(m), 689(w), 649(w), 623(w), 455(w) cm⁻¹.

**Crystal data** SuperNova diffractometer with Atlas CCD detector and MoK/α radiation source, wavelength = 0.71073 nm at University of Guelph; T = 150 K; tetragonal; P4_2/n; a = 24.38140(10), b = 24.38140(10), c = 3.64010(10) Å; V = 2163.87 Å³; Z = 8; R = 4.08%.
**Compound Name:** (4-(2', "-bipyrid-6'-yl)-1,2,3,5-dithiadiazolyl) antimony trichloride
SbCl$_3$(bipyDTDA)

**MW:** 487.44 g/mol

**Appearance:** Black-purple crystalline solid

**Lit. and/or notebook # and page:** MM-5-52

**First made on date:** July 30/15

**Made by:** Michelle Mills

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**Experimental data:**

**IR (KBr):** 3073(w), 1592(m), 1574(w), 1561(w), 1492(w), 1457(m), 1407(w), 1373(m), 1301(m), 1271(w), 1250(w), 1188(w), 1160(w), 1095(w), 1087(w), 1020(m), 940(w), 901(w), 815(m), 790(m), 760(w), 745(w), 737(w), 683(m), 676(m), 648(w), 641(m), 524(w), 497(w), 466(w), 437(m) cm$^{-1}$.

**Elemental Anal.** Anal Calcd for SbC$_{11}$H$_7$Cl$_3$N$_4$S$_2$: C, 27.10; H, 1.45; N, 11.49%. Found: C, 27.44; H, 1.56; N, 11.63%.

**Crystal data** SuperNova diffractometer with Atlas CCD detector and CuK/$\alpha$ radiation source, wavelength = 1.54184 nm at University of Guelph; $T = 150$ K; monoclinic; $P2_1/n$; $a = 8.08381(16)$, $b = 12.5808(2)$, $c = 15.0137(3)$ Å; $\beta = 93.7297(18)$ °; $V = 1523.67$ Å$^3$; $Z = 4$; $R = 7.9%.$
**Compound name:** 6,6'-bispersilylatedamidine 2,2'-bipyridine

**MW:** 673.36 g/mol

**Appearance:** Orange-brown solid

**Lit. and/or notebook # and page:** SM-4-2

**First made on date:** July 21/14

**Made by:** Scott Mackenzie

**Experimental date:**

$^1$H NMR (600 MHz, CDCl$_3$), $\delta$ (ppm): 8.49 (m) 7.87 (m) 7.32 (m) 0.21 (m).

**IR (KBr):** 2955(m), 2898(w), 1702(w), 1654(m), 1572(w), 1431(w), 1380(w), 1301(w), 1254(m), 1151(m), 1078(w), 1007(m), 842(s), 760(m), 719(w), 677(w), 631(w), 620(w) 434(w) cm$^{-1}$. 
**Compound name:** 6,6'-bis(1,2,3,5-dithiadiazolium) 2,2'-bipyridine dichloride
[bisDTDAbipy]Cl₂

**MW:** 433.36 g/mol

**Appearance:** Orange powder

**Lit. and/or notebook # and page:** SM-4-3

**First made on date:** July 22/14

**Made by:** Scott Mackenzie

**Experimental data:**

**IR (KBr):** 3057(br), 1686(m), 1648(w), 1638(w), 1618(w), 1578(m), 1561(w), 1509(w), 1434(w), 1399(w), 1380(w), 1274(w), 1171(w), 1082(w), 991(w), 896(w), 840(w), 812(m), 747(w), 634(w) cm⁻¹.
**Compound name:** 6,6'-bis(1,2,3,5-dithiadiazolyl) 2,2'-bipyridine (bisDTDAbipy)

**MW:** 362.46 g/mol

**Appearance:** Purple powder

**Lit. and/or notebook # and page:** SM-5-17

**First made on date:** July 25/14

**Made by:** Scott Mackenzie

**Experimental data:**

**IR (KBr):** 3052 (br), 1610 (w), 1585 (w), 1527 (w), 1458 (w), 1420 (w), 1382 (m), 1292 (w), 1265 (w), 1176 (w), 1114 (w), 995 (w), 958 (w), 886 (w), 848 (w), 823 (w), 782 (m), 747 (m), 709 (w), 631 (w), 619 (w), 545 (w), 471 (w) cm⁻¹.

**Mass Spectrum (High Resolution DART Ionization: 350 °C),** parent ion assigned as m/z 363.0 (M=C₁₂H₈N₆S₄) 65%.
Acq. Data Name: 150414_5161

MS Tune Method Name: Average(MS[1] Time:3.06..3.11)-1.0*Average(MS[1] Time:0.13..0.26)

SM-4-17 DART @350C

DART Ionization

AIMS Mass Spectrometry Laboratory
Department of Chemistry - U of T

AccuTOF

4/14/2015 10:39:33 AM

ION MODE: POSITIVE
**Compound name:** 4-(2', 2''-bipyrid-6'-yl)-1,2,3,5-dithiadiazolyl tris(hexafluoroacetylacetonato) La(III)  \( \text{La(hfac)}_3(\text{bipyDTDA}) \)

**MW:** 1019.38 g/mol

**Appearance:** red crystalline solid

**Lit. and/or notebook # and page:** MM-5-6

**First made on date:** May 6/15

**Made by:** Michelle Mills

**Experimental data:**

**IR (KBr):** 1650(s), 1601(w), 1577(m), 1530(m), 1489(m), 1427(w), 1382(w), 1254(s), 1211(ms), 1145(s), 1097(m), 1012(w), 948(w), 850(w), 800(m), 783(m), 740(w), 693(w), 659(m), 631(w), 583(m), 528(w), 456(w) cm\(^{-1}\).

**Elemental Anal.** Anal calcd for \( \text{LaC}_{26}\text{H}_{10}\text{F}_{18}\text{N}_{4}\text{O}_{6}\text{S}_{2} \): C, 30.36; H, 0.99; N, 5.50%. Found: C, 30.86; H, 1.16; N, 5.39%.
**Compound name:** 4-(2', 2''-bipyrid-6'-yl)-1,2,3,5-dithiadiazolyl tris(hexafluoroacetylacetono) Ce(III) Ce(hfac)₃(bipyDTDA)

**MW:** 1020.60 g/mol

**Appearance:** Red crystalline solid

**Lit. and/or notebook # and page:** SM-5-40

**First made on date:** April 7/15

**Made by:** Scott Mackenzie

**Experimental data:**

**IR (KBr):** 1649(m), 1602(w), 1578(w), 1529(w), 1488(m), 1428(w), 1383(w), 1254(ms), 1208(m), 1143(s), 1097(w), 1013(w), 949(w), 852(w), 800(m), 783(w), 740(w), 692(w), 678(w), 659(m), 631(w), 583(w), 527(w), 458(w) cm⁻¹.

**Elemental Anal.** Anal calcd for CeC₂₆H₁₀F₁₈N₄O₆S₂: C, 30.60; H, 0.99; N, 5.49%. Found: C, 30.80; H, 1.10; N, 5.29%.

**Crystal data** SuperNova diffractometer Atlas CCD detector and MoK/α radiation source, wavelength = 0.71073 nm at University of Guelph; T = 150 K; monoclinic; P2₁/c; a = 13.2266(2), b = 18.9303(4), c = 29.8769(6) Å; β = 102.523(2) °; V = 7302.71 Å³; Z = 8; R = 4.84%.
**Compound name:** 4-(2', 2''-bipyrid-6'-yl)-1,2,3,5-dithiadiazolyl tris(hexafluoroacetylacetonato) Pr(III)  Pr(hfac)$_3$(bipyDTDA)

**MW:** 1021.39 g/mol

**Appearance:** Red crystalline solid

**Lit. and/or notebook# and page:** SM-4-34

**First made on date:** Sept. 9/14

**Made by:** Scott Mackenzie

**Experimental data:**

**IR (KBr):** 1649 (s), 1602(w), 1578(w), 1556(w), 1556(w), 1489(m), 1429(w), 1383(w), 1348(w), 1254(s), 1207(m), 1143(s), 1098(m), 1013(w), 852(w), 800(m), 783(w), 771(w), 749(w), 740(w), 692(w), 659(m), 584(m), 527(w), 459(w) cm$^{-1}$.

**Elemental Anal.** Anal Calcd for PrC$_{26}$H$_{10}$F$_{18}$N$_4$O$_6$S$_2$: C, 30.57; H, 0.99; N, 5.49%. Found: C, 30.80; H, 1.08; N, 5.29%.

**Crystal data** SuperNova diffractometer with Atlas CCD detector and MoK/$\alpha$ radiation source, wavelength = 0.71073 nm at University of Guelph; T = 150 K; monoclinic; P2$_1$/c; a = 13.19653(10), b = 18.89007(19), c = 29.9155(3) Å; $\beta$ = 102.6935(8)°; V = 7274.2 Å$^3$; Z = 8; R = 4.05%.
**Compound name:** 4-(2', 2'-bipyrid-6'-yl)-1,2,3,5-dithiadiazolyl tris(hexafluoroacetylacetonato) Dy(III) \( \text{Dy(hfac)}_3(\text{bipyDTDA}) \)

**MW:** 1042.98 g/mol

**Appearance:** Red crystalline solid

**Lit. and/or notebook # and page:** SM-5-37

**First made on date:** March 27/15

**Made by:** Scott Mackenzie

**Experimental data:**

**IR (KBr):** 1654(s), 1604(w), 1555(w), 1492(m), 1431(w), 1390(w), 1347(w), 1255(s), 1208(m), 1142(s), 1101(w), 1015(w), 951(w), 856(w), 800(m), 783(w), 741(w), 692(w), 661(m), 632(w), 586(m), 527(w) \( \text{cm}^{-1} \).

**Crystal data** SuperNova Dual Atlas- CCD radiation source MoK/\( \alpha \), wavelength = 0.71073 nm at University of Guelph; \( T = 150 \) K; monoclinic; \( \text{P2}_1/\text{n} \); \( a = 13.11211(16), b = 18.5866(3), c = 29.5181(4) \) Å; \( \alpha = 90, \beta = 98.3185(12), \gamma = 90 ^\circ \); \( V = 7118.16 \) Å³; \( Z = 8 \); \( R = 6.6\% \).
Appendix B
Crystallographic Data Tables
<table>
<thead>
<tr>
<th><strong>Compound</strong></th>
<th><strong>bipyDTDA</strong></th>
<th><strong>SbCl₃(bipyDTDA)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C₁₁H₇N₄S₂</td>
<td>C₁₁H₇N₄S₂Sb</td>
</tr>
<tr>
<td><strong>MW</strong></td>
<td>259.33</td>
<td>487.44</td>
</tr>
<tr>
<td><strong>Space Group</strong></td>
<td>P₄₂/n</td>
<td>P₂₁/n</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td><strong>V (Å³)</strong></td>
<td>2163.87</td>
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</tr>
<tr>
<td><strong>Density (g/cm³)</strong></td>
<td>1.592</td>
<td>2.125</td>
</tr>
<tr>
<td><strong>R (%)</strong></td>
<td>4.08</td>
<td>7.9</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>24.38140(10)</td>
<td>8.08381(16)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>24.38140(10)</td>
<td>12.5808(2)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>3.64010(10)</td>
<td>15.0137(3)</td>
</tr>
<tr>
<td><strong>α (Å)</strong></td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>β (Å)</strong></td>
<td>90</td>
<td>93.7297(18)</td>
</tr>
<tr>
<td><strong>γ (Å)</strong></td>
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<td>90</td>
</tr>
<tr>
<td><strong>T (K)</strong></td>
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<td>150</td>
</tr>
<tr>
<td>Compound</td>
<td>Ce(hfac)$_3$(bipyDTDA)</td>
<td>Pr(hfac)$_3$(bipyDTDA)</td>
</tr>
<tr>
<td>------------------------------</td>
<td>------------------------------------------------------------</td>
<td>------------------------------------------------------------</td>
</tr>
<tr>
<td>Formula</td>
<td>C$<em>{26}$H$</em>{10}$CeF$_{18}$N$_4$O$_6$S$_2$</td>
<td>C$<em>{26}$H$</em>{10}$F$_{18}$N$_4$O$_6$PrS$_2$</td>
</tr>
<tr>
<td>MW</td>
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<td>1021.39</td>
</tr>
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<td>Space Group</td>
<td>P2$_1$/c</td>
<td>P2$_1$/c</td>
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<tr>
<td>Z</td>
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<td>8</td>
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<tr>
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<tr>
<td>R (%)</td>
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<tr>
<td>T (K)</td>
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<td>150</td>
</tr>
<tr>
<td>Compound</td>
<td>Dy(hfac)$_3$(bipyDTDA)</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------</td>
<td></td>
</tr>
<tr>
<td><strong>Formula</strong></td>
<td>C$<em>{26}$H$</em>{10}$DyF$_{18}$N$_4$O$_6$S$_2$</td>
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</tr>
<tr>
<td><strong>Space Group</strong></td>
<td>P2$_1$/n</td>
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</tr>
<tr>
<td><strong>Z</strong></td>
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</tr>
<tr>
<td><strong>V (Å$^3$)</strong></td>
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<td><strong>Density (g/cm$^3$)</strong></td>
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<td><strong>b (Å)</strong></td>
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<tr>
<td><strong>c (Å)</strong></td>
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<tr>
<td><strong>γ (Å)</strong></td>
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</tr>
<tr>
<td><strong>T (K)</strong></td>
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