Synthesis and Magnetic Properties of 1,2,3-Dithiazolyl Coordination Complexes

by

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A Thesis
presented to
The University of Guelph

In partial fulfilment of requirements
for the degree of
Master of Science
in
Chemistry

Guelph, Ontario, Canada

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SYNTHESIS AND MAGNETIC PROPERTIES OF 1,2,3-DITHIAZOLYL COORDINATION COMPLEXES

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University of Guelph, 2012

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This thesis provides the first example of coordination of a 1,2,3-dithiazolyl (1,2,3-DTA) ligand through a N, O bidentate pocket that is reproducible in high purity and bulk quantities. More importantly, it reports the first magnetometry measurements on metal complexes of a 1,2,3-DTA ligand.

The radical ligand 1,2,3-dithiazolyl-6,7-dimethyl-1,4-naphthoquinone (6,7-Me2DTANQ) has been prepared and fully characterized. Coordination complexes of 6,7-Me2DTANQ have also been prepared and the resulting species’ structural and magnetic properties are presented. The transition metal ions Ni$^{2+}$ and Mn$^{2+}$ produce volatile trinuclear M(hfac)$_2$-Rad-M(hfac)$_2$-Rad-M(hfac)$_2$ complexes. The spin ground state of the trinuclear Mn complex $S_T = 13/2$ results from antiferromagnetic (AFM) coupling. Short sulfur-sulfur contacts and sulfur-oxygen contacts between trinuclear complexes produce weak AFM coupling interactions between trimer units. The lanthanide ions Nd$^{3+}$, Gd$^{3+}$ and Dy$^{3+}$ produce volatile [Ln(hfac)$_3$-Rad]$_n$ complexes. The spin ground state of the Gd polymer is $S_T = 3$ per monomeric unit due to Gd$^{3+}$–radical AFM coupling.
Acknowledgements

I would like to thank everyone who has helped me through my academic career. I would like to extend a special thank you to Prof. Kathryn E. Preuss as she has been a highly influential person towards achieving my academic success. Her door has always been open to me, regardless of how busy she may be. As a supervisor, she has offered me critical guidance and support in both my research and education. As a person, she has been understanding and enthusiastic, and is always willing to offer me advice about life. I would like to sincerely thank Kathryn for being an outstanding supervisor and mentor.

I have been fortunate to work in the Preuss Research Group alongside other gifted chemists. In particular, I would like to thank my mentors: Ian S. Morgan, Chad Smithson, Dan MacDonald, and Elisa Fatila. I am the chemist I am today because of their teachings. I would also like to thank the other graduate students in my lab: Christian Carello, Adam Maahs and Yi Ting Lee for their support and friendship. Graduate studies have given me the excellent opportunity to meet incredible people and to build lasting friendships. The unforgettable experiences that I have shared with these friends are ones that I will truly cherish. Graduate school has been a rewarding and fulfilling part of my life, and there is no better substitute for the skills and assets that I have gained from it.

I would also like to thank my parents: Kevin and Lynne, and my brothers: Michael and Stephen for their love and support. My family has been the most influential people in my life. They have shaped the person that I am today, and for this I am truly thankful. Additionally, I wish to thank Jerry and Wendy Greenfield for their kindness and support. It is the combined generosity of my family and Jerry and Wendy that made it
possible for me to complete my last few months of graduate school.

First and foremost, I am forever thankful to my partner Jamie Greenfield. She is the single most important person in my life and my love for her keeps me going. I cannot emphasize how supportive and understanding she has been throughout my graduate studies. She has contributed significantly towards helping me finishing my thesis by editing it and providing helpful suggestions. Furthermore, her sensibility has kept me grounded and on track, while her positivity has held my spirits high and motivated. To a greater extent, she has stood by me through the hard times, and has been there to share the good ones. I cannot express how much your help and love has meant to me.
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<td>Boltzmann Constant</td>
</tr>
<tr>
<td>$l$</td>
<td>orbital angular momentum quantum number</td>
</tr>
<tr>
<td>$L$</td>
<td>total orbital angular momenta</td>
</tr>
<tr>
<td>LT</td>
<td>low temperature</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>$M$</td>
<td>magnetization</td>
</tr>
<tr>
<td>M</td>
<td>molar</td>
</tr>
<tr>
<td>$m/z$</td>
<td>parent ion</td>
</tr>
<tr>
<td>mp</td>
<td>melting point</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>MS/MS</td>
<td>tandem mass spectrometry</td>
</tr>
<tr>
<td>$MW$</td>
<td>molar weight</td>
</tr>
<tr>
<td>NITR</td>
<td>2-R 4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NRC</td>
<td>neutral radical conductor</td>
</tr>
<tr>
<td>obbz</td>
<td>oxamido bis(benzoate)</td>
</tr>
<tr>
<td>$O_h$</td>
<td>octahedral symmetry</td>
</tr>
<tr>
<td>ox</td>
<td>oxidation</td>
</tr>
<tr>
<td>PBE0</td>
<td>Perdew–Burke–Ernzerhof exchange-correlation method</td>
</tr>
<tr>
<td>PXRD</td>
<td>powder X-ray diffraction</td>
</tr>
<tr>
<td>$R^2$</td>
<td>correlation value</td>
</tr>
<tr>
<td>red</td>
<td>reduction</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>RIC</td>
<td>radical ion conductors</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>$S$</td>
<td>resultant spin angular momenta</td>
</tr>
<tr>
<td>$s$</td>
<td>spin angular momentum quantum number</td>
</tr>
<tr>
<td>$\hat{S}$</td>
<td>spin operator</td>
</tr>
<tr>
<td>SCE</td>
<td>saturated calomel electrode</td>
</tr>
<tr>
<td>SN</td>
<td>thiazyl fragment</td>
</tr>
<tr>
<td>SOMO</td>
<td>singly occupied molecular orbital</td>
</tr>
<tr>
<td>SQUID</td>
<td>superconducting quantum interference device</td>
</tr>
<tr>
<td>STP</td>
<td>standard temperature and pressure</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>T</td>
<td>tesla</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Curie temperature</td>
</tr>
<tr>
<td>TCNE</td>
<td>tetracyanoethylene</td>
</tr>
<tr>
<td>TCNQ</td>
<td>7,7,8,8-tetracyano-p-quinodimethane</td>
</tr>
<tr>
<td>TEMPO</td>
<td>2,2,6,6-tetramethylpiperidine-N-oxyl</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>trityl</td>
<td>triphenylmethyl</td>
</tr>
<tr>
<td>$T_N$</td>
<td>Neel temperature</td>
</tr>
<tr>
<td>uB3LYP</td>
<td>unrestricted Becke-3-Lee-Yang-PARR method</td>
</tr>
<tr>
<td>V</td>
<td>Volt</td>
</tr>
<tr>
<td>V</td>
<td>volume</td>
</tr>
<tr>
<td>Z</td>
<td>number of formula units per unit cell</td>
</tr>
</tbody>
</table>
$z$  nearest neighbours

$\chi$  molar magnetic susceptibility

$\chi_v$  magnetic susceptibility per volume
CHAPTER 1

THEORY
1.1 Magnetism

1.1.1 General magnetism

Magnetism is the phenomenon observed when a material interacts with a magnetic field. Magnetic materials can be either repelled (diamagnetic interaction) or attracted (paramagnetic and other magnetic interactions) to an applied magnetic field.\(^1\) Magnetism is intrinsically related to the spin of an electron. The term spin appears throughout this thesis and it is used to refer to spin angular momentum. Spin angular momentum is a quantum-mechanical property that defines the state of a single electron.\(^2,3\)

For a single electron, the spin angular momentum is represented by the quantum number \(s = \frac{1}{2}\). The direction of the vector, \(m_s\), defines the electron’s spin as either up (+\(\frac{1}{2}\)) or down (-\(\frac{1}{2}\)).\(^4\) The “spin-up” and “spin down” states are depicted in Figure 1.01.

Electrons in atoms and molecules are also spatially quantized, described by orbitals which possess discrete orientations relative to each other. In order to understand how this relates to magnetic properties, it is convenient to use a vector treatment where the orbital angular momentum quantum number, \(l\), defines the magnitude of this vector. For any particular value of \(l\) there exists a defined number of \(m_l\) values that give the possible orientations of the vector projection.\(^4\) An example of \(l = 2\) is given in Figure 1.01.

The interaction of an electron’s orbital and spin magnetic moments is referred to as spin orbit coupling. The net result of these moments is the total angular momentum, \(j\), as illustrated in Figure 1.01.\(^3\) In terms of the vector model, \(m_j\) is the vector sum of \(m_l\) and
In order to calculate the total momentum \( J \) in a multielectron system, the \( j \) value of each electron must be calculated and summed. This method of obtaining \( J \) is referred to as \( j-j \) coupling. For lighter hydrogen-like atoms, Russel-Saunders coupling is a simpler alternative method to obtain \( J \).\(^5\) Russel-Saunders coupling is calculated by summing the total orbital angular momenta \( L \) (sum of \( l \) for all the electrons), and the spin angular momenta \( S \) (sum of \( s \) for all electrons).

Figure 1.01 Vector models of (a) spin angular momentum \( m_s = \pm \frac{1}{2} \), (b) orbital angular momentum with \( m_l = 2, 1, 0, -1, -2 \), and (c) spin orbit coupling of magnetic moments (\( \mu \)).\(^3\(^,\)^4\)

All atom based materials respond to an external applied magnetic field, \( H \), to acquire some magnetization, \( M \).\(^6\) The material’s magnetic susceptibility per volume, \( \chi_v \), is equal to:

\[
\frac{\delta M}{\delta H} = \chi_v
\]  

(1.1)
Dividing $\chi_v$ by the density, $d$, of the substance and multiplying by the molecular weight, $MW$, produces the molar susceptibility, $\chi$: \(^7\)

$$\frac{\chi_v}{d} \times MW = \chi$$ \hspace{1cm} (1.2)

The molar susceptibility ($\chi$) is expressed in units of cm\(^3\)•mol\(^{-1}\) or emu•mol\(^{-1}\) and can be dependent on the temperature and the applied magnetic field. When a sufficiently weak field is applied, $\chi$ can be assumed to be independent of $H$ and the result is the weak field approximation.\(^8\)

$$\frac{M}{H} = \chi$$ \hspace{1cm} (1.3)

The ratio $M/H$ provides a measure of how magnetizable a material is in the presence of an applied magnetic field. A number of different types of magnetic susceptibilities can be observed, but four classes are of general importance, namely, diamagnetism, paramagnetism, ferromagnetism (FM) and antiferromagnetism (AFM).\(^9\) The magnetic behaviours corresponding to these four classifications are described in Table 1.01.

<table>
<thead>
<tr>
<th>Type</th>
<th>Sign</th>
<th>Magnitude</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetism</td>
<td>-</td>
<td>$10^{-6}$ emu</td>
<td>Field induced, paired electron circulations within bonds and lone pairs</td>
</tr>
<tr>
<td>Paramagnetism</td>
<td>+</td>
<td>$0$ to $10^{-4}$ emu</td>
<td>Magnetic moment of the electrons</td>
</tr>
<tr>
<td>Ferromagnetism</td>
<td>+</td>
<td>$10^{-4}$ to $10^{-2}$ emu</td>
<td>Spin alignment (↑↑) of moments on adjacent atoms</td>
</tr>
<tr>
<td>Antiferromagnetism</td>
<td>+</td>
<td>$0$ to $10^{-4}$ emu</td>
<td>Cancellation (↑↓) of moments on adjacent atoms</td>
</tr>
</tbody>
</table>
Bulk critical magnetic phenomena such as FM and AFM are based on long range cooperative ordering of spins, whereas bulk diamagnetism has no long range ordering of spins. The classification of a substance can be elucidated by measuring the field dependence of $\chi$ as a function of temperature. The plot depicted in Figure 1.02 illustrates magnetic susceptibility as a function of temperature. These types of plots are generated in an experiment in which a sample is cooled in the presence of an external field, and the $\chi$ response is measured. Several solid-state methods can be employed in this type of experiment but typically the modern convention is to use a superconducting quantum interference device (SQUID) magnetometer.

**Figure 1.02** Ideal ferromagnetic, paramagnetic, and antiferromagnetic behaviour in a plot of $\chi$ versus $T$ with a static applied field.
FM and AFM are critical phenomena, that is, their magnetic behaviour exhibits a phase transition below a critical temperature where large domains of spins behave cooperatively.\(^4\) In a \(\chi\) versus temperature plot of an antiferromagnet, the maximum temperature is referred to as the Neel temperature.\(^1\) At temperatures below the Neel temperature, the cooperative alignment of spins locked in a low-magnetization orientation occurs.\(^3\) In a \(\chi\) versus temperature plot of a ferromagnet, the temperature where a break from paramagnetic behaviour occurs is referred to as the Curie temperature. Below the Curie temperature cooperative alignment of spins locked in a high-magnetization orientation occurs.

### 1.1.2 Molecular magnetism

Molecular magnetism is a field of research that focuses on the design and study of materials which are composed of discrete molecules.\(^9,10\) Materials that possess magnetic properties derived from their constituent molecules can be more versatile than ionic solids that form traditional magnetic materials.\(^11\) The versatility of molecular materials is attributed to the principle that molecules are “tunable” and can be readily tailored by conventional syntheses to achieve desired properties in the final bulk material.

Research in molecular magnetism was spurred by organic conductors.\(^12\) It has been postulated that, just as organic materials can be created to possess metal-like conducting properties, there is the potential to also create organic materials that possess ferromagnetic properties.\(^13\) The “building block” approach has achieved considerable
success towards creating magnetic materials. This strategy commonly employs the introduction of magnetic metal ions into organic molecular systems.

The work of Prof. Joel Miller provides a relatively well known example of the organometallic building block approach towards molecular magnetic materials. The Miller Group synthesized charge transfer salts with the formula \([\text{MCp}^\ast_2]^+[\text{TCNE}]^-\) and \([\text{MCp}^\ast_2]^+[\text{TCNQ}]^-\) (\(\text{Cp}^\ast = \text{pentamethyl-cyclopentadienide (1.01)}\), \(\text{TCNQ} = 7,7,8,8\)-tetracyano-p-quinodimethane (1.02), and \(\text{TCNE} = \text{tetracyanoethylene (1.03)}\) and \(M = \text{Cr, Mn, Fe, Co}\)) which ordered ferromagnetically at low temperature. They also found that using the vanadium ion, they could produce the complex \(\text{V[TCNE]}_x\cdot y\text{CH}_2\text{Cl}_2\) (where the stoichiometry of \(x\) and \(y\) are approximately 2 and 0.5, respectively) which is a room temperature magnet. Unfortunately this complex could only be formed as a black amorphous precipitate and Miller later attributed the room temperature magnetism to Ni nanoparticles. They have since reported a new example of a room temperature molecular magnet.

The introduction of paramagnetic metal ions into organic molecular systems also offers the potential for diverse coordination chemistry. The application of inorganic coordination chemistry to synthesize molecular magnetic species was pioneered by Prof. Olivier Kahn and Prof. Marc Drillion. The Kahn Group produced numerous examples of paramagnetic metal ions bridged by organic ligands. These coordination
complexes have paramagnetic metal ion centers that experience superexchange coupling (closed-shell organic species) that arises from orbital overlap between metal and ligand. The reader is encouraged to consult Prof. Olivier Kahn’s book, *Molecular Magnetism*, for a detailed description of the types of coupling interactions.

Through the judicious selection of metal ions and ligands, a number of dinuclear, trinuclear and ferrimagnetic chain complexes were obtained by the Kahn Group. In some cases, the resulting coordination complexes were ferromagnetically ordered at low temperatures. For instance, the mixed metal complex \( \text{MnCu(obbz)} \cdot 5\text{H}_2\text{O} \), (1.04), (obbz = oxamido bis(benzoate)) has a ferromagnetic transition around \( T_c = 14 \text{ K} \).

![MnCu(obbz)•5H2O (1.04)](image)

### 1.2 Metal-radical approach

#### 1.2.1 Strategy

The “metal-radical approach” was first articulated by Prof. Dante Gatteschi. This strategy uses open-shell organic (radical) ligands to mediate spin coupling interactions between transition metals. The Gatteschi Group explored the metal-radical approach by
employing nitronyl nitroxide radicals as their open-shell ligands. Using 2-R 4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NITR, 1.05) (R = Me, Et, iPr, nPr, and Ph), they first synthesized metal-radical ferrimagnetic chains with the general formula \( \text{M}^{2+}(\text{hfac})_2(\text{NITR}) \) (hfac\(^-\) = hexafluoroacetylacetonato (1.06) and \( \text{M}^{2+} = \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+} \)).\(^{33-39}\) One example is the coordination polymer \( [\text{Mn}^{II}(\text{hfac})_2(\text{NITiPr})]_n \) which has an observed ferromagnetic transition around \( T_c = 7.6 \) K.\(^9\)

The metal-radical approach is the strategy that our research group has adopted to produce molecule based magnetic materials. We have adapted Gatteschi’s original idea but using a different radical ligand in place of nitronyl nitroxide radicals. The type of ligand we have chosen to use is the topic of Chapter 2. Our investigations are not limited to just transition metal complexes but also include lanthanide metal complexes. The metal-radical complexes that I have synthesised will be discussed in Chapter 3.

### 1.2.2 Coupling interactions

If two spin centers, A and B, interact with each other through bonding or space, then the local spin states, \( S_A \) and \( S_B \), are described to be coupling to produce a number of resultant spin states, \( S \), with different energies, \( E(S) \). For instance, if the two spin centers \( S_A \) and \( S_B \) both have a single unpaired electron (\( S_A = S_B = \frac{1}{2} \)) then the states \( S = 0 \) and \( S = \)}
1 would be used to describe the entire system. The energy gap separating $E(S = 0)$ and $E(S = 1)$ is defined as:

$$J = E(S = 0) - E(S = 1)$$ (1.4)

The spin coupling constant, $J$, is used to describe the energy difference between states.\(^{40,41}\) A stronger coupling interaction leads to a larger energy difference between the two states, while a weaker interaction leads to a smaller energy gap. For a two electron system (i.e. $S_A = S_B = \frac{1}{2}$), $J$ measures the energy separation between a triplet state ($S = 1$) and a singlet state ($S = 0$). Depending which spin state is lower in energy, the $S = 1$ or $S = 0$, $J$ is assigned either a negative or positive value. When $S = 0$ is the ground state then $J$ is negative and when $S = 1$ is the ground state then $J$ is positive (Figure 1.03).\(^6,40\)

The sign of the coupling constant ($J$) can be predicted from the spin centers’ valence orbitals, i.e. the ones that contain unpaired electrons. This is because the nature of the coupling interaction (AFM or FM) depends on the symmetry of the interacting orbitals with respect to one another.\(^9,41\) If the orbitals have orthogonal overlap then Hund’s rule of maximum multiplicity applies. The result is that the spins align parallel, and ferromagnetic coupling arises. Alternatively, if the orbitals have non-orthogonal overlap, then the Pauli Exclusion Principle applies. In this case the result is that the spins align antiparallel, and antiferromagnetic coupling arises. Figure 1.03 shows that these two cases can be easily visualized by a simple orbital scheme. The simplified example chosen in Figure 1.03 is a singly occupied $p_z$ orbital of a weak field ligand bound to, either, the singly occupied $d_{x^2}$ or $d_{xz}$ orbital of a metal in octahedral symmetry ($O_h$).\(^42\)
Therefore, the sign of the coupling between a radical ligand coordinated to a metal ion can be easily deduced on the basis of orbital overlap considerations. Orthogonal overlap results in a positive \( J \) and non-orthogonal overlap results in a negative \( J \).\textsuperscript{43}

![Orbital scheme](image)

**Figure 1.03** Orbital scheme for (a) a metal \( d_{z^2} \) and a ligand \( p_z \) with orthogonal overlap for which (b) Hund’s Rule of maximum multiplicity predicts a triplet ground state \( (J > 0) \) and (c) of a metal \( d_{x^2-y^2} \) and a ligand \( p_z \) with non-orthogonal overlap for which (d) The Pauli Exclusion Principle predicts a singlet ground state \( (J < 0) \).\textsuperscript{42}

Experimentally, the value of \( J \) can be obtained by fitting the curve from a \( \chi T \) versus temperature plot (for example **Figure 1.04**) using a phenomenological Hamiltonian, \( \hat{H} \).\textsuperscript{41,44} For instance for a two electron system, where the two magnetic
centers are identical \( S_A = S_B = \frac{1}{2} \) and are in the absence of an applied magnetic field \( H = 0 \), the spin Hamiltonian describing the low lying states may be written mathematically as:

\[
\hat{H} = -J(\hat{S}_A \cdot \hat{S}_B)
\]  \hspace{1cm} (1.5)

where \( \hat{S}_A \) and \( \hat{S}_B \) are the spin operators. The reader should note that there are four different conventions on how to write the spin Hamiltonian. The form of the spin Hamiltonian presented in Equation 1.5 fits the explanation for the energy difference between triplet and singlet energy levels, as shown in Figure 1.03. However, the following Hamiltonian will now be used throughout the rest of this Thesis

\[
\hat{H} = -2J(\hat{S}_A \cdot \hat{S}_B)
\]  \hspace{1cm} (1.6)

where this form of the spin Hamiltonian is used as a mathematical convenience for deriving the total energy values.

In molecular species that contain more than two interacting magnetic centers, there will be more than one intramolecular \( J \). For instance, in a linear A1-B-A2 trinuclear compound, there are two equal A-B interactions \( (J) \) and one A-A interaction \( (J') \). If the local spins are \( S_{A1} = S_{A2} = S_A \) and \( S_B \), then in zero field \( (H = 0) \) and neglecting local anisotropies and anisotropic interactions, the spin Hamiltonian describing the low lying states may be written mathematically as:

\[
\hat{H} = -2J(\hat{S}_{A1} \cdot \hat{S}_B + \hat{S}_{A2} \cdot \hat{S}_B) - 2J(\hat{S}_{A1} \cdot \hat{S}_{A2})
\]  \hspace{1cm} (1.7)
It is often possible to characterise coupling behaviour (FM, AFM, and non-interacting) and sign of the coupling constants ($J$) by simple inspection of a $\chi T$ versus temperature plot. In a $\chi T$ vs. T plot, FM coupling (+$J$) is characterized by increasing $\chi T$ with decreasing temperature; whereas AFM coupling (-$J$) is characterized by decreasing $\chi T$ with decreasing temperature.\textsuperscript{1,6,8} Non-interacting spin centers have a single value of $\chi T$ throughout the range of temperatures, as shown in Figure 1.04. It is also possible to model coupling interactions in a particular $\chi T$ vs. T plot using the van Vleck Equation in order to determine the value of $J$.\textsuperscript{6}

![Figure 1.04 Ferromagnetic, antiferromagnetic, and non-interacting coupling interactions in a plot of $\chi T$ versus temperature.\textsuperscript{1,8}](image-url)
The coupling that occurs between paramagnetic centers influences the long range ordering of spins in bulk solid state material. For long range ordering to occur in a molecular system, the interacting spin centers must couple in a correlated fashion. FM coupled systems have spins aligned in the same direction resulting in a net magnetic moment. AFM coupled systems have spins aligned in opposite directions such that magnetic moments either have complete cancelation (no net magnetic moment) or incomplete cancellation. Incomplete cancelation of an AFM coupled system is referred to as ferrimagnetism and occurs because opposing spins are unequal such that there remains a spontaneous magnetization (Figure 1.05).

![Spin coupling in molecular systems](image)

**Figure 1.05** Spin coupling in molecular systems resulting in (a) antiferromagnetic ordering, (b) ferromagnetic ordering, and (c) ferrimagnetic ordering.

### 1.2.3 Stable radicals

In order to achieve a coordination complex using a radical ligand, a so-called “stable” radical species must be used. There are a variety of molecular building blocks available to produce stable radicals, which could potentially be used as spin bearing ligands. A general overview of stable radicals and some of the most common species is pertinent.
Radicals are subvalent compounds, that have one less bond than expected based on the valence bond theory. Valency is a core principle that guides the prediction of chemical structures and bonding. In essence, valency can be thought of as the “bond-forming capability” parameter and it offers a rationalization for the non-existence (instability) of species with incomplete valencies. This point offers a rationale to explain why radical containing molecules are commonly thought of as reactive and short-lived. That is, radicals will readily react with other molecules to achieve a standard valence count. Radical species readily undergo reactions, such as dimerization, hydrogen abstraction, or disproportionation, due to there being little to no activation barrier blocking their progress towards more thermodynamically favourable reaction products. It is worth noting that often the term stability refers to this thermodynamic concept in regards to radicals stability with respect to the reaction products. However stability can also refer to kinetically stability and it really depends on who is writing and what they intend the term to mean. Also, due to the transient existence of most radical species, they are typically described as being unstable.

Initially the term stable was proposed to describe a radical molecule that is sufficiently unreactive such that it can be handled and stored under ambient conditions and remain as the pure compound with no more precautions than would be used for commercially available chemicals. This definition implies that a stable radical is kinetically inert (high activation energy) in a particular environment under standard temperature and pressure (STP) conditions even though the possible reaction products (e.g., the products from reactions with molecular oxygen) might be thermodynamically
favourable. In the context of the current body of stable radicals, the term stable can be used to describe any compound that can be isolated and then stored as the pure substance for a prolonged period of time, but not necessarily in the presence of oxygen-containing or wet ambient atmosphere. If the radical is not stable enough to isolate and store, but it can be experimentally observed through spectroscopic techniques for prolonged periods of time, then it is described as persistent.

The vast majority of stable radicals contain their unpaired electrons in a π-type orbital that is perpendicular to the local molecular framework. These species are classified as π radicals. The most famous stable (in air) π organic radicals are triphenylmethyl (trityl, 1.07), 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO, 1.08) and N,N-diphenyl-N′-picrylhydrazyl (DPPH, 1.09). Examples of common building blocks used to produce stable (not necessarily in air) π radicals include but are not limited to: verdazyls (1.10), nitroxides (1.11), nitronyl nitroxides (1.05), and phenoxyls (1.12). Stable π radicals can also be obtained by using the thiazyl fragment (SN). The diversity of radicals afforded by utilizing the SN unit will be discussed in Chapter 2.
Currently, the majority of spin-bearing ligands are derived from a variety of semiquinone and nitroxide derivatives. Our research group is actively pursuing spin-bearing ligands based on the 5-membered ring thiazyls 1.13 and 1.14. Chapter 2 will introduce thiazyl chemistry. Chapter 3 will present the molecule of interest in this thesis, a π-radical ligand that incorporates 1.14. Chapter 4 will focus on metal complexes of the ligand introduced in Chapter 3. Chapter 5 will introduce a novel molecule that was initially designed to be a thiazyl radical-anion ligand, but which could not be used for this intended purpose due to its unique properties. Finally, Chapter 6 will summarize the conclusions of this thesis.
1.3 References


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CHAPTER 2

THIAZYLs
2.1 Sulfur-nitrogen heterocycles

2.1.1 SN unit

The SN unit is the building block of a family of stable radical species known as thiazyls. The unsaturated fragment -S=N- readily forms catenated species that constitute a diverse variety of compounds that exhibit unusual structures and properties. The structures of SN compounds vary from acyclic polymeric and oligomeric species to cyclic ring species.\(^1\) Thiazyls can be binary species of sulfur-nitrogen or heteroatomic species of sulfur-nitrogen with additional elements. The most notable property of compounds composed of unsaturated SN fragments is the propensity for them to form a variety of cyclic structures.\(^2\) These systems range from four to ten membered rings that include cations, anions and neutral species. Some binary SN heterocycles 2.01, 2.02, 2.03, 2.04, and 2.05 are illustrated below. The nature of a SN heterocycle characterized as aromatic, anti-aromatic or a radical system depends on the number of SN fragments used. Interestingly, the most stable systems are the ones that conform to the Hückel \((4n + 2)\pi e^-\) rule, with \(n = 1, 2,\) and 3 producing stable species.\(^3\) However, conjugated SN building units are more electron rich than their conjugated carbon-carbon counterparts (more \(\pi\) electrons than atomic centres) and as a result, the \(\pi\)-framework of conjugated SN heterocycles are weaker and more prone to distortions from planarity.\(^4,5\)
Interest in compounds containing SN linkages originated with the discovery of the metallic\textsuperscript{6} and superconducting\textsuperscript{7} properties of polythiazyl (SN)\textsubscript{x}, \textbf{2.06}, in the early 1970s. The polymer (SN)\textsubscript{x} is composed of repeating units of SN that are connected by inter-chain sulfur interactions (\textbf{Figure 2.01}).\textsuperscript{8} It is interesting to note that this material is currently the only known metallic polymer that does not require charge transfer (CT) in order to generate carriers. The conductive behavior can be attributed to the electronic configuration of the SN unit, which is a 3\pi electron system with an unpaired electron in the \pi* orbital as illustrated in \textbf{Figure 2.01}. The high dimensionality of inter-chain sulfur interactions of (SN)\textsubscript{x} then produces a solid state structure with a partially filled metallic band. It should be mentioned now that a complete explanation of molecular conductivity (thiazyl or other) is outside the scope of this thesis. The reader can refer to the following references for an in depth explanation of conductivity.\textsuperscript{9-13}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{\textbf{Figure 2.01} (a) Frontier Molecular Orbital (FMO) of the -S=N- radical with the corresponding band structure of 1-D (Sn)\textsubscript{x} and the polymeric structure of \textbf{2.06} showing inter-chain contacts.\textsuperscript{8}}
\end{figure}
The (SN)$_x$ polymer is not merely a stepping stone in the exploration and development of compounds containing formally unsaturated SN linkages.\textsuperscript{14-16} It has also entertained some practical applications. For instance, when (SN)$_x$ is used as a barrier electrode in ZnS junctions, it increases (factor of 100 compared to gold) the quantum efficiency of the blue-emission. It has also been shown to increase the efficiency of GaAs solar cells by up to 35\%\textsuperscript{17} Unfortunately, its implementation into industry is currently nonviable because the synthesis of the material involves the explosive compounds, tetrasulfur dinitride, 2.07, (S$_4$N$_4$) and disulfur dinitride, 2.01 (S$_2$N$_2$). S$_2$N$_2$ is usually prepared from passing gaseous S$_4$N$_4$ over silver metal at high temperature and low pressure.\textsuperscript{18} In the solid state, S$_2$N$_2$ at 0 °C converts on the order of several weeks into the SN$_x$ polymer.\textsuperscript{19} The slow rates of polymerization are another obstacle to the industrial use of (SN)$_x$.

Binary heterocyclic compounds, such as (SN)$_x$, S$_4$N$_4$ and S$_2$N$_2$, form a small but growing class of compounds that contain unsaturated SN linkages.\textsuperscript{20} The tetramer, S$_4$N$_4$, is an orange solid that possesses an unusual half-chair six-membered ring.\textsuperscript{3,5} The cage-like structure of S$_4$N$_4$ has equal bond lengths (1.62 Å) with two weak transangular S-S interactions of ca. 2.60 Å at room temperature.\textsuperscript{2} S$_4$N$_4$ serves as the quintessential sulfur-nitrogen compound, first detected in 1835, just ten years after the discovery of benzene.\textsuperscript{21,22} S$_4$N$_4$ also serves as an important source of many other SN compounds, including S$_2$N$_2$ as previously discussed. The dimer, S$_2$N$_2$, is a colorless solid that exists as
a cyclic square planar molecule.\textsuperscript{3,5} The monomer NS\textsuperscript{•} can be generated by electrical discharge in gaseous mixtures of sulfur and nitrogen.\textsuperscript{14,23,24} However, the NS\textsuperscript{•} gas has a transient existence owing to its extreme reactivity; therefore, it converts to (SN)\textsubscript{x} upon condensation.\textsuperscript{5} In general, unsaturated binary thiazyl compounds are difficult to handle after their reduction from their corresponding cationic salts because they become increasingly sensitive to moisture, oxygen, heat or shock. These challenges make them less attractive candidates for synthetic exploration.

Fortunately, introducing additional elements, such as carbon or phosphorus, into the SN unit creates hybrid heteroatomic species that are much easier to handle (i.e less prone to detonation and hydrolysis).\textsuperscript{20} The relative stability of these hybrids is achieved by virtue of lowering the sulfur and nitrogen content. The introduction of other elements is also advantageous because it allows the use of a wider array of spectroscopic methods (eg. \textsuperscript{1}H, \textsuperscript{13}C, and \textsuperscript{31}P NMR). Most importantly, the incorporation of other elements into the SN unit leads to far more extensive chemistry, which in turn offers many new possibilities for design.

The hybrids can be treated as two distinct categories: (a) \textit{organic} thiazenes (by introducing carbon) or (b) \textit{inorganic} thiazenes (by introducing other inorganic elements). Although the classification is artificial, it is convenient for this thesis since it has a narrow focus on the heterocyclic thiazyl compounds that incorporate carbon. Organothiazene radicals are related to organic heterocyclic thiazene derivatives by a single electron reduction. Broadly speaking there are four main structural types of organic heterocyclic thiazenes: (a) 8-atom 10\(\pi\)e\textsuperscript{−} azocines (2.04, 2.08, 2.09, 2.10, 2.11, and 2.12), (b) 7-atom 10\(\pi\)e\textsuperscript{−} azepines (2.03, 2.13, 2.14, and 2.15), (c) 6-atom 8\(\pi\)e\textsuperscript{−} azines
(2.02, 2.16, 2.17, 2.18, 2.19, and 2.20), and (d) 5-atom 6π atoms (2.21, 2.22, 2.23, 2.24, and 2.25). Examples of the four classes (a-d) are presented in Figure 2.02. The next chapter will focus on the five-membered-ring species of organic 7π thiazene radicals.

Figure 2.02 Known cyclic organothiazenes with their corresponding isoelectronic binary compounds.  

2.1.2 Five-membered-ring thiazyls

There are a wide variety of known and theoretical isoelectronic thiazyl species that exist as five-membered-ring heterocycles. Planar five-membered-ring thiazyl species have a 7π electron system that is stabilized by resonance. The resonance occurs through a conjugated SN π system that is strongly linked together by two factors: 1) the small electronegativity difference between sulfur and nitrogen and 2) the large overlap of the adjacent sulfur 3pπ and the nitrogen 2pπ orbitals (comparable to that between two
conjugated carbon 2π orbitals). The unpaired electron of thiazyl rings resides in a π-antibonding molecular orbital. Typically, the unpaired electron is delocalized over the ring with large α spin densities localized on the sulfur and nitrogen atoms.¹

Five-membered-ring species of organothiazyls are related to the binary species 1,2,4,3,5-trithiadiazolyl radical cation, S₃N₂⁺⁺⁺ (2.26).⁵ It was one of the first five-membered ring species to be structurally characterized, after being isolated as a hexafluoroarsenate salt.²⁶ The introduction of carbon into the S₃N₂⁺⁺⁺ ring architecture offers a number of structural combinations as depicted in Figure 2.03.¹ Replacing the N=S⁺ fragment of 2.26 with a *S=C-X fragment (where X is Cl, CF₃ or a second CNS₃⁺⁺⁺ ring) creates a relatively rare species, the trithiazolyl radical cation (2.27).²⁷-³⁰ Replacing one of the S⁺ fragments of 2.26 with the isoelectronic C-R fragment produces the dithiadizolyl (DTDA) family of relatively stable radical species, including 1,2,3,4-DTDA (2.28) and 1,2,3,5-DTDA (2.29). In terms of design, both 2.28 and 2.29 can have an aromatic ring, saturated alkyl or other substituents as an R group. The family of DTDA radicals are well known stable radicals which have been studied extensively. The reader is directed to the following reviews and articles by Prof. Rawson for more information on DTDA radicals.³¹-³⁴ Lastly, replacing the N=S⁺ fragment of 2.26 with the isoelectronic R-C=C-R fragment generates the dithiazolyl (DTA) family of stable radical species, including 1,3,2-DTA (2.30) and 1,2,3-DTA (2.31).

Of the five-membered-ring species presented in Figure 2.03, only 1,3,2-DTA and 1,2,3-DTA are capable of fusing to an aromatic ring in the R-C=C-R location.³⁵ When 2.30 and 2.31 are ring-fused to an appropriate aromatic system, the conjugated nature of system facilitates a greater π-delocation of the unpaired spin density. When a DTA
radical is based on 2.30, the spin density is primarily concentrated on the S-N-S unit. Alternatively, a DTA radical based on 2.31 has significant spin density residing on one of the carbon atoms of the ring, which allows for spin density to be delocalized throughout the entire resonance stabilized molecule. The ability to fuse a variety of aromatic groups which act as “electron sinks” and pull electron density off the 1,2,3-DTA ring is the major design advantage of this ring system over the 1,3,2-DTA ring.

![Diagram of thiazyl radicals and structural relationship](image)

**Figure 2.03** Examples of known five-membered-ring thiazyl radicals and their structural relationship to 1,2,4,3,5-trithiadiazolyl radical cation, $\text{S}_3\text{N}_2^+$.

### 2.1.3 1,2,3-Dithiazolyl ring

In naming a thiazyl ring, the preceding numbers indicate the positions of the sulfur, nitrogen and carbon atoms relative to each other. Priority is given to sulfur and counting proceeds in the direction that will give the heaviest atoms the lowest numbers. For the 1,2,3-DTA moiety (2.31) the numbering scheme is presented in **Figure 2.04**. In **Figure 2.04** it is apparent that a resonance structure exists where the radical can be placed on the C5 position. The pioneering work in this field was done by Mayer who
identified a number of 1,2,3-DTA radicals by electron spin residence (ESR) spectroscopy studies.\textsuperscript{36,37} Mayer demonstrated that 1,2,3-DTA compounds could generate persistent ESR signals when the appropriate substituents were fused at the C4-C5 position.\textsuperscript{38-40}

Figure 2.04 (a) Numbering scheme for a 1,2,3-DTA and (b) resonance structures of a 1,2,3 DTA ring.

Figure 2.05 (a) Single electron reduction of the 4,5-dichloro-1,2,3-dithiazolylium chloride (2.32) to produce the C–C σ bond intermediate, followed by another single electron reduction to afford tetrathiadiazafulvalene (2.34), (b) 4-chloro-5-pentafluorophenyl-1,2,3-dithiazolyl (2.34), and (c) Cl\textsubscript{2}C\textsubscript{3}NS(ClC\textsubscript{2}NS\textsubscript{2}) (2.35).

Placing an \textit{R}-group at only the C4 position of a 1,2,3-DTA produces relatively unstable species. Because of the significant spin density at the C5 position, 1,2,3-DTA
species that are unsubstituted at the C5 position have a tendency to irreversibly dimerize in the solid state. For instance, when 4,5-dichloro-1,2,3-dithiazolium chloride (2.32) is reduced, a C-C σ bond is formed through the C5 position, producing the neutral compound 2.33, as shown in Figure 2.05. However, irreversible dimerization can be prevented by steric bulk at the C5 position, as demonstrated by the compounds 4-chloro-5-pentafluorophenyl-1,2,3-dithiazolyl (2.34), and (c) Cl₂C₃NS)(ClC₂NS₂) (2.35).

The strategy of fusing an aromatic ring to 1,2,3-DTA at both the C4 and C5 positions prevents molecules from undergoing irreversible dimerization by way of delocalizing the unpaired electron. The conjugated nature of these systems allows for the expansion of the spin density over a larger area and lowers the spin density at the C5 position in the process. This strategy also affords more stable radical species. Recall from Chapter 1, that the term stable refers to anything that can be stored as a pure substance for a prolonged period of time. It has been observed that delocalizing the electron over a larger area can raise the temperature at which these systems thermally decompose. Some examples of stable fused 1,2,3-DTA systems include 2.36, 2.37, and 2.38.

To reiterate, ring fused 1,2,3-DTA radical species are stable in the solid state for an extended period of time, sometimes even in air. Some of this stability can be attributed to that fact that, like most thiazyl compounds, 1,2,3-DTA radicals exist as π-dimers arrays in the solid state. In general, thiazyl dimerization generally produces a closed
shell singlet ground state and consequently quenches their solid state paramagnetic properties.\textsuperscript{1,33} However there do exist examples of thiazyl compounds that exhibit thermally excited triplet states at room temperature despite being dimerized in the solid state.\textsuperscript{48,49} ESR spectra can be obtained from dimerized thiazyl compounds, that lack a solid state ESR signal, by dissolving them in solution.\textsuperscript{50} This observation demonstrates that the dimers dissociate in solution to give rise to paramagnetic monomers. This dissociation is governed by a monomer-dimer equilibrium.\textsuperscript{1,51,52} Thiazyl $\pi$-$\pi$ dimerizations have been likened to hydrogen bonding in terms of their energetics, reversibility, and capacity to influence crystal packing motifs.\textsuperscript{1}

The counting of the $\pi$ electrons in 2.31 gives a neutral 7$\pi$ system.\textsuperscript{20} Due to the odd electron count of 2.31, it is an open shell doublet species, which means that the system exists with an unpaired electron. The 1,2,3-DTA ring can theoretically exist in two other oxidation states related to 2.31 by the addition or removal of an electron, which are the 1,2,3-DTA cation (2.39) and the 1,2,3-DTA anion (2.40) as shown in Figure 2.06.\textsuperscript{1,35}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure2.06.png}
\caption{The potential redox states of a 1,2,3-DTA ring.}
\end{figure}

The synthesis of ring fused 1,2,3-DTA salts has been known for many decades. Substituted 1,2,3-benzodithiazolium chlorides (2.41) were first reported by Herz in 1922.\textsuperscript{53} Since then, the treatment of primary aromatic amines, their salts, or $N$-acyl derivatives (2.42) with an excess of sulfur monochloride ($S_2Cl_2$) in preparation of 1,2,3-DTA cations (2.41 and 2.43), has been referred to as a Hertz reaction.\textsuperscript{54} The Herz
reaction is often accompanied by the chlorination of the benzene backbone. When deactivating groups, such as NO$_2$, COOH, SO$_3$H and H, are attached \textit{para} relative to the nitrogen, a Cl atom will be substituted onto this position. In contrast, donating groups \textit{para} to the nitrogen, such as Br, Me$_2$N, RO and R, will not be displaced by a Cl atom.$^{55}$ A representative reaction of both cases is provided in Figure 2.07. The mechanism of the Herz reaction is purely speculative and the hypotheses put forth thus far do not account for both the chlorination and ring closure steps.$^{55-57}$

![Figure 2.07 Herz reaction, with route (a) showing R groups that are replaced by a chlorine atom and route (b) showing R groups that remain unchanged.](image)

The common solvent of choice for Hertz reactions is CH$_3$CN because the resulting chloride salts are typically sparingly soluble in this solvent. The product can be easily separated from the reaction mixture via filtration. The tendency for polar solvents like CH$_3$CN to readily absorb water from the air can lead to some decomposition of the chloride salt. Hydrolysis of a Herz salt, such as 2.44, results in the formation of 3H-1,2,3-sulphoxide (2.45), shown in Figure 2.08.$^{57}$ Due to the susceptibility of Herz salts to moisture, it is common practice to perform Herz reactions under dry and inert atmosphere.

The 1,2,3-DTA radical species is afforded by a single electron reduction of the Herz salt. Depending on the specific 1,2,3-DTA species, the choice of reducing agent
varies. A common reducing agent for sulfur-nitrogen systems is triphenylantimony (SbPh₃) because it is convenient to use and it is relatively inexpensive.⁵⁸,⁵⁹ A half molar equivalent of SbPh₃ is used to reduce one equivalent of Herz salt, Figure 2.08. This produces the biproduct triphenylantimony chloride (SbPh₃Cl₂). SbPh₃Cl₂ is readily soluble in polar organic solvents, whereas radical products tend to be insoluble so that the desired product can usually be collected by filtration. Once the 1,2,3-DTA radical has been generated, it should be treated as air sensitive. A recent study showed that exposing an open shell 1,2,3-DTA radical to triplet O₂ can produce a disulfide bridging species (2.47), as depicted in Figure 2.08.⁶⁰

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Figure 2.08 Reaction scheme of (a) hydrolysis of Herz salt,⁵⁷ (b) reduction of Herz salt⁵⁸,⁵⁹ and (c) oxidation of 1,2,3-DTA radical, where R groups are tBu groups.⁶⁰
2.2 References


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CHAPTER 3

LIGAND
3.1 Ligand

3.1.1 Motivation

Our group is primarily interested in studying paramagnetic properties of a variety of thiazyl species and their corresponding coordination complexes. From a historical perspective, the Preuss group has a significant amount of experience working with metal coordination complexes of 1,2,3,5-DTDAs. Accomplishments include the first N-coordinated DTDA species (4-(2′-pyridyl)-1,2,3,5-dithiadiazolyl, 3.01),\(^1\) and the smallest supramolecular unit of a coordinated DTDA species (4-(benzoxazol-20-yl)-1,2,3,5-dithiadiazolyl, 3.02).\(^2\) Our group has shown that a DTDA ligand (4-(2′-pyrimidyl)-1,2,3,5-dithiadiazolyl, 3.03) can be used to mediate magnetic coupling between two paramagnetic metal centers.\(^3\) Additionally, we completed a series of first row transition metal complexes of 3.01.\(^4\) Our previous work has provided considerable insight into the behaviour of metal-thiazyl compounds and provides the foundation for our new research goal: the use of 1,2,3-DTA compounds as ligands.

A major contributor in the advancement of DTA ring systems is Dr. Oakley. His findings have established a framework upon which new thiazolyl materials can be based. Although his research is highly relevant to our group’s related DTA systems, it has concentrated primarily on DTA systems prepared as neutral radical conductors (NRCs).\(^5\)\(^\text{11}\) In fact, most of the current work done on DTA radicals has been directed towards their use as NRCs with additional efforts focusing on their use as radical ion conductors.
(RICs)\textsuperscript{12-15} and organic magnets\textsuperscript{16-21}. Relatively little work has been done on the coordination of DTA species.\textsuperscript{22-25} Recently we reported the first case of the coordination of a neutral 1,2,3-DTA species to a metal.\textsuperscript{26} This chapter will now focus on the design, preparation and investigation of a 1,2,3-DTA spin bearing ligand suitable for coordination to a metal.

\subsection*{3.1.2 Ligand design}

A ligand designed to perform a variety of functions must incorporate several features. The proposed molecule, 1,2,3-dithiazolyl-6,7-dimethyl-1,4-naphthoquinone (6,7-Me\textsubscript{2}DTANQ, \textbf{3.04}), possesses three major features that are necessary for its function: 1) a radical bearing component 2) an extended \(\pi\)-system and 3) a chelation site.

![Figure 3.01](attachment:image.png)

\textbf{Figure 3.01} (a) Bidentate and monodentate sites of 2.51 and (b) resonance structures of \textbf{3.04} obtained from electron pushing.

The 7\(\pi\) DTA ring is the radical bearing component, which functions to impart spin on the ligand. The extended \(\pi\)-system of \textbf{3.04} allows for the delocalization of the spin density and imparts stability to the molecule. \textbf{Figure 3.01} shows the possible resonance structures of \textbf{3.04}. Additionally, the electronegative elements that are incorporated into \textbf{3.04} assist in pulling the radical away from the DTA ring and redistributing the spin at
another atomic sites. A bidentate site and a monodentate site, as shown Figure 3.01, impart 3.04 with a strong tendency to coordinate metal ions in an oligomeric or polymeric arrangement.

Recall from Chapter 1 that when the p-orbital overlaps with the d-orbital of the metal, the relative orientation dictates the type of coupling (antiferromagnetic or ferromagnetic). The incorporation of a chelation site not only serves as a way to improve a ligand’s affinity for metal ions, but it also serves as a key approach to fix the orientation of ligand orbitals with respect to the metal magnetic orbitals.¹ The chelation site will allow 3.04 to coordinate metal ions in a particular orientation and should also aid in interpreting the subsequent coupling interactions.²⁷,²⁸

The molecule, 6,7-Me₂DTANQ (3.04) is based on the unmethylated parent molecule 1,2,3-dithiazolyl-1,4-naphthoquinone (DTANQ, 3.05). Mayer first reported DTANQ in the literature in 1981.²⁹ It was characterized by ESR and to our knowledge it has not been reported in the literature since. DTANQ is a structural isomer of the 1,2,3-dithiazolyl-1,4-naphthoquinone recently reported by Passmore.³⁰ We have since made and fully characterized DTANQ.³¹ DTANQ is the work of my colleague, Ian Morgan. The reader is encouraged to refer to his thesis for information regarding its properties and characterization.

To further describe the behaviour of 6,7-Me₂DTANQ, it is convenient to envision it in three components: 1) DTA ring (3.06), 2) quinone moiety (3.07) and 3) methylated
naphthalene backbone (3.08), as depicted in Figure 3.02. This chapter will entail a brief
description of the purpose of each component.

![Figure 3.02 Assembly of 1) DTA ring, 2) quinone and 3) methylated naphthalene to
give 6,7-Me2DTANQ (2.51).]

3.1.3 1,2,3-DTA moiety

The singly occupied molecular orbitals (SOMOs) of a 1,2,3-DTA ring and a
1,2,3,5-DTDA ring are presented in Figure 3.03. The SOMOs of the 1,2,3-DTA and
1,2,3,5-DTDA ring systems are $\pi^*$ type orbitals.\textsuperscript{32} The 1,2,3,5-DTDA ring has a node at
the C4 position which results in localization of the $\alpha$-spin on the sulfur and nitrogen
atoms of the thiazyl ring. The spin density localized on the 1,2,3,5-DTDA ring
encourages these systems to dimerize.\textsuperscript{32,33} Also, the node at the C4 position of 1,2,3,5-
DTDA ring systems prevents the possibility of designing a conjugated organic backbone
to allow delocalization of the SOMO.\textsuperscript{16}

The 1,2,3-DTA ring has $\alpha$-spin at the C5 position such that substituent effects are
more likely to play an important role in determining the electronic spin density
distribution.\textsuperscript{16,32} This is highlighted by the variations in N-hyperfine coupling constants
and g-tensors observed in EPR studies.\textsuperscript{34} This suggests that with the appropriate ring conjugated system fused to the C4 and C5 positions of a 1,2,3-DTA, the electron spin density can be drawn away from the thiazyl ring. The potential to redistribute spin density from the 1,2,3-DTA ring onto other electronegative atoms is a major design feature for a 1,2,3-DTA based radical ligand in order for it to facilitate spin coupling interaction between coordinated metals ions.

![Figure 3.03 SOMOs of (a) 1,2,3,5-DTDA and (b) 1,2,3-DTA, calculated using Gaussian 09: Revision A.02. Method was uB3LYP and basis set was 6-31G(d,p).\textsuperscript{35}](image)

DTDA and DTA dimerization in solid state involves the interaction of the SOMOs.\textsuperscript{32} The $\pi-\pi$ interactions of the thiazyl SOMOs produce the intermolecular contacts that give rise to the dimerization effect. These intermolecular contacts usually occur through the $\pi^*$ orbitals of the sulfur atoms, to form a $\sigma$ bond. If the intermolecular separation is within the sum of the van der Waals radii of S (3.7 Å)\textsuperscript{36}, then the associated thiazyl radicals are considered dimerized and this usually produces a closed shell singlet ground state.\textsuperscript{33}

The representative dimer motifs for both 1,2,3,5-DTDA and 1,2,3-DTA moieties are presented in **Figure 3.04**. These modes of dimerization include the trans-
antarafacial,\textsuperscript{37} twisted-cofacial,\textsuperscript{38} and cis-cofacial\textsuperscript{39}. There is also the less common trans-cofacial dimerization mode for the 1,2,3,5-DTA.\textsuperscript{32} The majority of 1,2,3,5-DTDA systems have S-S dimerization in the region of 2.9-3.1 Å, which is well within the sum of the van der Waals radii of sulfur.\textsuperscript{33} The relative orientation and overlap of the thiazyl magnetic orbitals has an influence on whether FM or AFM coupling will occur.\textsuperscript{40} For instance, with the trans-antarafacial dimerization mode it is possible to have orthogonal (FM coupling) overlap or non-orthogonal (AFM exchange interaction) overlap of the π* orbitals depending on how far ‘slipped’ the neighbouring thiazyl rings are relative to one another.

![Diagram of common modes of dimerization](image)

**Figure 3.04 Common modes of dimerization possible for 1,2,3,5-DTDA and 1,2,3-DTA species.**\textsuperscript{32,33,37-39}

The incorporation of electronegative atoms and steric groups into 1,2,3-DTA and 1,2,3,5-DTDA species can influence how and if dimerization occurs. The attachment of electronegative functional groups, such as CN, Br, F, NO\textsubscript{2}, etc., to the fused substituent of a 1,2,3,5-DTDA, has produced molecules that pack as discrete radicals in the crystal structure.\textsuperscript{41-43} With the introduction of electronegative functional groups into 1,2,3,5-DTDA molecules, it is now possible for the electropositive sulfur atoms to establish
electrostatic interactions (e.g., CN\textsuperscript{\delta-} ... S\textsuperscript{\delta+}). Sterics influences DTDA and DTA dimerization by determining how atoms of the thiazyl rings establish the \(\pi-\pi\) intermolecular contacts.

Figure 3.05 Possible dimerization modes for 4-chloro-5-pentafluorophenyl-1,2,3-dithiazolyl molecule, 2.34.\(^{38}\)

In addition, sterics influences how DTDA and DTA dimerization can occur. An example of the influence of sterics on dimerization is demonstrated by 4-chloro-5-pentafluorophenyl-1,2,3-dithiazolyl (2.34).\(^{38}\) The molecule 2.34 is a non-ring fused species of 1,2,3-DTA, and it provides a good model for the effect sterics can have on dimerization. The mode of dimerization for 2.34 is twisted-cofacial and occurs through the S1 atoms of both 1,2,3-DTA rings. Of the possible dimerization modes presented in Figure 3.05, the twisted cofacial S1-S1 is the least favourable electronically because the S1 atoms become hypervalent with a C=S double bond. Either a twisted-cofacial dimerization mode through the S2 atoms generating hypervalent S2 atoms with an S=N double bond, or a delocalized cis-cofacial mode would be electronically more favorable. For 2.34, only the cofacial dimerization mode prevents steric hinderance between the Cl atoms and the \(\text{C}_6\text{F}_5\) group.
### 3.1.4 Quinone moiety

Given that the proposed molecule 6,7-Me₂DTANQ features a *para*-quinone component, it seems appropriate to briefly discuss a few general characteristics of *p*-quinones. There is an extensive amount of literature on *p*-quinones and for a more comprehensive review on the chemistry of quinones and their related quinonoid compounds the reader is encouraged to refer to the series by Patai.⁴⁴,⁴⁵

Quinones are redox active, having three possible oxidation states: 1) quinone, 2) semiquinone, and 3) catecholate. These oxidation states can be interconverted by the addition or subtraction of a single electron, as illustrated using 1,4-benzoquinone (3.09) in Figure 3.06.³²,⁴⁶ The electron transfer can be achieved chemically with a reducing/oxidizing agent or electrochemically with an applied voltage.

![Figure 3.06: Oxidation states accessible for 1,4-benzoquinone: (a) quinone, (b) semiquinone and (c) catecholate.⁴⁶](image)

The semiquinone oxidation state is of particular interest because it is a radical species. The semiquinone oxidation state of 1,4-benzoquinone is actually a relatively reactive species that only exists transiently due to the large spin densities on the carbon sites of the phenyl substituent.³² More persistent radicals can be generated by attaching bulky groups to the reactive carbon sites.⁴⁷
A significant property of semiquinones is their ability to delocalize radicals, as shown Figure 3.07. Quinones can afford stable radical semiquinone species when conjugated to an extended \( \pi \) system, which provides stabilization via resonance.\(^{48} \) For instance, in Figure 3.07 it is clear that p-naphtho- semiquinone (3.12) has more possible resonance structures than p-benzo- semiquinone (3.09) ergo the radical is more delocalized. The ability of naphthoquinone to delocalize and therefore stabilize an unpaired electron is a common phenomena found in nature. Biological systems have evolved to use modified napthoquinone molecules to perform important functions such as electron transport and radical detoxification.\(^{49} \)

![Resonance structures](image)

**Figure 3.07** Resonance structures of (a) \( p \)-benzosemiquinone and (b) \( p \)-naphthosemiquinone.

Quinononate ligands are able to act as non-innocent ligands. When a quinononate ligand coordinates, it can therefore exist in either the catecholate or semiquinone oxidation state, depending on the nature of the metal.\(^{50} \) In transition metal complexes of catecholate ligands and semiquinone ligands, sometimes the metal and quinone orbital
energies is sufficiently close to permit switching between oxidation states. The shifts in charge distribution are controlled by the entropy of the system and allow for reversible charge transfer between quinononate ligands and the metal via valence tautomerism.

For diamagnetic metal-catecholate complexes, a charge transfer may lead to an easily detectable high-spin paramagnetic metal-semiquinone species, as shown in Figure 3.08.

For a quinononate such as 3.13, which is coordinated to a metal ion, the oxidation of its corresponding catecholate to a semiquinone and the reduction of $M^{3+}$ to $M^{2+}$, can be accompanied by an observable spin crossover at high temperature (3.14).

![Figure 3.08 Valence tautomerization for a metal-quinononate complex.](image)

Returning to the resonance structures of 6,7-Me$_2$DTANQ depicted in Figure 3.01, one of the possible resonance structures resembles that of a semiquinone. The semiquinone resonance structure has unpaired spin on the monodentate oxygen coordination site (Figure 3.01). It is the contribution of both semiquinone and dithiazolyl resonance structures which enables 6,7-Me$_2$DTANQ to mediate magnetic coupling with multiple metal centers. To demonstrate this postulation with certainty, computational calculations were performed to determine how a quinone moiety affects the electronic structures of 6,7-Me$_2$DTANQ.

All calculations were done using density functional theory (DFT), employing the unrestricted Becke-3-Lee-Yang-Par (uB3LYP) method and 6-31G(d,p) basis set as provided in Gaussian 09 software. uB3LYP/6-31G(d,p) was selected for the method.
and basis set because it has thus far provided us with reasonable estimates of molecular properties.\textsuperscript{46,54-56} It is necessary that the method and basis set are reliable in establishing trends between the related molecules of interest. Although a larger basis set could have yielded a more accurate calculation, the 6-31G(d,p) basis set was sufficient for our purposes. This thesis does not claim to be a formal computational study of the molecular systems and as such, the results included from computational calculations are however informative and provide a better understanding of molecular properties.

The SOMOs and the spin density distribution for 6,7-Me\textsubscript{2}DTANQ (3.04) and DTANQ (3.05) are graphically presented in Figure 3.09 and Figure 3.10, respectively. The two SOMOs look nearly identical and the methyl groups do not make a big difference to the $\pi$ system. However, the methyl group will influence the $\sigma$ system and should improve $\sigma$ donation. Additionally, the SOMO of 3.04 nicely reflects the predictions made from the simple resonance line drawings in Figure 3.01.

It is important that the atoms involved in coordination have access to some amount of spin density and from Figure 3.09 and Figure 3.10 this is clearly the case for 6,7-Me\textsubscript{2}DTANQ and DTANQ. In Table 3.01, the amount of spin density that is localized on the electronegative N3 and O9 atoms and is relatively large (24\% and 13\% respectively) compared to the other atoms present in the molecules. Also, for both 6,7-Me\textsubscript{2}DTANQ and DTANQ, it is apparent that the quinone’s O4 atom creates a chelation site with respect to the 1,2,3-DTA’s N4 atom, while the other oxygen atom, O9, creates a monodentate coordination site. Both coordination sites possess atoms that have access to spin density but it is also important to consider atomic charges. From the Mulliken atomic charges presented in Table 3.01, it is possible to discern that the atoms N3, O4,
and O9, have negative values. While the exact value of the charge and the way charge is treated is not so important, it is essential that the atoms intended to participate in binding positive metal ions have a charge that is both negative and relatively large.

![Calculated singly occupied molecular orbitals (SOMOs)](image1)

**Figure 3.09** Calculated singly occupied molecular orbitals (SOMOs) for a) 6,7-Me₂DTANQ and b) DTANQ using uB3LYP/6-311G(d,p).³⁵

![Calculated spin density distribution](image2)

**Figure 3.10** Calculated spin density distribution for a) 6,7-Me₂DTANQ and b) DTANQ using uB3LYP/6-311G(d,p).³⁵
Table 3.01 Calculated Mulliken atomic spin densities and Mulliken atomic charges given as percentages for 6,7-Me$_2$DTANQ and DTANQ. Calculations were done using uB3LYP/6-311G(d,p).$^{35}$ The values below do not have hydrogens summed into the heavy atoms.

<table>
<thead>
<tr>
<th>Atom Label</th>
<th>Spin Density (%)</th>
<th>Charge (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>DTANQ</td>
</tr>
<tr>
<td>S1</td>
<td>23.8377</td>
<td>23.9715</td>
</tr>
<tr>
<td>S2</td>
<td>20.7357</td>
<td>21.0118</td>
</tr>
<tr>
<td>O4</td>
<td>-1.9694</td>
<td>-2.0859</td>
</tr>
<tr>
<td>C4</td>
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<td>1.0369</td>
</tr>
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</tr>
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<tr>
<td>C7</td>
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</tr>
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<td>C8</td>
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<td>1.3157</td>
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<tr>
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<td>1.4097</td>
<td>1.2588</td>
</tr>
<tr>
<td>C13</td>
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<td>-0.7862</td>
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<tr>
<td>C14</td>
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<td>-</td>
</tr>
<tr>
<td>C15</td>
<td>0.0345</td>
<td>-</td>
</tr>
</tbody>
</table>

3.1.5 Methyl groups

Methyl groups were incorporated into the design of to 6,7-Me$_2$DTANQ (3.04) to overcome the drawbacks of the unmethylated parent molecule DTANQ (3.05) which is a poor ligand. We postulated that bulk coordination eluded DTANQ for the following reasons: 1) DTANQ is too insoluble in the solvents that are suitable for coordination reactions and 2) the oxygen and nitrogen atoms of DTANQ presumably do not have sufficient sigma donor character to facilitate coordination syntheses.$^{26}$ The addition of
methyl groups, at the 6,7-positions of DTANQ significantly improved solubility while simultaneously increasing its sigma donor ability. This strategy has been very successful in facilitating the coordination of 6,7-Me₂DTANQ, which has been reproducibly used in large scale coordination syntheses. A number of metal complexes of 6,7-Me₂DTANQ have been achieved and characterized by magnetometry, X-ray crystallography, and elemental analysis. The results for the metal complexes are presented in Chapter 4.

3.2 Characterization

3.2.1 Infrared spectroscopy

Infrared (IR) spectroscopy was primarily used in this research to identify the functional groups present in the reactants and the products. The IR spectrum of 2-amino-3-bromo-6,7-dimethyl-1,4-naphthoquinone (3.15) contains amine bond stretches indicating that this compound contains a primary amine. In Figure 3.11, two medium intensity bands occur at frequencies of 3461 and 3322 cm⁻¹. These bands correspond to N-H asymmetric and symmetric bond vibrations.⁵⁷

The IR spectra of 6,7-Me₂DTANQ (3.04) and 6,7-dimethyl-4,9-dioxo-naphtho[1,2-d][1,2,3]dithiazol-2-ium chloride (3.16) contain a C=O stretch located in the range of 1690-1655 cm⁻¹, which indicates that these compounds contain a quinone carbonyl. In Figure 3.12, one strong intensity band occurs at a frequency of 1686 cm⁻¹ for compound 3.16. Compound 3.04 has a very similar IR to 3.16, although there is some shifting of the bands (Figure 3.13). The strong intensity carbonyl band occurs at a
frequency of 1670 cm\(^{-1}\) for \textbf{3.04}. These particular bands arise from symmetrical C=O bond vibrations.\textsuperscript{57}

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{3.11.png}
\caption{3.11 IR transmittance spectra from 4000-500 cm\(^{-1}\) for compound 3.15.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{3.12.png}
\caption{3.12 IR transmittance spectra from 4000-500 cm\(^{-1}\) for 3.16.}
\end{figure}
The carbonyl stretch was also a good diagnostic IR band to track all isolated products in the multi-step synthesis towards 6,7-Me$_2$DTANQ. The typical range of transmittance for a quinone carbonyl ranges between 1690-1655 cm$^{-1}$. The typical range of absorption can shift dramatically due to interference or perturbation caused by the addition or subtraction of nearby electronegative atoms and/or changes in the spatial geometry of the molecular backbone. A number of factors influence where a C=O band will occur, including: mass differences between neighbouring atoms, inductive effects, mesomeric effects, steric, and even hydrogen bonding. The shifts in the carbonyl stretch that occurred during the multi-step synthesis of 6,7-Me$_2$DTANQ are apparent when looking at the IRs compared in Figure 3.14.
Figure 3.14 IR transmittance spectra from 2000-400 cm$^{-1}$ of products isolated during the multi-step synthesis of 6,7-Me$_2$DTANQ. The carbonyl peaks are indicated with asterisks.
3.2.2 Electron spin resonance

X-band electron paramagnetic resonance experiments were performed on cells prepared in a glovebox using dry, degassed CH₂Cl₂ to exclude air and moisture. Compound 6,7-Me₂DTANQ was obtained in the cell by reducing 3.16 with triphenyl antimony in situ. The expected three line coupling pattern to a single ¹⁴N nucleus, as seen in Figure 3.15, was observed with a g value of 2.0095. Slight hyperfine coupling to the protons of 6,7-Me₂DTANQ was also observed. The coupling constants were determined by spectral simulation using Winsim 2002. The simulation had the best correlation value (R² = 0.993679) when performed with three spin sites: one ¹⁴N and two unique ¹H. Two ¹H coupling constants provided the best fit to the data. Computational values were calculated using uB3LYP/6-311G(d,p) in Gaussian 03 software for Windows. The calculated (uB3LYP/6-311G(d,p)) coupling values provide an adequate fit to the simulated values. Table 3.02 summarizes the simulated and computational coupling constant values.

Table 3.02 ESR values of 2.51 in dry, degassed CH₂Cl₂ using X-band EPR at room temperature. Simulated coupling constant values were obtained from modeling the experimental spectrum using Winsim 2002 and calculated coupling constants using uB3LYP/6-311G(d,p) from Gaussian 03.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Simulated (G)</th>
<th>Calculated (G)</th>
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<td>a_N</td>
<td>4.46177</td>
<td>4.85551</td>
</tr>
<tr>
<td>a_H</td>
<td>0.32360</td>
<td>0.16534</td>
</tr>
<tr>
<td>a_H</td>
<td>0.52888</td>
<td>0.59823</td>
</tr>
<tr>
<td>g value</td>
<td>2.00950</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 3.15 X-band ESR spectrum of a) 6,7-Me₂DTANQ (g = 2.0095) in CH₂Cl₂ and b) simulation to model coupling constants of 6,7-Me₂DTANQ. Coupling constants are provided in Table 3.02.

### 3.3.3 Cyclic voltammetry

Cyclic voltammetry (CV) is commonly used to characterize redox active species. In a CV experiment the working electrode potential is ramped linearly versus time until a set potential is reached, at which point the working electrode's potential ramp is inverted. Depending on the experiment, the working electrode's potential ramp can be inverted several times during a CV run. The typical CV scan is a plot of the current ($i$) vs. potential ($E$) at the working electrode, where waves in potential indicate that a redox process is occurring.
Figure 3.16 CV of 6,7-Me₂DTANQ (2.0 mM) in 10mL CH₂Cl₂ and 100 mM (n-Bu)₄NPF₆ electrolyte, swept first in the cathodic direction (100mA), as indicated by the arrow. The cathodic peaks labelled $E_c^0$ and $E_c^-$ represent reductions to the radical and the anion, respectively. The anodic peaks labelled $E_a^0$ and $E_a^-$ represent oxidations to the radical and the anion, respectively. Peak potential values are references vs. SCE.

The cells used for CV experiments were prepared in a glovebox using dry solvent. Experiments were performed using Pt wire working, counter and reference electrodes, 100 mM (n-Bu)₄NPF₆ electrolyte and 2.0 mM analyte, at a scan rate of 100 mV/s. The ferrocene/ferrocenium (fc/fc⁺) redox couple ($E_{1/2}^{(fc/fc⁺)} = +400$ mV vs. SCE in CH₃CN and $E_{1/2}^{(fc/fc⁺)} = +460$ mV vs. SCE in CH₂Cl₂)⁶⁰,⁶¹ was used as an internal reference and thus all data are reported vs. SCE.
Figure 3.17 CV of 6,7-Me₂DTANQ (2.0 mM) in 10mL CH₃CN and 100 mM (n-Bu)₄NPF₆ electrolyte, swept first in the cathodic direction (100mA), as indicated by the arrow. The cathodic peaks labelled $E_c^0$ and $E_c^-$ represent reductions to the radical and the anion, respectively. The anodic peaks labelled $E_a^0$ and $E_a^-$ represent oxidations to the radical and the anion, respectively. Peak potential values are references vs. SCE.

The CV of 6,7-Me₂DTANQ in CH₂Cl₂ is presented in Figure 3.16. The peak to peak potential separation for 6,7-Me₂DTANQ in CH₂Cl₂ is $\Delta E_{pp}^{(0/1+)} = 86$ mV and $\Delta E_{pp}^{(1-/0)} = 108$ mV. In CH₂Cl₂, the two reversible oxidation processes correspond to $E_{1/2}^{(0/1+)} = +860$ mV and $E_{1/2}^{(1-/0)} = -320$ mV. The CV of 6,7-Me₂DTANQ in CH₃CN is presented in Figure 3.17. The peak to peak potential separation for 6,7-Me₂DTANQ in CH₃CN is $\Delta E_{pp}^{(0/1+)} = 96$ mV and $\Delta E_{pp}^{(1-/0)} = 111$ mV. In CH₃CN the two reversible oxidation processes correspond to $E_{1/2}^{(0/1+)} = +811$ mV and $E_{1/2}^{(0/-1)} = -410$ mV.
In Figure 3.17 the CV has a weaker signal to background compared to Figure 3.16 because 6,7-Me₂DTANQ is much less soluble in CH₃CN than CH₂Cl₂. However, it was necessary to use CH₃CN to compare 6,7-Me₂DTANQ to other related systems since this is the standard solvent for CVs of many thiazyl compounds. Also, in the CVs displayed in Figure 3.16 and Figure 3.17, the half-wave reduction potentials $E_{1/2}^{(0/1+)}$ and $E_{1/2}^{(1-0)}$ are shifted relative to one another through solvent effects. The observed shifts are caused by increasing the dielectric constant of the dipolar aprotic solvent, which shifts the reduction potentials towards more positive values. In short, an increase in the dielectric constant of the solvent (in this case from CH₂Cl₂ to CH₃CN) is accompanied by better solvation of the species that is produced electrochemically.

3.2.4 X-ray crystallography

The single-crystal X-ray data of an orange plate of 3.15, grown from ethanol, was collected at 150 K by Dr. Soldatov using a Cu X-ray source. The space group of 3.15 is monoclinic C2/c with unit cell dimensions as follows: $a = 7.72070(7)$, $b = 13.73969(16)$, $c = 21.1400(2)$ Å, $\beta = 94.0880(10)^{\circ}$, and $V = 2236.83(4)$ Å³. The final refined model fit the data with an $R$ value of 3.29 %. The smallest representative formula unit of the crystal structure was chosen to be a single molecule of 3.15 and half a water molecule (C₁₂H₁₀BrNO₂•0.5(H₂O)), which yields a $Z$ equal to 8. The stoichiometry per unit cell is 8 molecules of 3.15 for every 4 molecules of water. An individual unit of 3.15 hydrate and the packing of atoms in a single unit cell are displayed in Figure 3.18.
Figure 3.18 Crystal structure fragments showing a) one asymmetric unit of 3.15 hydrate and b) four molecules of 3.15 hydrogen bonding to one water molecule.

The single-crystal X-ray data of a purple plate of 3.04, grown by dynamic sublimation, was collected at 150 K by Dr. Lough using a Mo X-ray source. The space group of 3.04 is monoclinic $P2_1/c$ with unit cell dimensions as follows: $a = 11.055(2)$, $b = 7.9789(16)$, $c = 13.222(3)$ Å, $\beta = 113.03(3)^\circ$, $V = 1073.32(4)$ Å$^3$. The final refined model fit the data with an $R$ value of 4.28 %. The smallest representative formula unit of the crystal structure was chosen to be a single molecule of 3.04 ($C_{12}H_8NO_2S_2$), which yields a $Z$ equal to 4. Figure 3.19 represents an individual unit of 3.04 and shows the dimerization. The dimerization mode of 3.04 is established through a short intermolecular S-O contacts (3.111(3) Å).
Figure 3.19 Crystal structure fragments showing a) one asymmetric unit of 6,7-Me₂DTANQ and b) dimerization mode of 6,7-Me₂DTANQ illustrated through a solid yellow line between S-O atoms.

3.2.5 Magnetometry

Our collaborator Dr. Rodolphe Clérac conducted magnetic susceptibility measurements on 6,7-Me₂DTANQ using a Quantum Design MPMS-XL SQUID magnetometer. The measurements of 6,7-Me₂DTANQ were performed on a polycrystalline sample (8.3 mg) introduced in a sealed polyethylene bag (3 × 0.5 × 0.02 cm; 28.6 mg respectively) under argon in a glovebox. The dc measurements were conducted from 300 to 1.8 K and between -7 T and 7 T applied dc fields and results indicated that 6,7-Me₂DTANQ is diamagnetic. The $M$ vs $H$ measurement was performed at 100 K to confirm the absence of ferromagnetic impurities in the sample. Experimental data were corrected for the sample holder and for the diamagnetic contribution of the sample.
3.3 Discussion

3.3.1 Solution redox

The half-wave reduction potentials $E_{1/2}^{(0/1+)}$ and $E_{1/2}^{(1-/0)}$ for 6,7-Me$_2$DTANQ have been assigned as the radical-cation and anion-radical respectively. Both $E_{1/2}$ couples are considered reversible and stable at the scan rate of 100 mV/s. Note that the strict definition of reversible redox is $\Delta E_{pp} = 59$ mV in aqueous solution. The one electron redox waves in CVs carried out in aprotic solvents with a $\Delta E_{pp} > 59$ mV can be termed quasireversible.\textsuperscript{63,64} However, thiazly species with a $\Delta E_{pp} \approx 100$ mV are often referred to as reversible.\textsuperscript{44,47,63-67,65} The half-way reduction potentials, in CH$_3$CN, for oxidation and reduction of 6,7-Me$_2$DTANQ, are compared to that of a series of related compounds in Table 3.03.

Table 3.03 Half-wave reduction potentials in mV, of compounds related to 6,7-Me$_2$DTANQ. Values were obtained by CV experiments done in CH$_3$CN and referenced to SCE. \textsuperscript{a} Reversible behavior. \textsuperscript{b} Irreversible behavior

<table>
<thead>
<tr>
<th>Compound</th>
<th>3.04</th>
<th>3.05</th>
<th>3.20\textsuperscript{65}</th>
<th>2.36\textsuperscript{39}</th>
<th>3.12\textsuperscript{44}</th>
<th>3.21\textsuperscript{56}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{1/2}^{(ox)}$</td>
<td>811 $^a$</td>
<td>920 $^a$</td>
<td>518 $^a$</td>
<td>207 $^a$</td>
<td>-</td>
<td>790 $^a$</td>
</tr>
<tr>
<td>$E_{1/2}^{(red)}$</td>
<td>-410 $^a$</td>
<td>-280 $^a$</td>
<td>-400 $^a$</td>
<td>-910 $^b$</td>
<td>-600 $^a$</td>
<td>-30 $^a$</td>
</tr>
</tbody>
</table>

There are typically two distinct electrochemical reversible reduction steps possible for $p$-quinones: first radical anion ($0/-1$) and second dication ($-1/-2$).\textsuperscript{44} To clarify,
the $E_{1/2}$(red) of -600 mV given in Table 3.03 for $p$-naphthoquinone (3.12) corresponds to the first reversible couple $(0/-1)$. On the other hand, for simple aromatically fused DTA compounds, the cation-neutral radical $(+1/0)$ is electrochemically reversible but the reduction to the anion $(0/-1)$ is not. This is the case for naphthalene-1,2,3-dithiazolyl (2.36) which has a reversible peak at 207 mV $(+1/0)$, and an irreversible peak at -910 mV $(0/-1)$, reflecting the ease of reductive cleavage of the S-S bond. The addition of electron withdrawing groups into the backbone of a DTA is necessary to stabilize the negative charge and allow access to a reversible neutral radical-anion $(0/-1)$ couple.

A general description of the effects of electron affinity on $E_{1/2}$ values of substituted arenes is needed to interpret the potential shifts presented in Table 3.03. Upon reduction, the incoming electron either enters the lowest unoccupied molecular orbital (LUMO) of a closed shell species or the SOMO of an open shelled species. Regardless, an increase in electron affinity (EA) results in a lower LUMO/SOMO and therefore, an improved ease of reduction. With increasing EA the more the redox processes will shift towards anodic potentials. The introduction of electron withdrawing groups to a substituted aromatic compound increases EA, whereas the introduction of electron donating groups decreases EA. Thus, the introduction of methyl groups to DTANQ shifts the $E_{1/2}^{(0/1+)}$ and $E_{1/2}^{(1/-0)}$ values towards cathodic potentials.

The radical of a semiquinone primarily occupies the molecular $\pi^*$ LUMO, thus delocalizing it over the entire conjugated system, while the negative charge is localized at the two oxygen atoms. Molecules that contain the semiquinone structure have localized charge on electronegative atoms and will have a decrease in EA with increasing conjugation. The order of EAs for quinones is benzoquinone $>$ naphthoquinone $>$
anthroquinone. This order is the reverse for simple arenes because increasing conjugation allows the radical anions to delocalize across the entire \( \pi \) system. The order of EAs for arenes is benzene < naphthalene < anthracene. This effect leads to more anodic half-wave potentials for naphthalene-1,2,3-dithiazolyl (2.36) compared to the \( p \)-naphthoquinone-DTA and \( o \)-naphthoquinone-DTA species.

### 3.3.2 Solid state

The single crystal X-ray data for the purple plates of 6,7-Me\(_2\)DTANQ were collected at 150 K and its solution revealed that it is dimerized in the solid state (Figure 3.19). The crystal structures of DTANQ and its structural isomer 1,3,2-dithiazolyl-1,4-naphthoquinone (3.20)\(^{65}\), collected at low temperature are also known and can serve as standards to compare 6,7-Me\(_2\)DTANQ. The crystals of 6,7-Me\(_2\)DTANQ and DTANQ were prepared similarly, by dynamic vacuum sublimation on a three-stage furnace, with only one major difference. For DTANQ there were two different crystals produced: red crystals and green crystals. Both the red and green crystals had their structures determined by X-ray analysis. The difference between the red and green crystals is in their dimerization modes. This section will now focus on the differences between the intramolecular bonds and intermolecular interactions in the crystal structures of the closely related molecules 6,7-Me\(_2\)DTANQ (purple), DTANQ (red and green) and 3.20.
It is no surprise that the structures of $6,7\text{-Me}_2\text{DTANQ}$ (purple), DTANQ (red and green) and $3.20$ are all dimerized, as this is generally the case for thiazyl-based radicals unless they have been explicitly designed to do otherwise. However, in contrast to other thiazyl-based radicals, $6,7\text{-Me}_2\text{DTANQ}$ and DTANQ (green) are dimerized through an entirely new motif. This new dimerization mode is characterized by a short intermolecular S-O contact. The bond distances of the S-O bond dimerization modes for $6,7\text{-Me}_2\text{DTANQ}$ and DTANQ are 3.111 Å and 3.190 Å, respectively. These values are both are within the sum of the van der Waals radius for S-O (1.85 Å + 1.4 Å)$^{36}$. Also of interest, DTANQ can also dimerize through an additional motif. The green crystals have the S-O dimerization motif, whereas the red crystals dimerize in a cis-cofacial dimerization mode. The red crystals have a S-S bond length of 3.531 Å, which is within the sum of the van der Waals radius for S-S (1.85 Å +1.85 Å)$^{36}$. Molecule $3.20$ dimerizes in a trans-cofacial mode, through 3.244 Å S-S intermolecular contacts, which once again,
are within the sum of the van der Waals radius for S-S. The modes of dimerization for 6,7-Me₂DTANQ (purple), DTANQ (red and green) and 3.20 are shown in Figure 3.21.

![Figure 3.21 Dimerization modes present in the crystal structures of a) 6,7-Me₂DTANQ (purple), b) DTANQ (green) c) DTANQ (red), and d) 1,3,2-dithiazoyl-1,4-naphthoquinone (3.20).](image)

The S-O dimerization can occur for 6,7-Me₂DTANQ and DTANQ because they are hybrid semiquinones. The O-radical resonance form allows significant spin density to be distributed onto the carbonyl oxygen, as shown previously in the calculated spin density diagram (Figure 3.10). The Passmore Group performed density functional theory (DFT) calculations (PBE0/6-311G(d)) on 3.20, which revealed a different situation for this quinone-like DTA molecule. Their calculations demonstrate that the spin density distributions are localized on the 1,3,2-DTA ring, suggesting that it is a non
This observation may explain why 3.20 dimerizes in the cis-cofacial mode as opposed to the S-O dimerization characterized by our hybrid semiquinone species. The S-O intermolecular contact imparts diamagnetism upon 6,7-Me₂DTANQ and DTANQ (green) as they both display diamagnetic behaviour with applied magnetic fields.

The important structural parameters of 6,7-Me₂DTANQ, DTANQ (red and green) and 3.20 are summarized in Table 3.04. The atomic labels for the molecules’ atoms are presented in Figure 3.22. There are subtle differences in the intramolecular bond lengths. The largest noticeable difference is in the C2-C3 carbon fusing location. The 1,3,2-DTA structure has a considerably shorter C2-C3 bond length than that of the 1,2,3-DTA structures. This differences suggests that the C2-C3 bond in 3.20 has more cross-conjugation to the two flanking carbonyls than those of the 1,2,3-DTA structures. Even so, the C=O bonds are relatively similar across all structures, with substituent having little effect on this particular bond length.

![Figure 3.22 Crystallographic atomic labels for a) 6,7-Me₂DTANQ, b) DTANQ and c) 1,3,2-dithiazolyl-1,4-naphthoquinone (3.20).](image)
Table 3.04 Selected structural parameters of the crystal structures of DTANQ (3.05) and the closely related compounds 6,7-Me₂DTANQ (3.04) and 1,3,2-dithiazolyl-1,4-naphthoquinone (3.20). Collected at \(^a\) 150 K, \(^b\) 198 K, \(^c\) 100 K.

<table>
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<th>Intramolecular Distances (Å)</th>
<th>Compound</th>
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<th>3.05 (green)</th>
<th>3.20(^{65})</th>
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<tbody>
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<td>O1-C1</td>
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<td></td>
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<td>1.21(1)</td>
<td>1.221(2)</td>
<td>1.224(3)</td>
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<tr>
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<td></td>
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<td>1.38(1)</td>
<td>1.413(2)</td>
<td>1.354(3)</td>
</tr>
<tr>
<td>C6-C7</td>
<td></td>
<td>1.413(5)</td>
<td>1.38(1)</td>
<td>1.391(3)</td>
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</tr>
<tr>
<td>S1-C2</td>
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<td>1.73(1)</td>
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<tr>
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<tr>
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<td>2.066(5)</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>1.645(2)</td>
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<td>Intermolecular Distances (Å)</td>
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<td>3.05 (red)</td>
<td>3.05 (green)</td>
<td>3.20(^c)</td>
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<tr>
<td>S1-S2</td>
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<td>3.389</td>
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<td>S1-S1</td>
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<tr>
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<td></td>
<td>3.111</td>
<td>3.190</td>
<td>3.151</td>
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The effect of introducing methyl groups into DTANQ leads to some predictable outcomes in terms of bond lengths. That is, 6,7-Me₂DTANQ has a lengthening of the S1-C2 bond and a shortening of the C3-N3 bond relative to DTANQ. This is likely due to
extra electron density via the methyl groups, which perturbs the aromatic system. There is also a lengthening of the C6-C7 bond in 6,7-Me₂DTANQ compared to DTANQ. Again, this change is expected to occur with the attachment of electron donating groups.

3.4 Experimental

3.4.1 General considerations

Where indicated, reactions performed under Ar\(_{(g)}\) atmosphere were achieved using standard Schlenk and glove box techniques. Solvents were dried on a SP-1 Stand Alone Solvent Purification System from LC Technology Solutions Inc, using molecular sieves. All commercial reagents were used as received, with the exception of active manganese(IV) dioxide which was activated by heating\(^{68}\) at 100 °C for a minimum of 24 h prior to use, and triphenyl antimony which was recrystallized from acetonitrile. The reagents 2,3-dimethylbutadiene and p-benzoquinone were purchased from Acros Organics. The reagents active manganese(IV) dioxide (Fluka Analytical, catalogue number 63548-250G-F and Lot#BCBB3894), MnCl\(_2\)·4H\(_2\)O, triphenyl antimony and S\(_2\)Cl\(_2\), were obtained from Sigma Aldrich. 6,7-Dimethyl-5,8,9,10-tetrahydronaphthoquinone\(^{69}\) (3.17), 2,3-dibromo-6,7-dimethyl-1,4-naphtho-quinone\(^{70}\) (3.19) were prepared according to literature methods. IR (KBr pressed pellet) spectra were recorded on a Nicolet 4700 FT-IR spectrometer at 4 cm\(^{-1}\) resolution. X-band EPR spectra were recorded on a Bruker EMX spectrometer. CV data were collected using a BASi Epsilon-EC Bioanalytical Systems, Inc. Version 2.10.73_USB, 2009. CV cells were prepared in a glove box using dry solvent. NMR spectra were recorded on a Bruker
Avance-400 spectrometer at 298 K. Elemental analyses were performed by MHW Labs, Phoenix, AZ, USA. Crystal data for 6,7-Me₂DTANQ was collected by Dr. Alan Lough at the University of Toronto on a Nonius Kappa-CCD System and solved by Dr. Michael Jennings. Crystal data on 3.15 were collected by Dr. Dmitriy Soldatov at the University of Guelph on a SuperNova diffractometer with Atlas CCD detector and solved by David J. Sullivan.

### 3.4.2 Syntheses

**Figure 3.23 Synthetic Route for target compound 6,7-Me₂DTANQ.**

6,7-Dimethyl-1,4-naphthoquinone (3.18). A modification of the procedure reported by Mashraqui and Keehn\(^7\) was used. Dry toluene (185 mL) was added to a solid mixture of 1 (4.9625 g, 26.085 mmol) and activated MnO₂ (23.01 g, 301.5 mmol) under Ar\(_\text{(g)}\) atmosphere. The resulting solution was refluxed for 3 h, then filtered hot through Celite. The filtrate was collected and the solids on the Celite plug were washed with anhydrous ethanol, which was then added to the filtrate. Evaporation of the solvent from the filtrate
afforded the crude product 3.18, which was recrystallized from anhydrous ethanol to give a yellow crystalline product. Yield: 3.2242 g (17.312 mmol, 66%). mp: 113-116 °C. IR(KBr) ν/cm⁻¹: 2952 (w), 2918 (w), 2849 (w), 1666 (s), 1599 (s), 1560 (w), 1508 (w), 1449 (m), 1392 (m), 1360 (w), 1341 (m), 1328 (s), 1309 (s), 1262 (w), 1220 (w), 1202 (w), 1143 (m), 1099(w), 1072 (w), 1057 (s), 1019 (m), 995 (w), 971(w), 902 (w), 837 (s), 805 (w), 768 (w), 712 (w), 626 (w), 512 (m), 499 (m), 471 (w), 450 (m), 426 (m), 412 (w). ¹H NMR: (400 MHz, CDCl₃, 25 °C, ppm) δ 2.39 (6 H, s, CH₃), δ 6.88 (2 H, s, CH), δ 7.81 (2 H, s, CH).

2-Amino-3-bromo-6,7-dimethyl-1,4-naphthoquinone (3.15). A modification of the procedure reported by Hoover and Day was used for this preparation. A suspension of 3.19 (3.3563 g, 97.567 mmol) was heated to reflux in anhydrous ethanol (200 mL) under Ar(g) atmosphere. Concentrated (28%) NH₄OH(aq) (4.50 mL) was added and the mixture was refluxed under ammonia atmosphere (sealed system with a balloon of NH₃(g)) for 8 h. The solution was cooled in an ice bath and the resulting orange precipitate was recovered by filtration and washed with deionized water. The product, 3.15, was dried in vacuo overnight. Yield: 2.7128 g (96.826 mmol, 99%). mp: 226-228 °C. IR(KBr) ν/cm⁻¹: 3528 (m), 3461 (m), 3423 (m), 3322(s), 3073 (w), 2973 (w), 2946 (w), 2919 (w), 1831 (w), 1794 (w), 1682 (s), 1631 (s), 1606 (s), 1588 (s), 1566(s), 1448 (m), 1405 (m), 1386 (m), 1367 (s), 1330 (s), 1297 (s), 1240 (w), 1201 (w), 1178 (w), 1064 (w), 1023 (w), 1000 (w), 964 (m), 916 (w), 899 (w), 801 (m), 760 (w), 744 (s), 688 (w), 676 (w), 622 (m), 577 (m), 549 (m), 499 (m), 446 (w), 426 (m). ¹H NMR: (400 MHz, CDCl₃, 25 °C, ppm) δ 2.35 (3 H, s, CH₃), δ 2.37 (3 H, s, CH₃), δ 7.78 (1 H, s, CH), δ 7.88 (1 H, s, CH). Crystal
**data:** SuperNova diffractometer Atlas-CCD detector radiation source CuKα, wavelength = 1.5418 Å at University of Guelph; \( T = 150(2) \) K; monoclinic; \( C2/c \); \( a = 7.72070(7), b = 13.73969(16), c = 21.1400(2) \) Å; \( \beta = 94.0880(10)^\circ \); \( V = 2236.83(4) \) Å\(^3\); \( Z = 8; R = 3.29\% \).

6,7-Dimethyl-4,9-dioxo-naphtho[1,2-d][1,2,3]dithiazol-2-ium chloride (3.16). Excess \( \text{S}_2\text{Cl}_2 \) (6.00 mL, 74.8 mmol) was added to a solution of 3.15 (4.1079 g, 14.665 mmol) in dry CH\(_3\)CN (45 mL) under Ar\( _\text{(g)} \) atmosphere. The reaction mixture was refluxed for 3 h. The resulting orange slurry was filtered warm to isolate a fine precipitate, which was washed with dry CH\(_3\)CN (6 mL). The product, 3.16, was an orange powder which was dried \textit{in vacuo}. Crude yield: 3.8674 g (12.987 mmol, 89%). IR(KBr) ν/cm\(^{-1}\): 3035 (w), 3014 (w), 2953 (w), 2921 (w), 1686 (s), 1671 (s), 1593 (s), 1558 (w), 1452 (m), 1407 (w), 1396 (m), 1374 (m), 1292 (s), 1226 (w), 1194 (s), 1172 (w), 1094 (s), 1032 (s), 994 (m), 938 (w), 918 (s), 906 (m), 852 (s), 819 (w), 804 (w), 774 (w), 748 (w), 729 (s), 691 (m), 643 (m), 603 (w), 583 (w), 539 (m), 503 (m), 466 (w), 439 (m), 424 (m).

6,7-Dimethyl-4,9-dioxo-naphtho[2,3-d][1,2,3]dithiazolyl (3.04). Triphenyl antimony (0.6130 g, 1.7365 mmol) was added to a suspension of 3.16 (1.0336 g, 3.4710 mmol) in dry CH\(_3\)CN (20 mL) under Ar\( _\text{(g)} \) resulting in an instant color change from orange to purple. The slurry was stirred for 0.5 h at RT and then the purple precipitate way isolated from the green solution by filtration. The fine purple solid 3.04 was washed with dry CH\(_3\)CN (10 mL) and dried \textit{in vacuo}. Crude yield: 0.8370 g (3.1906 mmol, 92%). A portion of the crude product (0.1453 g, 0.5539 mmol) was purified by sublimation under
dynamic vacuum ($10^{-5}$ Torr) using a four stage gradient tube furnace (175, 95, 70, 30 °C) to generate purple crystals of 1. Sublimation yield: 0.0930 g (0.355 mmol, 64%).

**IR(KBr) v/cm$^{-1}$**: 3326 (w), 3049 (w), 2969 (w), 2944 (w), 2916 (w), 1670 (s), 1602 (m), 1593 (w), 1574 (s), 1550 (m), 1535 (m), 1500 (w), 1458 (w), 1448 (w), 1421 (s), 1401 (w), 1380 (w), 1375 (w), 1350 (s), 1305 (w), 1282 (s), 1259 (s), 1193 (s), 1178 (m), 1078 (m), 1034 (m), 995 (m), 940 (w), 892 (m), 815 (s), 760 (m), 740 (m), 723 (m), 693 (m), 683 (m), 639 (m), 594 (w), 574 (m), 530 (w), 506 (w), 482 (w), 454 (w), 438 (w), 417 (m).

**Crystal data**: Nonius Kappa, CCD, radiation source MoK$\alpha$, wavelength = 0.71073 Å at University of Toronto; $T = 150(2)$ K; monoclinic; $P2_1/c$; $a = 11.055(2)$, $b = 7.9789(16)$, $c = 13.222(3)$ Å; $\beta = 113.03(3)^\circ$; $V = 1073.32(4)$ Å$^3$; $Z = 4$; $R = 4.28\%$.

**Elemental Anal.** Calc. for C$_{12}$H$_8$NO$_2$S$_2$: C, 54.94; H, 3.07; N, 5.34%. Found: C, 54.77; H, 3.01; N, 5.33%.
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4.1 Thiazyl coordination

4.1.1 DTDA coordination

Coordination of the 1,2,3-DTA ligand 1,2,3-dithiazolyl-6,7-dimethyl-1,4-naphthoquinone (6,7-Me₂DTANQ, 3.04) is the primary focus of this chapter. But first, 1,2,3,5-DTDA metal complexes merit a brief overview because the past accomplishments of the Preuss Group provide a rationale for exploring 1,2,3-DTA coordination.

The metal coordination of 1,2,3,5-DTDA species is achieved through either the sulfur or nitrogen atoms of the thiazyl ring. Previous work involved metal coordination of DTDA compounds to low valent metal ions through the sulfur atoms.¹ The first transition metal complex of a DTDA compound was reported by Banister and colleagues using the 4-phenyl-DTDA (4.01) radical reacted with Fe₂(CO)₉ or Fe₃(CO)₁₂.² However further investigation by Dr. Boeré revealed that upon formation of the Fe complex 4.02, the thiazyl ring of 4.01 underwent S-S bond cleavage and nitrogen protonation to become the closed shell imine species, 3-H-1,2,3,5-dithiadiazoline.³⁴ The Banister group has since achieved S-coordination of a DTDA species to a transition metal by reacting 4.01 with a molar equivalent of [CpNi(CO)]₂ (Cp = η⁵-cyclopentadienyl ring) to give the di-nickel complex 4.03.⁵ The metal complex 4.03 is similar to 4.02 apart from the DTDA nitrogen, which bears no hydrogen, and hence remains an open shell coordinated species. Sulfur-metal coordination of DTDA species is typically accompanied by S-S bond breakage, which is characterized by increased S-S bond distance.⁶ Even so, there are examples of DTDA coordination to a low valent Cr where the S-S bond remains intact but the DTDA species is no longer a radical.⁷
Studies involving 4-(2'-pyridyl)-1,2,3,5-DTDA (3.01) were carried out by Nigel Hearns of the Preuss Group. Hearns demonstrated the utility of DTDA compounds as spin-bearing ligands that do not break the S-S bond. The DTDA ligand 3.01 was the first reported N-coordination of a DTDA species.

This milestone was achieved using two key strategies: 1) incorporating a chelation site into the DTDA ligand and 2) coordinating the DTDA ligand to hard, divalent metal species as opposed to soft, low valent metal species. Hard metal ions promote coordination of the relatively hard, electronegative nitrogen atoms of the DTDA ring over that of the relatively soft, electropositive sulfur atoms. The hardness of the divalent metal is enhanced by incorporating electron-withdrawing groups in the auxiliary ligand. Our choice of auxiliary ligand is hexafluoroacetylacetonate (hfac). We use the THF adduct of M(hfac) for transition metal coordinations because the THF molecules are labile and can be easily displaced by a thiazyl ligand.

Complexes of M(hfac) and 3.01 (4.04) reported by our group with the transition metal ions Co^{2+}, Fe^{2+} and Ni^{2+} exhibited either AFM or FM coupling interactions between ligand and metal center at low temperature. However, the transition metal complexes Cu^{2+} and Mn^{2+} of 4.04 exhibited no ligand-metal coupling interaction in the solid state because the nearest-neighbour DTDA rings are dimerized via close S-S contacts.
In general, thiazyl close contacts allow direct exchange between radicals. As the intermolecular distance between neighbouring DTDA rings decreases, the AFM exchange interaction increases, that is if the magnetic thiazyl π* orbitals have non-orthogonal overlap. Details about thiazyl dimerization, such as common modes of dimerization, are discussed in Chapter 3. Dimerization normally renders the 1,2,3,5-DTDA ligands diamagnetic so that the only remaining magnetic contribution is due to the metal centers. In most cases, this quenching of ligand spin is detrimental to thiazyl-metal complexes’ magnetic properties. However, there are some exceptions for DTDA-lanthanide complexes, in which thiazyl close contacts are desirable; the results of which are currently being prepared for publication.

The design of molecules incorporating chelating sites to promote coordination is only the first step towards studying the magnetic molecular systems of metal complexes containing open shelled thiazyl ligands. The next step is the introduction of design features that allow the thiazyl ligand, in its corresponding metal complex, to associate via intermolecular contacts with neighbouring complexes in the solid state.
4.1.2 Crystal packing

There are two possible design features that can be incorporated in a thiazyl ligand to alter close contacts in the corresponding metal complex: 1) multiple chelation sites and 2) electronegative substituents. In exploring these design features, our research group has discovered some interesting results.

First, by incorporating multiple chelation sites in the thiazyl ligand, the steric bulk of the M(hfac)$_2$ fragments affords multinuclear metal complexes that inhibit the usual dimerization motifs. For instance, Jian Wu$^{13}$ of the Preuss Group demonstrated that using a DTDA ligand, 4-(2’-pyrimidyl)-1,2,3,5-DTDA (3.03)$^{14}$, which incorporates two N-coordinating pockets, it is possible to achieve undimerized binuclear transition metal complexes. We reported the family of undimerized binuclear transition metal complexes (4.05) based on 3.03 and showed that these complexes (Mn$^{2+}$, Ni$^{2+}$, and Co$^{2+}$) mediate FM coupling between more than one paramagnetic metal center; both novel findings in the field of thiazyl radical chemistry.$^{15}$

![Diagram of 4.05 (M$^{2+}$ = Mn, Ni, Co) and 3.03](image)

Secondly, it has been postulated that the addition of electronegative moieties into thiazyl ligands directs intermolecular interactions, which interrupts typical dimer formation in the solid state metal complexes.$^{16-18}$ We explored this approach by modifying our DTDA ligand 3.01. We synthesized 4’-cyano-pyDTDA (4.06), 5’-cyano-
pyDTDA (4.07) and 5'-bromo-pyDTDA (4.08) and coordinated these ligands to Mn$^{2+}$ and Ni$^{2+}$. However, the introduction of the electronegative group did not provide predictable outcomes regarding whether or not the metal complexes were dimerized or undimerized. Our results demonstrate how difficult it is to predict and manipulate crystal packing in metal-DTDA complexes.

In our efforts to manipulate the crystal packing of thiazyl metal complexes, we discovered a key structural parameter for producing increased spin ground state molecular magnetic materials. Specifically, we sought to explain the solid state magnetic properties observed for a manganese complex of 4-(benzoxazol-2-yl)-1,2,3,5-dithiadiazolyl (3.02). Close inspection of the crystal structure of manganese complex of 3.02 suggests that the S-O close contacts between the 1,2,3,5-DTDA sulfur and hfac oxygen provide an exchange pathway for magnetic coupling. These intermolecular interactions are worth mentioning because a similar S-O close contact occurs in the 1,2,3-DTA metal complexes of 6,7-Me$_2$DTANQ.

4.1.2 DTA coordination

1,2,3-DTA coordination was pioneered by the Preuss Group. This thesis provides the first example of coordination of a 1,2,3-DTA ligand (6,7-Me$_2$DTANQ, 3.04) through a N, O bidentate pocket that is reproducible in high purity and bulk quantities. More
importantly, it reports the first magnetometry measurements on metal complexes of a 1,2,3-DTA ligand. For the first bi-oxygen coordinated 1,2,3-DTA (3.21), refer to the Thesis of my colleague Chad Smithson. As well, the first N, O coordinated 1,2,3-DTA ligand (DTANQ, 3.05) is reported in the Thesis of my colleague Ian Morgan.

![Chemical structures](images/structures.png)

The results presented in this chapter show that 6,7-Me₂DTANQ (3.04) can be used to produce organometallic thiazyl “chain-like” complexes that are undimerized in the solid state. Coordination polymers have been reported for nitronyl nitroxides and verdazyls. However, oligomeric radical ligand coordination complexes, such as those arising from the coordination of 6,7-Me₂DTANQ to transition metals, are rare. These multinuclear complexes arise because ligand 6,7-Me₂DTANQ has monodentate and bidentate coordination sites that are on opposing sides of the molecule. Additionally, both monodenate and bidentate sites have atoms that possess spin density, which leads to magnetic coupling between the radical ligand and all coordinated metal centers.

Following the convention of our previous research, 1,2,3-DTA ligands are coordinated to hard transition metals with hfac auxiliary ligands. We choose not to use alternative auxiliary ligands as it would not be possible to make comparisons with the related 1,2,3,5-DTDA complexes. Although ligand 3.04 has monodentate and bidentate coordination sites, the atoms of these sites have no direct charge and can only bind a metal ion through weak σ donation. Thus, the hfac supporting ligands are necessary to
promote successful coordination of 1,2,3-DTA ligands by withdrawing electron density away from the metal.

In addition, the hfac ligands serve an important role in promoting the solubility of the metal-DTA complexes. Although the 1,2,3-DTA ligand 6,7-Me₂DTANQ is more soluble than DTANQ, it still remains relatively insoluble in non-coordinating solvents. The ability of the M(hfac)₂ to solubilize the radical 6,7-Me₂DTANQ upon coordination shifts the reaction equilibrium towards completion. During the coordination reactions, performed in 1,2-dichloroethane (DCE), the solution mixture begins as a slurry of insoluble radical. As the reaction progresses, the slurry becomes a solution indicating that the coordination reaction for 6,7-Me₂DTANQ has reached completion. In contrast, coordination reactions for DTANQ appear to remain in equilibrium as the mixture remains a slurry.

4.1.3 Lanthanides

The lanthanide chemistry in our lab was pioneered by my colleague Elisabeth Fatila. Before her work, metal complexes of thiazyl radicals and lanthanide ions were not possible, primarily because no suitable starting materials were known. Lanthanide hydrate starting materials cannot be used because thiazyl radicals are water sensitive. Anhydrous Ln(hfac)₃ starting materials are required as coordination precursors. Reliable synthesis of three anhydrous Ln(hfa)₃(monoglyme) species (Ln = Eu²⁶, Gd²⁷, and Ho²⁸) was reported prior to our research. Recently, our group completed a series of fully characterized Ln(hfac)₃(monoglyme)ₙ complexes (Ln = La, Ce, Pr, Sm, Eu, Gd, Tb, Dy,
Er, and Tm) including supporting information for the preparation of the anhydrous starting material.\textsuperscript{29,30}

Trivalent lanthanide ions are generally incapable of strong exchange interaction due to the unpaired valence electrons being in the 4\textit{f} orbitals, which are closer to the nucleus and lie within the 5\textit{s}\textsuperscript{2} and 5\textit{p}\textsuperscript{6} orbitals.\textsuperscript{31} Therefore, the 4\textit{f} electrons are inner electrons and are less available for effective overlap with ligand orbitals. Thus Ln\textsuperscript{3+} magnetic properties are minimally influenced by the ligands. The exchange interaction in lanthanide complexes can be enhanced by using organic radical-based ligands.\textsuperscript{32} Only a select few radical molecules have been coordinated to lanthanide ions, including nitroxides\textsuperscript{33}, semiquinonates\textsuperscript{34,35} and one example of a verdazyl\textsuperscript{36}. Our group has expanded this list to also include thiazyls. The structural and magnetic properties of Ln(hfac)\textsubscript{3}(1,2,3,5-DTDA)\textsubscript{x} complexes were explored by my colleague Elisabeth Fatila and are pending publication.

My work demonstrates that 1,2,3-DTA can also be coordinated to lanthanide metals. I achieved examples of undimerized lanthanide coordination polymers bridged by a thiazyl radical by coordinating 6,7-Me\textsubscript{2}DTANQ to several Ln(hfac)\textsubscript{3}(monoglyme) starting materials.

\subsection*{4.1.4 Sublimation}

The volatility of our metal-thiazyl complex is necessary in order to employ sublimation techniques that produce a pure crystalline product for magnetic measurements. The hfac ligand plays another essential role in enhancing the volatility of coordination complexes. The metal complexes of 6,7-Me\textsubscript{2}DTANQ are volatile but
require high vacuum to afford any product from dynamic or static sublimations. Unlike the metal-DTDA complexes which can be sublimed at \(~1\times10^{-2}\) Torr, metal-DTA complexes must be sublimed at pressures of \(~1\times10^{-5}\) Torr. To achieve high sublimation yields for metal complexes of 6,7-Me₂DTANQ, we use oil diffusion pumps that provide the necessary vacuum for both dynamic and static sublimations.

Although the metal complexes of a 1,2,3-DTA ligand can be sublimed, they are subject to thermal decomposition at high temperatures. The metal complexes of 6,7-Me₂DTANQ are no different and pure material can be obtained if the sublimation temperature is kept below a certain value. Above this temperature, decomposition occurs and the ligand breaks apart from the M(hfac)₂ fragment. The temperature at which the metal complexes of 6,7-Me₂DTANQ decompose is dependent on the metal. Many dynamic sublimation attempts were performed to determine the ideal temperature, which is high enough to produce good yields but low enough to prevent decomposition. Sublimations of each particular metal complex were carried out by immediately setting the furnace to this ideal temperature. The ideal temperature gradients for each metal complex of 6,7-Me₂DTANQ are reported in the synthesis section of this chapter.

The volatile metal complexes of 6,7-Me₂DTANQ (Mn, Ni, Nd, Gd, and Dy) were dynamically sublimed on a programmable gradient furnace. Metal complexes obtained from dynamic sublimations were microcrystalline and were used for direct physical measurements (EA and magnetometry). The metal complexes of 6,7-Me₂DTANQ that were collected from dynamic sublimations, with the exception of the Mn complex, were not suitable for single crystal X-ray analysis. Instead, the single crystals for X-ray data collection were prepared from slow resublimations through a static sublimation process.
The static sublimation process involved several steps: 1) putting the dynamically sublimed product in the “bottom” of a glass tube, while preventing the sample from touching the sides of the glass using a tube-inside-tube technique. 2) putting the glass tube containing the sample under vacuum (10⁻⁵ Torr) for several days. 3) vertically sealing the “top” of tube with a flame. 4) putting the tube horizontally in a single temperature furnace, and 5) leaving the tube to sublime undisturbed for several weeks.

4.2 Results

4.2.1 Crystallography

Five different metal complexes using 6,7-Me₂DTANQ as the coordination ligand, have been characterized by X-ray crystallography: two transition metal complexes (Mn²⁺ and Ni²⁺) and three lanthanide metal complexes (Nd³⁺, Gd³⁺, and Dy³⁺). All crystal structures were solved and refined by Dr. Michael Jennings. Simple line drawings of the structures for transition metal complexes and lanthanide metal complexes are displayed in Figure 4.01 and Figure 4.02 respectively.
Figure 4.01 Structural formula of tri-nuclear $\text{M(hfac)}_3-(\text{6,7-Me}_2\text{DTANQ})-\text{M(hfac)}_3-(\text{6,7-Me}_2\text{DTANQ})-\text{M(hfac)}_3$ complexes, where $\text{M}^{2+}$ represents the d-block transition metal ions Mn$^{2+}$ and Ni$^{2+}$.

Figure 4.02 Structural formula of polymeric $[\text{Ln(hfac)}_3(\text{6,7-Me}_2\text{DTANQ})]_n$ complexes, where Ln$^{2+}$ represents the f-block lanthanide metal ions Nd$^{3+}$, Gd$^{3+}$ and Dy$^{3+}$.

The single crystal X-ray data for the Mn trimer 4.09 were collected at low temperature (150 K) by Dr. Lough on a brown needle using a Mo X-ray source. The brown needles were grown over 15 days by sublimation under dynamic vacuum ($10^{-5}$ Torr) using a four stage gradient tube furnace that was quickly brought up to the ideal temperature gradient (130, 90, 60, 40 °C). The space group of 4.09 is triclinic $P-1$ with
unit cell dimensions as follows: \( a = 12.178(2), \) \( b = 12.716(3), \) \( c = 12.809(3) \) Å, \( a = 69.55(3)^\circ, \) \( \beta = 76.62(3)^\circ, \) \( \gamma = 68.97(3)^\circ, \) and \( V = 1722.0(6) \) \( \text{Å}^3. \) The final refined model fit the data with an \( R \) value of 4.89 \%. The formula unit of the crystal structure of 4.09 is \((\text{C}_{54}\text{H}_{22}\text{F}_{36}\text{Mn}_{3}\text{N}_{2}\text{O}_{16}\text{S}_{4}),\) with \( Z \) equal to 1. Figure 4.03 shows the asymmetric unit, complete molecule, and crystal packing of 4.09. The Mn trimers are undimerized but have S-O (2.915 and 3.188 Å) and S-S (3.388 Å) close contacts.

Figure 4.03 Crystal structure of 4.09 showing a) one complete molecule of Mn trimer with fluorine and hydrogen atoms omitted for clarity and b) crystal packing between two trimers with intermolecular S-S and S-O contacts, represented by the green and orange dashed lines, respectively.
Figure 4.04 Crystal structure of 4.10 showing a) one complete molecule of Ni trimer with fluorine and hydrogen atoms omitted for clarity and b) crystal packing between two trimers with intermolecular S-S and S-O contacts, represented by the green and orange dashed lines, respectively.

The single crystal X-ray data for the Ni complex 4.10 were collected at low temperature (150 K) by Dr. Lough on a brown needle using a Mo X-ray source. The brown needles were grown by sublimation under static vacuum ($10^{-5}$ Torr) at 140 °C over 11 days. The space group of 4.10 is triclinic $P\overline{1}$ with unit cell dimensions as follows: $a = 12.1205(11)$, $b = 12.5589(11)$, $c = 12.6180(12)$ Å, $\alpha = 68.686(2)^\circ$, $\beta = 77.751(2)^\circ$, $\gamma = 69.302(2)^\circ$, and $V = 1666.1(3)$ Å$^3$. The final refined model fit the data with an $R$ value of 4.17 %. The formula unit of the crystal structure of 4.10 is (C$_{54}$H$_{22}$F$_{36}$Ni$_{3}$N$_{2}$O$_{16}$S$_{4}$), with Z
equal to 1. **Figure 4.04** shows the asymmetric unit, complete molecule, and crystal packing of **4.10**. The Ni trimers are undimerized but have S-O (2.927 and 3.435 Å) and S-S (3.348 Å) close contacts.

The single crystal X-ray data for the Nd complex **4.11** were collected at low temperature (150 K) by Dr. Soldatov on an orange plate using a Mo X-ray source. The orange plates were grown by sublimation under static vacuum (10^-5 Torr) at 144 °C over 1 week. The space group of **4.11** is triclinic *P*-1 with unit cell dimensions as follows: \(a = 9.1102(18)\), \(b = 12.498(3)\), \(c = 16.228(3)\) Å, \(\alpha = 76.95(3)^\circ\), \(\beta = 79.51(3)^\circ\), \(\gamma = 86.67(3)^\circ\), and \(V = 1769.7(6)\) Å³. The final refined model fit the data with an \(R\) value of 7.1 %. The formula unit of the crystal structure of **4.11** is \((C_{27}H_{11}F_{18}NdNO_8S_2)\), with \(Z\) equal to 2. **Figure 4.05** shows the asymmetric unit and a polymeric unit of **4.11**. Individual Nd polymer chains are separated from one another by the bulky hfac ligands, leaving the bridging 6,7-Me₂DTANQ ligands undimerized with no S or O close contacts.

![Crystal structure fragment of 4.11](image)

**Figure 4.05** Crystal structure fragment of 4.11 showing a polymeric unit of one Nd chain with fluorine and hydrogen atoms omitted for clarity.
The single crystal X-ray data for the Gd complex 4.12 were collected at low temperature (150 K) by Dr. Lough on an orange needle using a Cu X-ray source. The orange needles were grown by sublimation under static vacuum (10⁻⁵ Torr) where the furnace temperature was increased from 110°C to 146°C over a period of 19 days. The space group of 4.12 is triclinic P-1 with unit cell dimensions as follows: \( a = 8.9751(9) \), \( b = 16.741(2) \), \( c = 24.576(3) \, \text{Å} \), \( \alpha = 80.887(10)^\circ \), \( \beta = 84.937(11)^\circ \), \( \gamma = 75.917(9)^\circ \), and \( V = 3531.7(7) \, \text{Å}^3 \). The final refined model fit the data with an \( R \) value of 7.26%. The formula unit of the crystal structure of 4.12 is \( (\text{C}_{27}\text{H}_{11}\text{F}_{18}\text{GdNO}_{8}\text{S}_2) \), with \( Z \) equal to 4. Figure 4.06 shows the asymmetric unit and a polymeric unit of 4.12. Individual Gd polymer chains are separated from one another by the bulky hfac ligands, leaving the bridging 6,7-Me₂DTANQ ligands undimerized with no S or O close contacts.

**Figure 4.06** Crystal structure fragment of 4.12 showing a polymeric unit of one Gd chain with fluorine and hydrogen atoms omitted for clarity.
The single crystal X-ray data for the Dy complex 4.13 were collected at low temperature (150 K) by Dr. Soldatov on an orange prism using a Mo X-ray source. The orange prisms were grown by sublimation under static vacuum (10⁻⁵ Torr) at 144 °C over 1 week. The space group of 4.13 is triclinic P-1 with unit cell dimensions as follows: \(a = 8.9360(18)\), \(b = 12.249(2)\), \(c = 16.872(3)\) Å, \(\alpha = 81.42(3)^\circ\), \(\beta = 75.23(3)^\circ\), \(\gamma = 84.07(3)^\circ\), and \(V = 1761.6(6)\) Å³. The final refined model fit the data with an \(R\) value of 3.91 %. The formula unit of the crystal structure of 4.13 is \((\text{C}_{27}\text{H}_{11}\text{F}_{18}\text{DyNO}_8\text{S}_2)\), with \(Z\) equal to 2. Figure 4.07 shows the asymmetric unit and a polymeric unit of 4.13. Individual Dy polymer chains are separated from one another by the bulky hfac ligands, leaving the bridging 6,7-Me₂DTANQ ligands undimerized with no S or O close contacts.

Figure 4.07 Crystal structure fragment of 4.13 showing a polymeric unit of one Dy chain with fluorine and hydrogen atoms omitted for clarity.
4.2.2 Solid-state magnetometry

Currently, of the five metal complexes characterized by X-ray crystallography, magnetic measurements have been conducted on two, 4.09 (M = Mn) and 4.12 (M = Gd). Solid-state samples of the other three metal complexes, 4.10 (M = Ni), 4.11 (M = Nd), and 4.13 (M = Dy), have been appropriately prepared and currently await magnetic measurements. Our collaborator, Dr. Rodolphe Clérac, carried out all magnetic susceptibility measurements using a Quantum Design MPMS-XL SQUID magnetometer. Magnetic measurements of the Mn trimer (4.09) and Gd polymer (4.12) were performed on polycrystalline samples (17.8 mg and 9.0 mg respectively) introduced in a sealed polyethylene bag (3 × 0.5 × 0.02 cm) under argon in a glovebox. The dc measurements were conducted from 300 to 1.8 K (applied field of 1000 Oe) and between -7 T and 7 T applied dc fields. An $M$ vs $H$ measurement was performed at 100 K to confirm the absence of ferromagnetic impurities in the sample. Experimental data were corrected for the sample holder and for the diamagnetic contribution of the sample.

The magnetic properties of the Mn complex (4.09) are shown in Figure 4.08. It is clear that at 280 K, the $\chi T$ ($\chi$ defined as molar magnetic susceptibility (Equation 1.3) per mole of Mn trimer) product of 4.09 is 13.1 cm$^3$Kmol$^{-1}$. Upon cooling, the $\chi T$ product gradually decreases to 12.4 cm$^3$Kmol$^{-1}$ at 110 K, and then increases to a maximum of 15.5 cm$^3$Kmol$^{-1}$ at 14 K. This thermal behaviour is consistent with significant AFM coupling between the ligand and metal ion spins leading to a ferrimagnetic arrangement of the magnetic sites. Upon further cooling, the $\chi T$ product decreases sharply to a minimum of 4.7 cm$^3$Kmol$^{-1}$ at 1.8 K, indicating additional AFM intermolecular interactions.
Based on the crystal structure of 4.09 (Figure 4.03), the magnetic data can be thus modelled on the basis of the following isotropic Heisenberg Hamiltonian:

\[
\hat{H} = -2J_{\text{Mn1-Rad}} \{ \hat{S}_{\text{Mn1}} \cdot \hat{S}_\text{rad} + \hat{S}_{\text{Mn1(ii)}} \cdot \hat{S}_{\text{rad(ii)}} \} - 2J_{\text{Mn2-Rad}} \{ \hat{S}_{\text{Mn2}} \cdot (\hat{S}_\text{rad} + \hat{S}_{\text{rad(ii)}}) \}
\]  

(3.1)

Where \(J_{\text{Mn1-Rad}}\) and \(J_{\text{Mn2-Rad}}\) represent the exchange interactions between radical (\(S = 1/2\)) and Mn1 and Mn2 (\(S = 5/2\)) spins, respectively; and \(\hat{S}_i\) is the spin operator of each magnetic site. There exists no analytical expression for such a spin system. The reason, as explained by our collaborator Dr. Clérac, is that the diagonalization of the spin Hamiltonian is not possible, even in low field. Thus, it is not possible to obtain susceptibility expression via the Kambé method.

The magnetic data were simulated numerically by Dr. Clérac using Magpack software. Inter-complex interactions were introduced into the magnetic model to achieve an adequate fit of the \(\chi T\) experimental data collected between 280 and 1.8 K. The simulation yielded \(J_{\text{Mn1-Rad}/k_B} = -35(1)\) K, \(J_{\text{Mn2-rad}/k_B} = -13(1)\) K, \(zJ'/kB = -0.17(2)\) K, and \(g_{iso} = 2.05(2)\), suggesting an \(S_T = 13/2\) spin ground state for complex 4.09. Figure 4.08 also shows the high field magnetization (\(M\ vs.\ H\); normalized per trimer complex Equation 1.2) at 1.8K is saturated under 7 T at 13.4 \(\mu_B\) as is expected for an \(S_T = 13/2\) ground state.

\[\chi = \frac{\chi_{\text{Mn3Rad}}}{1 - \frac{2zJ'}{Ng^2\mu^2} \chi_{\text{Mn3Rad}}}\]
Figure 4.08 Magnetic measurement diagrams of Mn complex 4.09 showing a) Temperature (K) dependence of the magnetic susceptibility ($\chi T$) product at 1000 Oe (black circles indicate measured data and the red line represents best simulation obtained) and b) applied magnetic field ($H$) dependence of the magnetization ($M$) below 8 K.

The magnetic measurements of the Gd complex (4.12) are shown in Figure 4.09. It is clear that at 298 K, the $\chi T$ ($\chi$ defined as molar magnetic susceptibility (Equation 1.3) of single Gd(hfac)$_3$(6,7-Me$_2$DTANQ) unit) product of 4.12 is 8.75 cm$^3$Kmol$^{-1}$ at 1000 Oe. Decreasing the temperature, the $\chi T$ product (1000 Oe) continuously increases to 1.97 cm$^3$ K/mol at 1.8 K. This thermal behavior clearly indicates the presence of AFM interactions between the Gd$^{3+}$ center and radical ligand.
Figure 4.09 Magnetic measurement diagrams of Gd complex 4.12 showing a) Temperature (K) dependence of the magnetic susceptibility ($\chi T$) product at 1000 Oe (black circles indicate measured data and the red line represents best simulation obtained) and b) applied magnetic field ($H$) dependence of the magnetization ($M$) below 8 K.

Based on the crystal structure of 4.12 (Figure 4.06) the magnetic data can be thus modelled on the basis of the following isotropic Heisenberg Hamiltonian:

$$\hat{H} = -2J\{\hat{S}_{\text{Gd}} \bullet \hat{S}_{\text{rad}}\}$$  \hspace{1cm} (3.2)

Where $J$ is the Gd-radical interaction, and $S_i$ are the spin operators ($S_{\text{Gd}} = 7/2$ for Gd$^{3+}$, $S_{\text{Rad}} = 1/2$ for the 6,7-Me$_2$DTANQ radical). The theoretical expression of the magnetic susceptibility can be estimated with the van Vleck equation,$^{37}$ applying weak field
approximation.\(^2\) However, this model is not able to reproduce the experimental data below 50 K. Thus coupling interactions along the chain must be introduced to the magnetic model in order to fit the low temperature \(\chi T\) product.\(^2\)

The magnetic data were simulated\(^3\) by Dr. Clérac. An adequate simulation of the experimental data was obtained between 280 and 1.8 K, with \(J/k_B = -0.9(1)\) K, \(J'/k_B = -0.25(5)\) K and \(g_{av} = 2.09(5)\), suggesting an \(S_T = 3\) spin ground state for complex 4.12. Figure 4.09 also shows the high field magnetization (\(M\) vs. \(H\); normalized per trimer complex, Equation 1.2) at 1.8 K is saturated under 7 T at 6.3 \(\mu_B\) as is expected for an \(S_T = 3\) ground state.

4.2 Discussion

4.2.1 Structures and properties of metal complexes

The metal complexes of 6,7-Me\(_2\)DTANQ (4.09-4.13) demonstrate that a 1,2,3-DTA ligand is capable of coordinating two metal ions via a monodentate mode at atom O1 and a bidentate mode at atoms N3 and O4. From the crystal structures obtained thus far for transition metal (4.09-4.10) coordination complexes, the ligand 6,7-Me\(_2\)DTANQ seems to induce tri-nuclear (a metal:radical ratio of 3:2) architectures. Results are similar

\(\chi_{\text{dim}} \approx \frac{4N\mu_B^2g_{av}^2}{3k_BT} \frac{21 + 45e^{\frac{8J}{k_BT}}}{7 + 9e^{\frac{8J}{k_BT}}}\)

and the susceptibility due to intercomplex interactions:

\[\chi = \frac{\chi_{\text{dim}}}{1 - \frac{2J'}{Ng^2\mu_B^2} \chi_{\text{dim}}}\]

\(^2\) The van Vleck equation:
for lanthanide (4.11-4.13) coordination complexes, with 6,7-Me₂DTANQ giving polymeric (a metal:radical ratio of 1:1) architectures.

Bond lengths, bond angles, and torsion angles between transition metal ions (Ni and Mn) and 6,7-Me₂DTANQ ligand are presented in Table 4.01. These particular structural parameters are important because they can be used to interpret the measured AFM coupling (Figures 4.08) for the Mn complex (4.09). Both the bond angles and torsion angles in Table 4.01 differentiate whether the overlap of 6,7-Me₂DTANQ radical containing p-orbital is orthogonal or non-orthogonal with respect to Ni²⁺ and Mn²⁺ d-orbitals. As discussed in Chapter 1, the orthogonality of the overlap between metal d-orbitals and radical ligand p-orbitals is a key parameter in the type of magnetic coupling (AFM vs. FM) in transition metals.

Table 4.01 Bond lengths, bond angles, and torsion angles for the Ni and Mn coordination complexes of 6,7-Me₂DTANQ. Atom labels are shown in crystal structure Figures 4.03-4.04.

<table>
<thead>
<tr>
<th>Metal Center 1</th>
<th>Bond Lengths (Å)</th>
<th>Bond Angle</th>
<th>Torsion Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1-N3</td>
<td>2.330(3)</td>
<td>71.02°</td>
<td>4.49°</td>
</tr>
<tr>
<td>M1-O4</td>
<td>2.297(2)</td>
<td>77.27°</td>
<td></td>
</tr>
<tr>
<td>Ni1</td>
<td>2.098(2)</td>
<td>2.155(2)</td>
<td>3.93°</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal Center 2</th>
<th>Bond Lengths (Å)</th>
<th>Bond Angle</th>
<th>Torsion Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>M2-O1</td>
<td>2.203(2)</td>
<td>180.00°</td>
<td>59.76°</td>
</tr>
<tr>
<td>M2-O1</td>
<td>2.096(2)</td>
<td>180.00°</td>
<td>57.09°</td>
</tr>
<tr>
<td>Ni2</td>
<td>2.096(2)</td>
<td>180.00°</td>
<td>57.09°</td>
</tr>
<tr>
<td>Ni2</td>
<td>2.096(2)</td>
<td>180.00°</td>
<td>57.09°</td>
</tr>
</tbody>
</table>

There are three metal centers in the structure of the Mn coordination complex (4.09). These are Mn1 and Mn2 as seen in the crystal structure (Figure 4.03). The
coordination geometries of Mn2 and Mn1 are octahedral and nearly octahedral, respectively. The central Mn2 resides on an inversion center and has two 6,7-Me2DTANQ ligands coordinated in a monodentate fashion with a 180° angle between the two oxygen atoms (O1 and O4). Like many monodentate O-coordinated Mn\(^{2+}\) complexes of nitronylnitroxides\(^{40,41}\), the Mn-O bond is not in the ligand plane. The O1 atom of the 6,7-Me2DTANQ ligand coordinates the Mn2 in a monodentate fashion, with a torsional angle of C2-C1-O1-Mn2 = 59.76°. When a metal is coordinated outside of the ligand plane, it is difficult to determine the resulting orthogonality of the overlapping \(p\)- and \(d\)-orbitals because there are a number of possibilities. Some of the possibilities for 6,7-Me2DTANQ radical are illustrated in Figure 4.10.

On the other hand, the ligand 6,7-Me2DTANQ coordinates the Mn1 center in a bidentate fashion. Like many bidentate N-coordinated Mn\(^{2+}\) complexes of 1,2,3,5-DTDAs\(^{12,14}\), the chelated Mn\(^{2+}\) ion is in the ligand plane. The N3 and O4 atoms of 6,7-Me2DTANQ ligand coordinate the Mn1 in a bidentate fashion producing a slight torsional angle of 4.49° between the ligand plane and the metal equatorial plane. When a metal is chelated it has its \(d\)-orbitals orientated with the ligand’s \(p\)-orbitals such that the orthogonality of the resulting overlap is easy to determine. The bidentate coordination modes for 6,7-Me2DTANQ are compared to the monodentate modes in Figure 4.10.
Figure 4.10 Orbital diagrams of ligand $p$-orbital coordinated to metal $d$-orbital resulting in a-b) monodentate non-orthogonal overlap, where the M-O-C bond is not $180^\circ$ and c-d) bidentate orthogonal overlap, where the ligand and metal are fixed in the same plane.\textsuperscript{42}

The orientation of the overlap does not matter as much for a Mn$^{2+}$ magnetic center because the degenerate orbitals in the $t_{2g}$ and the $e_g$ set all contain one unpaired electron (Figure 4.11). AFM coupling usually occurs for radical-Mn complexes because there is a high probability that there will be non orthogonal $d\pi$-$p\pi$ overlap, regardless of monodentate ($e_g$ and $t_{2g}$) or bidentate ($t_{2g}$) coordination.\textsuperscript{24} However the coupling with the Ni trimer (4.10) may be different due to the d$^8$ electron filling, that is, assuming it has true octahedral symmetry (Figure 4.11).\textsuperscript{43} Unlike the Mn$^{2+}$ magnetic center, when a radical ligand is chelated to a Ni$^{2+}$ center, there is a higher likelihood of FM coupling.\textsuperscript{44,45}

In an octahedral Ni$^{2+}$ ion, the degenerate orbitals ($e_g$ set) that contain unpaired spins ($d_{z^2}$ and $d_{x^2-y^2}$) are fixed orthogonal to the $p$-orbitals of the ligand by virtue of chelation (Figure 4.10).
Figure 4.11 Spin states of octahedral symmetry a) Ni\(^{2+}\) and b) Mn\(^{2+}\).

The Ni trimer complex (4.10) packs in the same fashion as the Mn trimer (4.09) and therefore also possesses two distinct Ni centers. These centers are Ni1 and Ni2 as seen in the crystal structure (Figure 4.04). The coordination geometries of both Ni2 and Ni1 are octahedral. Again, the central Ni2 resides on an inversion center and has two 6,7-Me\(_2\)DTANQ ligands coordinated in a monodentate fashion with a 180° angle between the two oxygen atoms (O1 and O4). The torsion angle at which the Ni2 center is coordinated to the O4 atom of the ligand is C2-C1-O1-Ni2 = 57.09°. The resulting coupling between the Ni2 center and the 6,7-Me\(_2\)DTANQ is more difficult to predict since they do not lie in the same plane. However, the Ni1 center of the trimer exists in the same plane as 6,7-Me\(_2\)DTANQ (C3-C4-N3-Ni1 = 3.93°) and therefore FM coupling between paramagnetic ligand and Ni1 magnetic center is anticipated. A sample of 4.10 has been sent for magnetic measurement. Once the results are obtained, a more definite answer may be provided.

The 6,7-Me\(_2\)DTANQ bridging radical ligand acts to mediate magnetic coupling between the metal centres owing to the significant spin density at both the N3 and O4 atoms of the ligand (Figure 3.10 in Chapter 3). The AFM coupling interaction between
Mn1 and ligand is stronger than the coupling between Mn2 and ligand signified by the $J/k_B$ values of -35(1) K and -13(1) K, respectively. This is likely due to the larger spin density at the N3 vs. the O9, atom but may also be related to the atoms in-plane coordination motif. The spin system of the Mn trimer (4.09) is illustrated in Figure 4.12, and has a spin ground state of $S_T = 13/2$, which is the highest to date for any thiazyl-metal system.

![Spin System Illustration](image)

**Figure 4.12** A simplified illustration of a) the the spin system of an isolated Mn trimer and b) the coupling exchange between two Mn trimers.

There also exists an intermolecular exchange parameter ($J'/k_B = -0.17(2)$ K). Below 15 K, the $\chi T$ product decreases sharply to a minimum of 6.7 cm$^3$Kmol$^{-1}$ at 1.8 K (Figure 4.08), characterizing an intermolecular AFM interactions. The AFM exchange (Figure 4.12) occurs through a close S-S contact (3.388 Å) between nearby DTA rings of neighbouring trimer units (Figure 4.03) despite the existence of close S-O contacts (2.915 and 3.188 Å) which have been shown to direct FM exchange between...
neighbouring DTDA-Mn complexes. It is reasonable to assume that non-orthogonal overlap occurs between the SOMOs of 6,7-Me2DTANQ at this S-S contacts, establishing the mechanism of intermolecular AFM exchange in the Mn trimer (4.09).

The Ni trimer (4.10) also has similar close contacts (S-S = 3.348 Å and S-O = 2.927 Å). From the magnetic behaviour observed in the Mn complex, it is likely that the S-S close contact will mediate AFM exchange between Ni trimer units. Assuming that AFM exchange occurs between ligands and that FM coupling occurs between Ni and ligand, then Ni metal centers of neighbouring trimer units should have their spins aligned anti-parallel.

Bond lengths, bond angles, and torsion angles between lanthanide metal ions (Nd, Gd, and Dy) and 6,7-Me2DTANQ ligand are presented in Table 4.03. The coordination of 6,7-diMeDTANQ to Ln3+ metals gives polymeric structures. Such structures are common for coordinating a ligand with multiple oxygen coordination sites, and have been reported for both nitronylnitroxides and verdazyl. The crystal structures of 6,7-Me2DTANQ with the Ln3+ ions (Figure 4.05-4.07) are similar with subtle differences. The Gd structure differs from the Nd and Dy structure in that is has two distinct metal centers, although as seen in Table 4.02 the differences (bond angles and lengths) are essentially negligible. The coordination number of the Ln3+ complexes (4.11-4.13) is nine. The 6,7-Me2DTANQ ligand coordinates two Ln3+(hfac)3, one at its monodentate site (O1) and the other through its bidentate site (O4 and N3) to create infinite coordination chains. The coordination chains isolate 6,7-Me2DTANQ from forming any S-O or S-S close contacts by virtue of the steric bulk of the hfac auxiliary ligand.
Unlike the transition metal complexes, the lanthanide metal complexes coupling with a radical ligand cannot be predicted on a simple orbital overlap scheme. For lanthanides, the unpaired electrons occupy the f-orbitals, which are more core-like. Therefore the electrons that give rise to the magnetic properties are in orbital that are less available to overlap with ligand orbitals. The limited overlap between the valence orbitals of a lanthanide ion and ligand provides an explanation as to why the AFM coupling between Gd (4.12; $J/k_B = -0.9(1)$ K) and 6,7-Me$_2$DTANQ is weaker than that exhibited between Mn (4.09; $J/k_B = -35(1)$ K and -13(1) K) and 6,7-Me$_2$DTANQ. The AFM coupling which occurs within the polymeric Gd coordination complex can be viewed magnetically as a dimerization process occurring between Gd$^{3+}$ and the paramagnetic ligand centers, which strengthens with decreasing temperature. The spin ground state of 4.12 is $S_T = 3$, which is the product of AFM coupling between Gd$^{3+}$ and radical (Figure 4.13).

**Table 4.02 Bond lengths, bond angles, and torsion angles for the Nd, Gd, and Dy coordination complexes of 6,7-Me$_2$DTANQ (4.11-4.13).**

There are two distinct Gd centers in the unit cell with slightly different environment. Atom labels are shown in crystal structure Figures 4.05-4.07.

<table>
<thead>
<tr>
<th>Metal Center</th>
<th>Bond Lengths (Å)</th>
<th>Bond Angle</th>
<th>Torsion Angle</th>
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<tr>
<td></td>
<td>Ln-N3</td>
<td>Ln-O4</td>
<td>Ln-O1</td>
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<tr>
<td>Nd</td>
<td>2.680(8)</td>
<td>2.631(7)</td>
<td>2.454(7)</td>
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<tr>
<td>Gd</td>
<td>2.59(1)</td>
<td>2.60(1)</td>
<td>2.43(1)</td>
</tr>
<tr>
<td>Dy</td>
<td>2.60(1)</td>
<td>2.58(1)</td>
<td>2.43(1)</td>
</tr>
<tr>
<td></td>
<td>2.585(3)</td>
<td>2.586(3)</td>
<td>2.400(3)</td>
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</table>
Below 50 K, strong intermolecular AFM coupling is apparent. The intermolecular AFM coupling can be viewed magnetically as inter-trimer interactions along the radical-Ln$^{3+}$ chain.\textsuperscript{33} The inter-trimer interactions are illustrated in Figure 4.13.

\[
\begin{array}{c}
\text{radical} & \begin{array}{c}
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(a)

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\end{array} \\
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\text{AFM} & \text{AFM} & \text{AFM}
\end{array}
\]

(b)

Figure 4.13 A simplified illustration of a) the spin system of an isolated Gd polymer and b) the inter-trimer coupling exchange along the chain.

4.3 Synthesis

4.3.1 General considerations

All metal coordinations were performed under Ar$_{(g)}$ atmosphere using standard Schlenk and glove box techniques. 1,2-Dichloroethane (DCE) was dried on a SP-1 Stand Alone Solvent Purification System from LC Technology Solutions Inc, using molecular sieves (3 Å). All commercial reagents were used as received. Hexafluoroacetylacetonate (Hhfac) and dimethoxyethane (DME) were purchased from Alfa Aesar and Acros respectively and used as received. M(hfac)$_2$(THF)$_2$\textsuperscript{12} and Ln(hfac)$_3$(DME)$^{29}$ starting materials were prepared according to literature methods. 6,7-Dimethyl-4,9-dioxo-naphtho[1,2-d][1,2,3]dithiazolyl (3.04) was prepared according to the synthetic procedure
previously reported in Chapter 3. IR (KBr pressed pellet) spectra were recorded on a Nicolet 4700 FT-IR spectrometer at 4 cm$^{-1}$ resolution. Elemental analyses were performed by MHW Labs, Phoenix, AZ, USA. Crystal data for complex 4.09 was collected by Dr. Alan Lough at the University of Toronto on a Nonius Kappa-CCD System. Crystal data for complexes 4.10-4.11 were collected by Dr. Alan Lough at the University of Toronto on a Bruker APEX-II CCD. Crystal data for complexes 4.12-4.13 were collected by Dr. Dmitriy Soldatov at the University of Guelph on a SuperNova diffractometer with Atlas CCD detector. All crystal structures solutions and refinements were done by Dr. Michael Jennings. Magnetic susceptibility measurements were performed by Dr. Rodolphe Clérac using a Quantum Design MPMS-XL SQUID magnetometer.

4.3.2 Fully characterized complexes

Mn(hfac)$_2$-Rad-Mn(hfac)$_2$-Rad-Mn(hfac)$_2$ (4.09). Dry DCE (300 mL) was added to a solid mixture of Mn(hfac)$_2$(THF)$_2$ (0.4740 g, 0.773 mmol) and 3.04 (0.1997 g, 0.762 mmol), under inert atmosphere, generating a dark green slurry. After 1 h of gentle heating and stirring, an olive green solution, free of precipitates, was obtained. The solvent was removed in vacuo resulting in a dark green powder of 4.09. Crude yield: 0.5509 g of total mass was recovered. A portion of the crude product (0.2533 g) was purified by sublimation under dynamic vacuum ($10^{-5}$ Torr) using a four stage gradient tube furnace. The best yields were obtained by quickly ramping the furnace up to the ideal temperature gradient (130, 90, 60, 40 °C). Dynamic vacuum sublimation afforded dark emerald green crystals of 4.09. Sublimation yield: 0.0955 g (0.0494 mmol, 41%). IR(KBr) ν/cm$^{-1}$: 1645
Crystal data: Nonius Kappa CCD, radiation source Mo K\(\alpha\), wavelength = 0.71073 Å, at University of Toronto; \(T = 150(2)\) K; monoclinic, \(P-1\); \(a = 12.178(2), b = 12.716(16), c = 12.809(3)\) Å; \(\alpha = 69.55(3)^\circ, \beta = 113.03(3)^\circ, \gamma = 68.97(3)^\circ; V = 1722.0(6)\) \(\text{Å}^3\); \(Z = 1\); \(R = 4.89\%\). Elemental Anal. Calc. for \(\text{C}_{54}\text{H}_{22}\text{F}_{36}\text{Mn}_{3}\text{N}_{2}\text{O}_{12}\text{S}_{4}\): C, 33.57; H, 1.15; N, 1.45%. Found: C, 33.36; H, 1.32; N, 1.42%.

\(\text{Ni(hfac)}_2\text{-Rad-Ni(hfac)}_2\text{-Rad-Ni(hfac)}_2\) (4.10). Dry DCE (350 mL) was added to a solid mixture of \(\text{Ni(hfac)}_2(\text{THF})_2\) (0.4666 g, 0.756 mmol) and 3.04 (0.1981 g, 0.755 mmol), under inert atmosphere, generating a dark green slurry. After 1 h of gentle heating and stirring, a bright yellow solution, free of precipitates, was obtained. The solvent was removed in vacuo resulting in a dark green powder of 4.10. Crude yield: 0.4877 g of total mass was recovered. A portion of the crude product (0.2521 g) was purified by sublimation under dynamic vacuum (10\(^{-5}\) Torr) using a four stage gradient tube furnace. The best yields were obtained by quickly ramping the furnace up to the ideal temperature gradient (132, 100, 70, 40 °C). Sublimation yielded 0.0965 g (0.0497 mmol, 38%) of brown polycrystalline material. Static vacuum sublimation (10\(^{-5}\) Torr) afforded dark brown single crystals of 4.10. IR(KBr) v/cm\(^{-1}\): 1643 (s), 1573 (m), 1560 (w), 1532 (w), 1482 (m), 1420 (m), 1331 (w), 1301 (m), 1256 (s), 1198 (s), 1148 (s), 1099 (w), 1043 (w), 951 (w), 907 (w), 844 (w), 799 (s), 770 (w), 744 (w), 734 (w), 675 (s), 648 (w), 589 (s), 530 (w), 503 (w), 469 (w), 425 (w). Crystal data: Bruker APEX-II CCD, radiation
source Mo K\(\alpha\), wavelength = 0.71073 Å, at University of Toronto; \(T = 150(2)\) K; monoclinic, \(P\)-1; \(a = 12.1205(11), b = 12.5589(11), c = 12.6180(12)\) Å; \(\alpha = 68.686(2)°, \beta = 77.751(2)°, \gamma = 69.302(2)°; V = 1666.1(3) \text{Å}^3; Z = 1; R = 4.17\%.\) Elemental Anal. Calc. for \(C_{54}H_{22}F_{36}Ni_{3}N_{2}O_{12}S_{4}\): C, 33.38; H, 1.14; N, 1.44. Found: C, 33.47; H, 1.14; N, 1.56%.

**Nd(hfac)$_3$(6,7-diMeDTANQ) (4.11).** Dry DCE (300 mL) was added to a solid mixture of Nd(hfac)$_3$(DME) (0.2405 g, 0.281 mmol) and **3.04** (0.0735 g, 0.280 mmol), under inert atmosphere, generating a dark green slurry. After 1 h of gentle heating and stirring, a bright green solution, free of precipitates, was obtained. The solvent was removed *in vacuo* resulting in a dark purple powder of **4.11** (crude yield: 0.2386 g). The crude product (0.2386 g) was purified by sublimation under dynamic vacuum (10$^{-5}$ Torr) using a four stage gradient tube furnace. The best yields were obtained by quickly ramping the furnace up to the ideal temperature gradient (140, 100, 70, 40 °C). Sublimation yielded 0.0265 g (0.0258 mmol, 11%) of orange polycrystalline material. Static vacuum sublimation (10$^{-5}$ Torr) afforded orange single crystals of **4.11.** IR(KBr) ν/cm$^{-1}$: 1649 (s), 1611 (w), 1577 (w), 1560 (w), 1534 (w), 1492 (m), 1421 (w), 1353 (w), 1257 (s), 1207 (s), 1146 (s), 1098 (w), 1047 (w), 1021 (w), 996 (w), 950 (w), 900 (w), 864 (m), 806 (s), 762 (w), 741 (w), 694 (w), 685 (w), 660 (s), 641 (w), 585 (s), 528 (w), 463 (w), 421 (w).

**Crystal data:** SuperNova Atlas CCD, radiation source Mo K\(\alpha\), wavelength = 0.71073 Å, at University of Guelph; \(T = 150(2)\) K; monoclinic, \(P\)-1; \(a = 9.1102(18), b = 12.498(3), c = 16.228(3)\) Å; \(\alpha = 76.95(3)°, \beta = 79.51(3)°, \gamma = 86.67(3)°; V = 1769.7(6) \text{Å}^3; Z = 2; R =\)
Elemental Anal. Calc. for C$_{27}$H$_{11}$F$_{18}$NdNO$_8$S$_2$: C, 31.55; H, 1.08; N, 1.36. Found: C, 31.22; H, 1.40; N, 1.36%.

**Gd(hfac)$_3$(6,7-diMeDTANQ) (4.12).** Dry DCE (300 mL) was added to a solid mixture of Gd(hfac)$_3$(DME) (0.3905 g, 0.450 mmol) and 3.04 (0.1009 g, 0.385 mmol), under inert atmosphere, generating a dark green slurry. After 1 h of gentle heating and stirring, a bright green solution, free of precipitates, was obtained. The solvent was removed *in vacuo* resulting in a dark blue powder of 4.12 (crude yield: 0.4070 g). A portion of the crude product (0.2051 g) was purified by sublimation under dynamic vacuum (10$^{-5}$ Torr) using a four stage gradient tube furnace. The best yields were obtained by quickly ramping the furnace up to the ideal temperature gradient (136, 90, 70, 40 °C). Sublimation yielded 0.0714 g (0.0686 mmol, 35%) of orange polycrystalline material. Static vacuum sublimation (10$^{-5}$ Torr) afforded orange single crystals of 4.12. **IR(KBr)**

\[ \nu/\text{cm}^{-1}: 2963 \text{ (w)}, 2920 \text{ (w)}, 2852 \text{ (w)}, 1686 \text{ (w)}, 1650 \text{ (s)}, 1578 \text{ (w)}, 1561 \text{ (w)}, 1530 \text{ (w)}, 1499 \text{ (w)}, 1492 \text{ (w)}, 1478 \text{ (w)}, 1468 \text{ (w)}, 1451 \text{ (w)}, 1400 \text{ (w)}, 1383 \text{ (w)}, 1356 \text{ (w)}, 1313 \text{ (w)}, 1257 \text{ (s)}, 1209 \text{ (s)}, 1146 \text{ (s)}, 1099 \text{ (w)}, 1045 \text{ (w)}, 951 \text{ (w)}, 906 \text{ (w)}, 864 \text{ (w)}, 801 \text{ (m)}, 741 \text{ (w)}, 695 \text{ (w)}, 661 \text{ (m)}, 586 \text{ (m)}. \]

**Crystal data:** Bruker APEX-II CCD, radiation source Cu Kα, wavelength = 1.54178 Å, at University of Toronto; \( T = 147(2) \) K; monoclinic, \textit{P}1; \( a = 8.9751(9), b = 16.741(2), c = 24.576(3) \) Å; \( \alpha = 80.887(10)^{\circ}, \beta = 84.937(11)^{\circ}, \gamma = 75.917(9)^{\circ}; V = 3531.7(7) \) Å\(^3\); \( Z = 4; R = 7.26\%. \) **Elemental Anal.** Calc. for C$_{27}$H$_{11}$F$_{18}$GdNO$_8$S$_2$: C, 31.16; H, 1.07; N, 1.35. Found: C, 30.89; H, 1.41; N, 1.30%. 118
**Dy(hfac)$_3$(6,7-diMeDTANQ) (4.13).** Dry DCE (300 mL) was added to a solid mixture of Dy(hfac)$_3$(DME) (0.2803 g, 0.321 mmol) and 3.04 (0.0823 g, 0.314 mmol), under inert atmosphere, generating a dark green slurry. After 1 h of gentle heating and stirring, a bright green solution, free of precipitates, was obtained. The solvent was removed *in vacuo* resulting in a dark purple powder of 4.13 (crude yield: 0.3200 g). A portion of the crude product (0.1850 g) was purified by sublimation under dynamic vacuum (10$^{-5}$ Torr) using a four stage gradient tube furnace. The best yields were obtained by quickly ramping the furnace up to the ideal temperature gradient (140, 100, 70, 40 °C). Sublimation yielded 0.0188 g (0.0180 mmol, 10%) of orange polycrystalline material. Static vacuum sublimation (10$^{-5}$ Torr) afforded orange single crystals of 4.13. IR(KBr) $\nu$/cm$^{-1}$: 1654 (s), 1580 (m), 1559 (w), 1529 (w), 1500 (m), 1478 (w), 1400 (w), 1341 (w), 1313 (w), 1257 (s), 1254 (s), 1209 (s), 1144 (s), 1101 (w), 1045 (w), 998 (w), 952 (w), 906 (w), 836 (w), 797 (m), 766 (w), 741 (w), 734 (w), 691(w), 661 (s), 586 (m), 528 (w), 496 (w), 467 (w), 434 (w), 424 (w). **Crystal data:** SuperNova Atlas CCD, radiation source Mo K$\alpha$, wavelength = 0.71073 Å, at University of Guelph; $T$ = 150(2) K; monoclinic; $P-1$; $a = 8.9360(18)$, $b = 12.249(2)$, $c = 16.872(3)$ Å; $\alpha = 81.42(3)^{\circ}$, $\beta = 75.23(3)^{\circ}$, $\gamma = 84.07(3)^{\circ}$; $V = 1761.6(6)$ Å$^3$; $Z = 2$; R = 3.91%. **Elemental Anal.** Calc. for C$_{27}$H$_{11}$F$_{18}$DyNO$_8$S$_2$: C, 31.16; H, 1.06; N, 1.34. Found: C, 30.26; H, 0.93; N, 1.28%.

### 4.3.3 Partially characterized complexes

**Co(hfac)$_2$(6,7-diMeDTANQ) (4.14).** Dry DCE (300 mL) was added to a solid mixture of Co(hfac)$_2$(THF)$_2$ (0.2633 g, 0.427 mmol) and 3.04 (0.1094 g, 0.417 mmol), under inert atmosphere, generating dark green slurry. After 1 h of gentle heating and
stirring, a red solution, free of precipitates, was obtained. The solvent was removed *in vacuo* resulting in a dark green powder of 4.14. Crude yield: 0.2581 g, 84% of total mass was recovered (minus the mass contribution from THF placeholders). The crude product 0.2581 g) was obtained by sublimation under dynamic vacuum (10⁻⁵ Torr) using a four stage gradient tube furnace. Different sublimation attempts (138, 100, 60, 40 °C and 134, 90, 60, 40 °C) yielded both a black polycrystalline product (4.14) and purple crystals (3.04) in two landing zones. The two landing zones were not well separated and the IR spectrum of the sublimed black polycrystalline product suggests a mixture of 4.14 and 3.04. IR (KBr) v/cm⁻¹: 2963 (w), 2918 (w), 2849 (w), 1686 (w), 1676 (w), 1642 (s), 1590 (m), 1571 (w), 1560 (m), 1529 (w), 1509 (w), 1491 (w), 1476 (w), 1459 (w), 1302 (s), 1260 (s), 1204 (s), 1148 (s), 1097 (s), 1049 (s), 925 (w), 801 (s), 754 (w), 731 (w), 697 (w), 670 (m), 587 (m), 531 (w), 518 (w), 490 (w), 469 (w), 437 (w), 421 (w).

Ce(hfac)₃(6,7-diMeDTANQ) (4.15). Dry DCE (300 mL) was added to a solid mixture of Ce(hfac)₂(DME) (0.3520 g, 0.413 mmol) and 3.04 (0.1036 g, 0.394 mmol), under inert atmosphere, generating dark green slurry. After 1.5 h of gentle heating and stirring, a green solution, free of precipitates, was obtained. The solvent was removed *in vacuo* resulting in a brown solid plus some sticky green oil. Hexanes (75 mL) were added to the crude product and removed *in vacuo* to get sticky brown and green solids. Crude yield: 0.4036 g, 95%. A portion of the crude product (0.2570 g) was sublimed under dynamic vacuum (10⁻⁵ Torr) using a four stage gradient tube furnace. A yellow polycrystalline product was obtained by increasing the furnace temperature up to a maximum (190, 90, 70, 40 °C) over 5 days. The amount of sublimed product was only enough for
characterization by IR. IR (KBr) ν/cm:\n2962 (w), 2917 (w), 2849 (w), 1655 (s), 1584 (w), 1560 (w), 1533 (w), 1474 (s), 1407 (w), 1383 (w), 1344 (w), 1289 (m), 1257 (s), 1214 (s), 1145 (s), 1100 (m), 1057 (w), 1025 (w), 802 (s), 741 (w), 660 (s), 584 (m), 528 (w), 496 (w), 487 (w), 461 (w), 432 (m).

**Pr(hfac)$_3$(6,7-diMeDTANQ) (4.16).** Dry DCE (400 mL) was added to a solid mixture of Pr(hfac)$_2$(DME) (0.5215 g, 0.612 mmol) and 3.04 (0.1563 g, 0.596 mmol), under inert atmosphere, generating a dark green slurry. After 2 h of gentle heating and stirring, an orange solution, free of precipitates, was obtained. The solvent was removed in vacuo resulting in a sticky green solid. The sticky product eventually became a solid after being left under Ar$_{(g)}$ for 14 days. Crude yield: 0.4995 g, 71%. A portion of the sticky crude product (0.1230 g) was sublimed under dynamic vacuum (10$^{-5}$ Torr) using a four stage gradient tube furnace. By slowly increasing the furnace temperature over 8 days, an orange powder (175, 90, 70, 40 °C) and yellow polycrystalline product (200, 90, 70, 40 °C) were obtained. Sublimation yielded 0.0058 g (0.00566 mmol, 5%) of orange powder. Sublimed yellow product was not isolated or characterized. IR (KBr) ν/cm:\n2963 (w), 2918 (w), 2850 (w), 1649 (s), 1611 (w), 1578 (m), 1555 (m), 1529 (m), 1492 (s), 1396 (m), 1341 (w), 1313 (w), 1254 (s), 1217 (s), 1144 (s), 1100 (m), 1098 (w), 1044 (w), 950 (w), 904 (w), 835 (w), 798 (s), 766 (w), 741 (w), 734 (w), 660 (s), 584 (s), 528 (w), 493 (w), 464 (w), 447 (w), 433 (w), 422 (w).

**Lu(hfac)$_2$(6,7-diMeDTANQ) (4.17).** Dry DCE (400 mL) was added to a solid mixture of Lu(hfac)$_2$(DME) (0.4683 g, 0.528 mmol) and 3.04 (0.1370 g, 0.522 mmol), under inert
atmosphere, generating a dark green slurry. After 2 h of gentle heating and stirring, a green solution, free of precipitates, was obtained. The solvent was removed in vacuo resulting in a dark purple solid. Crude yield: 0.5153 g, 70%. A portion of the crude product (0.2500 g) was sublimed under dynamic vacuum (10⁻⁵ Torr) using a four stage gradient tube furnace. By increasing the furnace temperature 5°C over 2 days, a blue powder (140, 100, 70, 40 °C) and purple crystals (145, 100, 70, 40 °C) were obtained. The purple crystals were identified as 3.04 by IR. Sublimation yielded 0.0474 g (0.0337 mmol, 19%) of blue powder. IR (KBr) v/cm⁻¹: 2963 (w), 2919 (w), 2850 (w), 1654 (s), 1611 (w), 1578 (m), 1560 (m), 1534 (m), 1508 (m), 1501 (m), 1491 (w), 1477 (w), 1437 (w), 1391 (w), 1376 (w), 1259 (s), 1206 (s), 1146 (s), 1103 (m), 1035 (w), 899 (w), 876 (w), 801 (s), 742 (w), 729 (w), 686 (w), 662 (s), 589 (m), 528 (w), 500 (w), 472 (w), 453 (w), 436 (w), 422 (w), 417(w). Elemental Anal. Calc. for C₂₇H₁₁F₁₈LuNO₈S₂: C, 30.17; H, 1.25; N, 1.02. Found: C, 29.86; H, 1.85; N, 1.17%.

4.3.4 Unsuccessful coordinations

Cu(hfac)₂(6,7-diMeDTANQ) (4.18). Dry DCE (300 mL) was added to a solid mixture of Cu(hfac)₂(THF)₂ (0.2636 g, 0.424 mmol) and 3.04 (0.1103 g, 0.421 mmol), under inert atmosphere, generating dark green slurry. After 2 h of gentle heating and stirring, a green solution, free of precipitates, was obtained. The solvent was removed in vacuo resulting in a mixture of two distinctly different powders (green and purple). The IR of the green powder matches Cu(hfac)₂(THF)₂ and the IR of the purple powder matches 3.04. The IR spectra suggest that 3.04 will not coordinate to a Cu²⁺ ion.
4.4 Future work

Sublimation attempts of the Co complex (\textbf{4.14}) have so far resulted in both 6,7-\textit{Me}_2\textit{DTANQ} and \textbf{4.14} subliming together. The Co complex (\textbf{4.14}) cannot be studied by magnetometry if sublimed samples are contaminated with ligand. However, synthesis of the Co complex (\textbf{4.14}) were only attempted in a 1:1 ligand-to-metal ratio; before the realization that coordination of 6,7-\textit{Me}_2\textit{DTANQ} with transition metals preferentially gives trinuclear complexes. This stoichiometry puts the ligand in excess, relative to the metal starting material and this might be the reason for 6,7-\textit{Me}_2\textit{DTANQ} subliming along with \textbf{4.14}. If the coordination synthesis is carried out in a 3:2 metal-to-ligand ratio then the sublimation of \textbf{4.14} might work.

With the Ni complex of 6,7-\textit{Me}_2\textit{DTANQ}, clearly a trinuclear product (\textbf{4.10}) can be sublimed. But there is evidence that a monomeric Ni species might exist. My colleague Ian Morgan acquired a crystal structure of \textit{DTANQ} (\textbf{2.52}) coordinated to \textit{Ni(hfac)}\textsubscript{2} in a monomeric fashion. During sublimations of \textbf{4.10}, more than one product region has been observed. In some cases, both product regions were characterized as trimer, but there has been at least one instance where the IR, EA and PXRD suggest monomer. Yet we have not managed to isolate and fully characterize the monomer to date. It could be that a rigid octahedral coordination environment imposed by a \textit{d}^8 ion that makes the trimer less stable than for a \textit{d}^6 ion. This might explain why there is some evidence for complexes other than trimer in the case of \textit{Ni}^{2+} but not \textit{Mn}^{2+}. The monomer would have interesting properties and if it does exist, then it is worthwhile trying to isolate.
With the Ce complex (4.15), sublimation gave a low yield of product and required unusually high temperatures. Also, the Ce sublimation product was yellow instead of orange (Ln complexes 4.11-4.13 and 4.16). These unusual observations might have been a result of attempting to sublime sticky crude product instead of solid crude product. Future sublimation attempts should be attempted on crude 4.15 that has been given sufficient time to solidify. Although, the yellow product that was produced from the sublimation of 4.15 might actually be the desired product but it needs further characterization to verify this.

With the Pr complex (4.16), sublimations gave both an orange product and a yellow product. The orange product appears to be the desired product but it was in low yield. The yellow product sublimed at a higher temperature than the orange product and has not been identified. Complex 4.16 holds promise for full characterization but would require repeated sublimation attempts before enough material was collected for both EA and magnetometry. A similar yellow sublimation product existed for the Ce complex (4.15). Yellow sublimation products might be a result of moving left along the 4f block.

With the Lu complex (4.17), sublimations gave a blue film that has been confirmed by EA to be pure. However, the sublimed blue powder of 4.17 holds little promise of producing single crystals. Lu has a filled 4f orbital set and is magnetically inactive and therefore, the structure and magnetometry of 4.17 is desirable because it can assist in modeling the Dy (4.11) and Nd (4.13) complexes. Sublimations of the Dy complex (4.13) also produced a blue film (minor product) in addition to the polycrystalline orange solid (major product). This observation suggests that the Ln blue powder will not be isostructural to the sublimed orange Dy complex (4.13) but likely
related to the sublimed blue Dy complex. Blue sublimation products might be a result of moving right along the 4f block.
4.5 References


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CHAPTER 5

4-benzoyl-$5H$-1,2,3-dithiazol-5-one
5.1 Introduction

5.1.1 Reactivity

Monocyclic dithiazole chemistry is derived from 4,5-dichloro-1,2,3-dithiazolium chloride (Appel’s salt; 5.01).\(^1\)\(^-\)\(^3\) Appel’s salt is readily prepared from the reaction of chloroacetonitrile and sulfur monochloride (Figure 5.01) to afford a pale greenish-yellow solid.\(^4\) Appel’s salt is a stable compound in dry inert atmosphere, but it will react slowly with water and hydrogen sulfide (Figure 5.01) to form 4-chloro-1,2,3-dithiazol-5-one (5.02) and 4-chloro-1,2,3-dithiazole-5-thione (5.03), respectively.\(^5\) Indeed, the C5 position of 5.01 readily undergoes nucleophilic attack. However, this makes it a useful synthetic precursor to achieve a number of 5-substituted 1,2,3-dithiazolium chlorides.\(^6\) For instance, 5.01 readily reacts with anilines (Figure 5.01) to give stable 5-(arylimino)-4-chloro-5H-1,2,3-dithiazoles (5.04).\(^4\)

![Figure 5.01 Reaction of a) chloroacetonitrile and sulfur monochloride to give Appel's salt (5.01); and 5.01 with b) water, c) hydrogen sulfide, and d) substituted anilines.\(^5\)](image)
While the chlorine at the C5 position of 5.01 is easily substituted, the chlorine at the C4 position appears to be relatively inert. The substitution of the C4 via direct displacement of the chlorine atom was reported by Rees et al. The formation of dithiazolobenzoxazine (5.05) is thought to involve displacement of the chlorine atom at the C4 position through intermolecular nucleophilic attack by a phenoxide ion. However, there is no characterization data to validate this claim.

![Diagram](5.05)

For the related iminodithiazoles (5.04), replacement of the chlorine atom at the C4 position can be achieved through reaction with excess (6 equivalents) secondary alkylamines to give 5-(arylimino)-4-(dialkylamino)-5H-1,2,3-dithiazoles (5.06). The proposed mechanism (Figure 5.02) for the formation of 5.06 is ring-opening and subsequent recyclization, which does not proceed through direct displacement of the chlorine atom.

![Diagram](5.04_to_5.06)

**Figure 5.02** Proposed reaction mechanism of 5.04 with a secondary alkylamine to give 5-(arylimino)-4-(dialkylamino)-5H-1,2,3-dithiazole (5.06).

The reaction of monosubstituted acetonitriles and sulfur monochloride gives 5-substituted 1,2,3-dithiazolium chlorides. Utilizing this synthetic strategy, substituents with poor nucleophilicity (*ie* carbon-based backbones) can be placed at the C5 position of
1,2,3-dithiazolium chlorides. For example, reaction of pentafluorophenylacetonitrile with excess S$_2$Cl$_2$ gives 1,2,3-dithiazolium chloride (5.07) (Figure 5.03).\textsuperscript{9}

![Figure 5.03 Reaction of pentafluorophenylacetonitrile with S$_2$Cl$_2$ to give 5.07.]

**5.1.2 4-Substituted 1,2,3-dithiazol-5-ones**

Since the chlorine of the C4 position of 5.02 cannot be displaced by nucleophiles, an alternative synthetic strategy must be used to achieve the 4-substituted 1,2,3-dithiazol-5-one species. One such method was reported by Rees \textit{et al.}\textsuperscript{10} The reaction of acetophenone oxime (5.08) with an excess of sulfur monochloride gives an intermediate solid product (Figure 5.04). When the intermediate species is reacted \textit{in situ} with water, a 33\% yield of 4-phenyl-1,2,3-dithiazol-5-one (5.10) is achieved (Figure 4.04).\textsuperscript{11} Presumably, the intermediate species is 5.09, although it has not been fully characterized because it is difficult to purify. Alternatively, 5.09 can be reacted with a primary aromatic amine to give 4-phenyl-5-arylimino-1,2,3-dithiazole (5.11) in yields between 30-40\%.\textsuperscript{11} Possible mechanisms for the formation of 5.09 by conversion of acetophenone oxime and S$_2$Cl$_2$ into dithiazolium salt were proposed by Reese and are shown in Figure 5.05.\textsuperscript{11}
Figure 5.04 Reaction of a) acetophenone oxime with excess sulfur monochloride, followed by \textit{in situ} treatment of 5.09 intermediate with b) water and c) aniline.\textsuperscript{11}

Figure 5.05 Proposed reaction mechanisms for the formation of 5.09 from acetophenone oxime, whereby: a) the nitrogen lone pair attacks S\textsubscript{2}Cl\textsubscript{2} and b) the ene double bond of hydroxylamine tautomer attacks S\textsubscript{2}Cl\textsubscript{2}, to form the 5.12 intermediate species, which is subsequently chlorinated by S\textsubscript{2}Cl\textsubscript{2}, followed by acid-catalyzed aromatization.

Recently, Konstantinova \textit{et al.} reported a one-pot reaction to selectively obtain 4-substituted 1,2,3-dithiazol-5-ones and 1,2,3-dithiazole-5-thiones.\textsuperscript{12} Various
ethanoneoximes (5.13) can be reacted with $S_2Cl_2$ and pyridine in $CH_3CN$, followed by subsequent addition of formic acid or thioacetamide in the last stage of the reaction (Figure 5.06). Treatment with formic acid gives 1,2,3-dithiazol-5-ones (5.14), whereas treatment with thioacetamide gives 1,2,3-dithiazole-5-thiones (5.15). This synthetic variation to the methods previously reported by Rees et al.\textsuperscript{11} likely proceeds through a dithiazolium salt intermediate (5.16), related to 5.09, but with various $R$ groups in place of the phenyl substituent.

![Figure 5.06 One-pot reaction in CH$_3$CN to afford 4-substituted 1,2,3-dithiazol-5-ones (5.14) and 1,2,3-dithiazole-5-thiones (5.15).\textsuperscript{12}](image)

### 5.1.3 4-benzoyl-5$H$-1,2,3-dithiazol-5-one

This project began with the work of my colleague, David Petrone. The original goal was to synthesize 1,2,3-DTA ligand 4-acyl-5$H$-1,2,3-dithiazole-5-one (5.18). However, neither David nor I were able to obtain 5.18 using the one-pot synthetic procedure described by Konstantinova et al. (Figure 5.07).\textsuperscript{12} Instead of using the 2,3-butandione monoxime (5.17), I decided to try a different ethanoneoxime starting material. The one-pot procedure using $\alpha$-isonitroso-propiophenone (5.19) as the ethanoneoxime reagent, yielded the first instances of 4-benzoyl-5$H$-1,2,3-dithiazol-5-one (5.20) and 4-
benzoyl-5H-1,2,3-dithiazole-5-thione (5.21). The various reaction conditions for 5.20 and 5.21 are given in Figure 5.07.

Figure 5.07 Reaction conditions explored to afford the products 5.18, 5.20 and 5.21. All reactions gave a red oil, which required purification by column chromatography (Silica gel; light petroleum and then light petroleum/CH2Cl2 mixtures) before yields could be determined.

Following the exact preparation outlined by Konstantinova et al. gave 5.20. However, these conditions also gave 5.21 as byproduct (Figure 5.07). 5.20 was obtained as the major product by increasing the stoichiometric amount of formic acid from 5 to 11 equivalents. The best yield of 5.20 (19%) was achieved by use of the reagents S2Cl2, pyridine and formic acid in the ratio 3:5:11. The yield increased from 16% to 19% when
the remaining formic acid was quenched with a base (pyridine). The direct synthesis of 5.21 gave low yields (3%) and could not be achieved without 5.20 byproduct. No product was afforded when the reaction conditions were modified towards 5.21 by increasing the stoichiometric amount of thioacetamide or bringing the reaction mixture to reflux.

### 5.2 Results and Discussion

#### 5.2.1 Cyclic voltammetry

Cyclic voltammetry (CV) experiments were carried out on 4-benzoyl-5H-1,2,3-dithiazol-5-one (5.20) to determine its redox behaviour. Had the radical-anion oxidation state (Figure 5.08) of 5.20 been achieved, this reduced species may have served as an interesting radical ligand.

![Figure 5.08 Radical-anion oxidation states of 4-benzoyl-5H-1,2,3-dithiazol-5-one (5.20).](image)

The cells used for CV experiments were prepared in a glovebox using dry solvent. Experiments were performed using Pt wire working, counter and reference electrodes, 100 mM (n-Bu)4NPF6 electrolyte, and 3.0 mM analyte, at a scan rate of 100 mV/s. The ferrocene/ferrocenium (fc/fc⁺) redox couple \(E_{1/2}^{(fc/fc⁺)} = +400\text{ mV vs. SCE in CH}_3\text{CN}\)\(^{13,14}\) was used as an internal reference.\(^{13,14}\) In the entire electrochemical window of CH₃CN, which is approximately +3 to -3 V vs. SCE\(^{15}\) (with 100 mM (n-Bu)₄NPF₆ electrolyte and
Pt electrodes), there exists only one peak ($E_c^- = -1130$ mV), which is irreversible in nature. A representative CV of 5.20 in CH$_3$CN is shown in **Figure 5.09**.

![Figure 5.09 CV of 5.20 in CH$_3$CN swept first in the anodic direction (arrow). The single cathodic peak labelled $E_c^-$ represents an irreversible reduction to an unstable species.](image)

The electrochemical irreversibility of the cathodic peak is characteristic of the formation of a chemical species that is not stable. Although it does not rule out the possibility of a chemical reduction, if the reduced species is not stable in the time frame of the CV experiment (100 mV/s), then it certainly will not be stable long enough to isolate and be useful.$^6$ It is most likely that the species formed by reduction of 5.20 undergoes reductive cleavage.$^{16}$ The reduction potential needed to reduce 5.20 is surprisingly large at -1131 mV, which is just inside the reduction potential of cobaltocene in CH$_3$CN (-1330 mV)$^{13}$. 

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5.2.2 DSC and PXRD

Sublimed 4-benzoyl-5H-1,2,3-dithiazol-5-one (5.20), the purity of which was verified by EA, demonstrated a broad melting point (95-107 °C). After allowing the same sample to cool, the melting point range became narrow (105-107 °C). The new melting point falls within the higher end of the first observed melting point. Additionally, samples of 5.20 that had solvent (CH₂Cl₂) removed quickly gave a different narrow melting point, 95-97 °C, which falls within the lower end of the first observed melting point.

Given these melting point observations, it was proposed that 5.20 has two distinct crystal packing modes. Polymorphism is the ability of compounds to exist in multiple crystal forms, and is frequently encountered in the pharmaceutical industry. The higher melting point polymorph (105-107 °C; 5.20-highMP) indicates a more stable crystal packing form, while the lower melting point polymorph (95-97 °C; 5.20-lowMP) may be a metastable form.

To verify the existence of polymorphism, samples of 5.20 demonstrating melting point ranges of 95-107°C (5.20-mixMP), 95-97°C (5.20-lowMP) and 105-107 °C (5.20-highMP) were analyzed by combining differential scanning calorimetry (DSC) and X-ray powder diffraction (PXRD). A similar study was performed on antibacterial drug sulfanilamide (5.22). There exists three crystalline forms of 5.22: the α-, β-, and γ-forms. DSC was used to assign the enthalpy values associated with the α- to β- and β- to γ-transitions of sulfanilamide.

![5.22](image)
The yellow crystalline plates of the 5.20-mixMP sample were grown over three days by sublimation under dynamic vacuum (10⁻² Torr) using a three stage gradient tube furnace (70, 50, 30 °C). The yellow polycrystalline of the 5.20-lowMP sample was afforded by evaporating CH₂Cl₂ quickly by rotary evaporation. The yellow powder of the 5.20-highMP sample was produced from melting a portion of sublimed 5.20-mixMP in a hot water bath.

The diffraction patterns for 5.20-mixMP, 5.20-lowMP and 5.20-highMP were measured with a Mo X-ray source using a SuperNova diffractometer with Atlas CCD detector (Figure 5.10). Because PXRD patterns are measured on a bulk batch of sample, this characterization technique is useful to verify whether the sample is a single polymorph or a mixture.

It is clear that 5.20-lowMP and 5.20-highMP are indeed two different polymorphs since their unique lattices produce different diffraction patterns (Figure 5.10). The PXRD pattern for 5.20-mixMP suggests that purification by sublimation yields a mixture of both polymorphs, with 5.20-lowMP being the major product.
Figure 5.10 PXRD patterns of a) 5.20-highMP (MP = 105-107 °C), b) 5.20-lowMP (MP = 95-97 °C) and c) 5.20-mixMP (MP = 95-107 °C). Diffraction patterns were collected with a Mo X-ray source.

DSC is a thermoanalytical technique in which the difference in heat required to increase the temperature of a sample and a reference is measured as a function of temperature. DSC is often used to detect polymorphic forms because they typically have different melting points and heats of fusion. A TA instrument DSC Q2000 was used to conduct DSC experiments. Samples of varying mass (1.82-8.07 mg) were pressed into aluminum pans and DSC curves were recorded at 5 °C/min heating rate between -90 to
150 °C. The instrument was calibrated with an indium standard prior to carrying out experiments on samples of 5.20.

The representative DSC thermograms of 5.20-mixMP, 5.20-lowMP and 5.20-highMP, which will be referred to as traces (a) through (d), are given in Figure 5.11. DSC measurements on samples (4.86-6.23 mg) of the higher melting point polymorph (5.20-highMP) produce thermograms where there is only a single endotherm with an average onset temperature of 101.9(7) °C (3 measurements), which indicates uniform melting of the sample. A representative DSC thermogram of a sample of 5.20-highMP can be seen in trace (a) of Figure 5.11.

Samples of lower melting point polymorph (5.20-lowMP) display a dependency on sample size. DSC measurements on a small sample (1.82 mg) of 5.20-lowMP produced a single endotherm, with an onset temperature of 91.7 °C (single measurement). Trace (c) shows a representative example of a DSC thermogram displaying a single endotherm, which indicates uniform melting of 5.20-lowMP. However, when larger sample sizes (7.60-8.07 mg) of 5.20-lowMP were used for DSC measurements, the typical thermogram produced two distinct endotherms. Trace (b) illustrates that the initial endothermic process, which has an average onset temperature of 89.9(6) °C (four measurements), is followed by an exothermic process. The initial endothermic process corresponds to the melting of 5.20-lowMP, and the following exothermic process corresponds to the crystallization of newly-formed 5.20-highMP, which in this temperature range, is likely to be more stable than the liquid. Upon further heating, the second endotherm represents melting of the newly-formed 5.20-highMP.
Figure 5.11 Representative DSC thermograms shown as heat flow (W/g) vs. temperature (°C) of a sample of a) the higher melting point polymorph (5.20-highMP) with an observed endothermic process, b) the lower melting point polymorph (5.20-lowMP) with an observed endothermic-exothermic-endothermic process, c) the lower melting point polymorph (5.20-lowMP) with an observed endothermic process, and d) a mixture of both polymorphs (5.20-mixMP).
Typically, the polymorph with the higher melting point is associated with a higher enthalpy.\textsuperscript{18} Unfortunately, the enthalpy difference between 5.20-highMP and 5.20-lowMP could not be determined because both processes had enthalpy energies close to 112 J/g ± 3%. The 3% error is larger than the enthalpy difference between 5.20-highMP and 5.20-lowMP. The systematic error (± 0.3 J/g) due to the data spread is much smaller than the instrumental error (± 3%), such that experimental errors for these particular measurements can be ignored.

\subsection*{5.2.3 X-ray crystallography}

The single-crystal X-ray data for 5.20 were collected at low temperature (150 K) by Dr. Lough on a yellow plate using a Mo X-ray source. The yellow crystalline plates of 5.20 were grown over three days by sublimation under dynamic vacuum (10\textsuperscript{-2} Torr) using a three stage gradient tube furnace (70, 50, 30 °C). The space group of 5.20 is orthorhombic \textit{P}bc\textit{a} with unit cell dimensions as follows: \(a = 7.1753(14)\), \(b = 11.346(2)\), \(c = 22.898(5)\) Å, \(\alpha = 90°\), \(\beta = 90°\), \(\gamma = 90°\), and \(V = 1864.1(6)\) Å\textsuperscript{3}. The final refined model fit the data with an \(R\) value of 5.22%. The formula unit of the crystal structure of 5.20 is (C\textsubscript{3}H\textsubscript{5}NO\textsubscript{2}S\textsubscript{2}), with \(Z\) equal to 8. Figure 5.12 shows an ORTEP representation of 5.20.
Figure 5.12 Crystal structure of 4-benzoyl-5H-1,2,3-dithiazol-5-one (5.20).

PXRD was used to identify the crystal structure presented in Figure 5.12 as the low melting polymorph (5.20-lowMP). The diffraction pattern of 5.20-lowMP was simulated using the crystal structure (collected at low temperature) and compared to an experimental PXRD (collected at room temperature), as illustrated in Figure 5.13. The structure of the high melting point polymorph (5.20-highMP) is unknown and attempts to recrystallize 5.20-highMP as single crystals suitable for X-ray analysis have been unsuccessful to date.
Figure 5.13 Diffraction patterns that were a) experimentally collected (Mo X-ray source) on the low melting point polymorph (5.20-lowMP) and b) simulated (Mo Kα radiation) from the crystal structure.

The single-crystal X-ray data for 1,2,3-dithiazole-5-thione (5.21) were collected at low temperature (150 K) by Dr. Lough on a purple block using a Mo X-ray source. The purple crystals of 5.21 were grown by slow evaporation of CH₂Cl₂. The space group of 5.21 is orthorhombic $P2_12_12_1$ with unit cell dimensions as follows: $a = 8.7510(5)$, $b = 10.2750(6)$, $c = 10.9530(6)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, and $V = 984.86(10)$ Å³. The final refined model fit the data with an $R$ value of 3.93%. The formula unit of the crystal structure of 5.20 is (C₉H₅NOS₃), with $Z$ equal to 4. Figure 5.14 shows an ORTEP representation of 5.21.
5.3 Experimental

5.3.1 General considerations

All reactions performed under Ar\textsubscript{(g)} atmosphere were achieved using standard Schlenk line techniques. CH\textsubscript{3}CN was dried on a SP-1 Stand Alone Solvent Purification System from LC Technology Solutions Inc, using molecular sieves (3 Å). All commercial reagents were used as received. The reagents α-isonitroso-propiophenone, thioacetamide and S\textsubscript{2}Cl\textsubscript{2}, were obtained from Sigma Aldrich. The reagent formic acid was purchased from Fisher Scientific. The reagent pyridine was purchased from Acros Organics and used as received. IR (KBr pressed pellet) spectra were recorded on a Nicolet 4700 FT-IR spectrometer at 4 cm\textsuperscript{-1} resolution. CV data were collected using a BASi Epsilon-EC Bioanalytical Systems, Inc. Version 2.10.73_USB, 2009. CV cells were prepared in a
glove box using dry solvent. NMR spectra were recorded on a Bruker Avance-400 spectrometer at 298 K. Elemental analyses were performed by MHW Labs, Phoenix, AZ, USA. Electron impact GC/MS was done by Dr. Richard Smith at the University of Waterloo. Electron spray ionization MS/MS was done by Daniel Beach at the University of Guelph. Crystal data for 5.20 and 5.21 were collected by Dr. Alan Lough at the University of Toronto on a Nonius Kappa-CCD System and solved by Dr. Michael Jennings. PXRD on 5.20 were done by Dr. Dmitriy Soldatov at the University of Guelph on a SuperNova diffractometer with Atlas CCD detector.

5.3.2 Synthesis

4-Benzoyl-5H-1,2,3-dithiazol-5-one (5.20). A modification of the procedure reported by Konstantinova et al.\textsuperscript{12} was used. Pyridine (2.4 mL, 30 mmol) was added dropwise over ten minutes into a stirred solution (0 °C) of α-isonitroso-propiophenone (0.9941 g, 6.092 mmol) in CH\textsubscript{3}CN (100 mL) and S\textsubscript{2}Cl\textsubscript{2} (1.6 mL, 20 mmol) under argon to produce a yellow slurry. The mixture was stirred at 0 °C for 30 minutes and turned light orange. Formic acid (2.6 mL, 69 mmol) was added, the slurry turned dark orange and the mixture was stirred at 0 °C for 30 minutes. The mixture was allowed to warm up to room temperature and then refluxed for one hour, after which the slurry became red. Pyridine (5.6 mL, 69 mmol) was added to the mixture and stirred for 20 minutes at room temperature. Solvents were removed \textit{in vacuo} to afford a red oil plus some red solid. The red material was dissolved in a minimum of CH\textsubscript{2}Cl\textsubscript{2} and loaded onto a hexanes silica column. Product was eluted using a 50:50 CH\textsubscript{2}Cl\textsubscript{2}:hexanes mobile phase and the solvents were evaporated to give 0.4230 g yellow solid of 5.20 (1.894 mmol, 19%). A portion of
the crude product (0.2450 g) was purified by sublimation under dynamic vacuum ($10^{-2}$ Torr) using a three stage gradient tube furnace (70, 50, 30 °C). Sublimation yielded 0.1998 g (0.8948 mmol, 82%) of yellow crystalline material. **IR (KBr) ν/cm⁻¹:** 3257 (w), 3060 (w), 1991 (w), 1910 (w), 1831 (w), 1665 (s), 1603(s), 1595 (m), 1527 (w), 1475 (s), 1445 (m), 1321 (w), 1309 (m), 1292 (s), 1184 (m), 1159 (w), 1149 (m), 1081 (w), 1024 (w), 999 (w), 954 (m), 943 (m), 934 (w), 854 (w), 833 (m), 799 (m), 754 (m), 730 (s), 689 (s), 646 (s), 529 (w), 508(w), 459 (m), 440 (m), 425 (m). **$^1$H NMR:** (400 MHz, CDCl₃, 25 °C, ppm) δ 7.95 (2 H, d, CH), δ 7.65 (1 H, t, CH), δ 7.50 (1 H, t, CH). **$^{13}$C NMR:** (400MHz, CDCl₃, 25 °C, ppm) δ 187.8, 185.2 (2 C=O), δ 152.9, 135.3 (2 sp² quaternary C), δ 134.7, 130.2, 128.8 (5 CH, Ph). **Mass Spec:** (EI+, r.t., 1.45min); parent ion assigned as $m/z$ 222.99 (M = C₉H₅NO₂S₂)+ 12.36%; 194.98 (M – CO)+ 33.51%; 105.02 (C₇H₆O)+ 100.00%; 76.99 (C₆H₅)+ 43.86%; 51.00 (C₄H₃)+ 18.98%. **Crystal data:** Nonius Kappa CCD radiation source MoKα, wavelength = 0.71073 Å at University of Guelph; $T = 150(2)$ K; orthorhombic, Pbca; $a = 7.1753(14)$, $b = 11.346(2)$, $c = 22.898(5)$ Å; $α = 90.00^°$, $β = 90.00^°$, $γ = 90.00^°$; $V = 1864.1(6)$ Å³; $Z = 8$; $R = 5.22%$. **Elemental Anal.** Calc. for C₉H₅NO₂S₂: C, 48.41; H, 2.26; N, 6.27. Found: C, 48.60; H, 2.37; N, 6.20%. 

### 4-Benzoyl-5H-1,2,3-dithiazole-5-thione (5.21)

A modification of the procedure reported by Konstantinova et al.¹² was used. Pyridine (1.6 mL, 20 mmol) was added dropwise over ten minutes to a stirred solution (0 °C) of α-isonitroso-propiophenone (1.0624 g, 6.5110 mmol) in CH₃CN (100 mL) and S₂Cl₂ (1.6 mL, 20 mmol) under argon to produce a yellow slurry. The mixture was stirred at 0 °C for 30 minutes.
Thioacetamide (0.5421 g, 7.215 mmol) was added and the resulting red mixture was stirred at 0 °C for 30 minutes. The resulting red mixture was then stirred at room temperature for two hours and the solids were filtered. Solvents were removed from the filtrate in vacuo to afford a red oil. The red oil was dissolved in a minimum of CH$_2$Cl$_2$ and loaded onto a hexanes silica column. Product was eluted using a 70:30 CH$_2$Cl$_2$:hexanes mobile phase and the solvents were evaporated to give 0.0482 g red solid of **5.21** (0.201 mmol, 3%). **IR (KBr)** ν/cm$^{-1}$: 3330 (w), 3082 (w), 3064 (w), 1994 (w), 1973 (w), 1907 (w), 1820 (w), 1774 (w), 1750 (w), 1678 (s), 1593 (m), 1580 (w), 1490 (w), 1474 (w), 1449 (m), 1412 (w), 1341 (w), 1312 (m), 1275 (s), 1199 (s), 1174 (s), 1097 (s), 1070 (w), 1022 (w), 999 (w), 951 (s), 930 (w), 842 (w), 829 (m), 797 (s), 760 (m), 707 (m), 685 (s), 660 (s), 614 (w), 582 (m), 497 (w), 478 (w), 432 (w), 424 (w).

**$^1$H NMR:** (400MHz, CDCl$_3$, 25 °C, ppm) δ 7.85 (2 H, d, CH), δ 7.64 (1 H, t, CH), δ 7.49 (1 H, t, CH).

**$^{13}$C NMR:** (400MHz, CDCl$_3$, 25 °C, ppm) δ 188.0 (C=O), δ 205.7, 167.1, 134.6 (3 sp$^2$ quaternary C), δ 135.0, 129.9, 129.0 (5 CH, Ph).

**TOF MS/MS:** (ESI+, MeOH/H$_2$O + NH$_4$CH$_3$COO, r.t.); parent ion assigned as $m/z$ 239.97 (M = C$_9$H$_5$NOS$_3$H)$^+$ 39.12%; 161.93 (C$_9$H$_6$OS)$^+$ 69.32%; 105.04 (C$_7$H$_5$O)$^+$ 100.00%, 101.95 22.89%, 77.05 (C$_6$H$_5$)$^+$ 7.95%.

**Crystal data:** Nonius Kappa CCD, radiation source MoKα, wavelength = 0.71073 Å at University of Toronto; $T = 150(2)$K; orthorhombic, $P2_12_12_1$, $a = 8.7510(5)$, $b = 10.2750(6)$, $c = 10.9530(6)$ Å; $a = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$; $V = 984.86(10)$ Å$^3$; $Z = 4$; $R = 3.93\%$. 
5.4 Future work

Future work could involve attempting to coordination 5.20 as a neutral species. The CV of 5.20 (Figure 5.09) showed that the radical anion species is unstable and most likely not isolatable. However, it might be possible to stabilize the radical anion species of 5.20 through metal coordination. With the correct choice of metal, for instance trivalent europium, it might be possible to coordinate 5.20 plus reduce it. Additionally, 5.20 has an improved likelihood of coordinating to Eu$^{3+}$ because of lanthanide ions high affinity for oxygen.
5.5 References


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CHAPTER 6

CONCLUSIONS
6.1 Conclusions

The 1,2,3-DTA based radical ligand 1,2,3-dithiazolyl-6,7-dimethyl-1,4-naphthoquinone (6,7-Me₂DTANQ, 3.04) was synthesized and fully characterized. Relatively large scale coordination reactions using 6,7-Me₂DTANQ as the ligand were reproducible and gave high yields of metal complex. The metal complexes of 6,7-Me₂DTANQ were robust and volatile because of the use of hfac auxiliary ligand, such that sublimation produced pure crystalline material in amounts appropriate for subsequent experimental measurements. Five different metal complexes of 6,7-Me₂DTANQ were characterized by X-ray crystallography: two transition metal complexes (Mn²⁺ and Ni²⁺) and three lanthanide metal complexes (Nd³⁺, Gd³⁺ and Dy³⁺). 6,7-Me₂DTANQ was shown to be capable of coordinating a metal ion in both a monodentate and bidentate fashion. Coordination of 6,7-Me₂DTANQ with lanthanide ions produced coordination polymers, whereas coordination of 6,7-Me₂DTANQ with transition metal ions produced oligomers. Thus far, two metal complexes of 6,7-Me₂DTANQ were measured magnetically (Gd³⁺ and Mn²⁺) and these are the first examples of magnetic measurements on a coordination complex that contains a 1,2,3-DTA radical ligand. The 6,7-Me₂DTANQ ligand mediated magnetic coupling between the metal centres (monodentate and bidentate). Both the Gd and Mn complexes exhibited AFM coupling between 6,7-Me₂DTANQ ligand and metal centers. The trinuclear Mn complex had a ground state of $S_T = 13/2$, which is the highest to date for any thiazyl-metal system. The results of the trinuclear Mn complex have lead to a manuscript recently being accepted as a Chemical Communication.
The species 4-benzoyl-5H-1,2,3-dithiazol-5-one (5.20) was synthesized for the first time from a modified one-pot procedure and subsequently fully characterized. The biproduct of the reaction towards 5.20, 4-benzoyl-5H-1,2,3-dithiazole-5-thione (5.21) was also isolated and characterized. The crystalline form of 5.20 was found to have two polymorphs using DSC and PXRD.
APPENDIX A

COMPOUND DATA SHEETS
**Compound Name:** 6,7-dimethylnaphthalene-1,4-dione (modified prep, literature compound)

**MW:** 186.21 g/mol

**Appearance:**
Yellow crystalline

**Lit. and/or notebook # and page:**
DS03-27 pg 46
DS03-47 pg 72 (bulk)

**First made on date:**
Nov 25/10

**Made by:**
David Sullivan

**Synthesis and Structure:**

**Experimental Data:**

**MP:** 113-116°C

**IR(KBr) v/cm⁻¹:** 2952 (w), 2918 (w), 2849 (w), 1666 (s), 1599 (s), 1560 (w), 1449 (m), 1392 (m), 1360 (w), 1341 (m), 1328 (s), 1309 (s), 1262 (w), 1220 (w), 1202 (w), 1143 (m), 1099(w), 1072 (w), 1057 (s), 1019 (m), 995 (w), 971(w), 902 (w), 837 (s), 805 (w), 768 (w), 712 (w), 626 (w), 512 (m), 499 (m), 471 (w), 450 (m), 426 (m), 412 (w).

**¹H NMR** (400MHz, CDCl₃, 25 °C, ppm) δ: 2.39 (6 H, s, CH₃), 6.88 (2 H, s, CH), 7.81 (2 H, s, CH).
IR: KBr pressed pellet

NMR: $^1$H, CDCl$_3$, 400MHz, 16 Scans
**Compound Name:** 2-Amino-3-bromo-6,7-dimethyl-1,4-naphthoquinone (modified prep, literature compound)

**MW:** 280.12 g/mol

**Appearance:**
orange powder

**Lit. and/or notebook # and page:**
DS03-12 pg 23
DS03-51 pg 76 (bulk)

**First made on date:**
April 12/11

**Made by:**
David Sullivan

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**Experimental Data:**

**MP:** 226-228°C

**IR(KBr) v/cm⁻¹:** 3528 (m), 3461 (m), 3423 (m), 3322(s), 3073 (w), 2973 (w), 2946 (w), 2919 (w), 1831 (w), 1794 (w), 1682 (s), 1631 (s), 1606 (s), 1588 (s), 1566(s), 1448 (m), 1405 (m), 1386 (m), 1367 (s), 1330 (s), 1297 (s), 1240 (w), 1201 (w), 1178 (w), 1064 (w), 1023 (w), 1000 (w), 964 (m), 916 (w), 899 (w), 801 (m), 760 (w), 744 (s), 688 (w), 577 (m), 577 (m), 549 (m), 499 (m), 446 (w), 426 (m).

**¹H NMR** (400MHz, CDCl₃, 25 °C, ppm) δ: 2.35 (3 H, s, CH₃), 2.37 (3 H, s, CH₃), 7.78 (1 H, s, CH), 7.88 (1 H, s, CH).

**Crystal data:** (hydrate) collected on a SuperNova Atlas CCD, radiation source CuK\(\alpha\), wavelength = 1.5418 Å at University of Guelph, T = 150(2)K, monoclinic space group C2/c, \(a = 7.72070(7)\) Å, \(b = 13.73969(16)\) Å, \(c = 21.1400(2)\) Å, \(\beta = 94.0880(10)^\circ\), \(V = 2236.83(4)\) Å³, \(Z = 8\); \(R = 3.29\%\).
IR: KBr pressed pellet

NMR: $^1$H, CDCl$_3$, 400MHz, 16 Scans
**Compound Name:** 6,7-Dimethyl-4,9-dioxo-naphtho[1,2-\textit{d}][1,2,3]dithiazol-2-iium chloride (diMeDTANQ$^+$Cl$^-$)

**MW:** 297.78 g/mol

**Appearance:**

orange powder

**Lit. and/or notebook # and page:**

DS03-52 pg 77

**First made on date:**

April 14/11

**Made by:**

David Sullivan

**Experimental Data:**

$\text{IR(KBr)}$ $\text{v/cm}^{-1}$: 3035 (w), 3014 (w), 2953 (w), 2921 (w), 1686 (s), 1671 (s), 1593 (s), 1558 (w), 1452 (m), 1407 (w), 1396 (m), 1374 (m), 1292 (s), 1226 (w), 1194 (s), 1172 (w), 1094 (s), 1032 (s), 994 (m), 938 (w), 918 (s), 906 (m), 852 (s), 819 (w), 804 (w), 774 (w), 748 (w), 729 (s), 691 (m), 643 (m), 603 (w), 583 (w), 539 (m), 503 (m), 466 (w), 439 (m), 424 (m).
IR: KBr pressed pellet
**Compound Name:** 6,7-Dimethyl-4,9-dioxo-naphtho[1,2-d][1,2,3]dithiazolyl (diMeDTANQ•)

**MW:** 262.33 g/mol

**Appearance:**
Purple powder (amorph)
Purple blocks (subl)

**Lit. and/or notebook # and page:**
DS03-14 pg 25 (amorph)
DS04-03 pg 4 (subl, passed EA)

**First made on date:**
April 22/11

**Made by:**
David Sullivan

**Experimental Data:**

**IR(KBr) ν/cm⁻¹:** 3326 (w), 3049 (w), 2969 (w), 2944 (w), 2916 (w), 1670 (s), 1602 (m), 1593 (w), 1574 (s), 1550 (m), 1535 (m), 1500 (w), 1458 (w), 1448 (w), 1421 (s), 1401 (w), 1380 (w), 1375 (w), 1350 (s), 1305 (w), 1282 (s), 1259 (s), 1193 (s), 1178 (m), 1078 (m), 1034 (m), 995 (m), 940 (w), 892 (m), 815 (s), 760 (m), 740 (m), 723 (m), 693 (m), 683 (m), 639 (m), 594 (w), 574 (m), 530 (w), 506 (w), 482 (w), 454 (w), 438 (w), 417 (m).

**Elemental Anal.** Calc. for C₁₂H₈NO₂S₂: C, 54.94; H, 3.07; N, 5.34. Found: C, 54.77; H, 3.01; N, 5.33%.

**Crystal data:** collected on a Nonius Kappa CCD radiation source MoKα, wavelength = 0.71073 Å at University of Toronto, T = 150(2)K, monoclinic space group P2₁/c, a = 11.055(2), b = 7.9789(16), c = 13.222(3) Å, β = 113.03(3)°, V = 1073.4(4) Å³, Z = 4, R = 4.28 %.
IR: KBr pressed pellet
**Compound Name:** Mn Trimer [Mn₃(hfac)₆(diMeDTANQ•)₂]

**MW:** 1931.77 g/mol

**Appearance:**
green powder (crude)
emerald green blocks (subl)

**Lit. and/or notebook # and page:**
DS03-57 pg 82 (crude)
DS03-26 pg 45 (subl, passed EA)

**First made on date:**
May 30/11

**Made by:**
David Sullivan

**Experimental Data:**

**IR(KBr) ν/cm⁻¹:** 1645 (s), 1576 (m), 1561 (w), 1534 (w), 1479 (m), 1407 (m), 1307 (m), 1255 (s), 1200 (s), 1147(s), 1094 (m), 1041 (w), 906 (w), 836 (w), 806 (s), 800 (s), 767 (w), 742 (w), 734 (w), 665 (s), 648 (w), 585 (s), 527 (w), 511 (w), 499 (w), 485 (w), 472 (w), 459 (w), 441 (w), 428 (w), 415 (w), 411 (w).

**Elemental Anal.** Calc. for C₅₄H₂₂F₃₆Mn₃N₂O₁₂S₄: C, 33.57; H, 1.15; N, 1.45. Found: C, 33.31; H, 1.31; N, 1.22%.

**Crystal data:** collected on a Nonius Kappa CCD radiation source MoK\(\alpha\), wavelength = 0.71073 Å at University of Toronto, T = 150(2)K, triclinic space group P-1, \(\alpha = 12.178(2)\), \(b = 12.716(16)\), \(c = 12.809(3)\) Å, \(\alpha = 69.55(3)°\), \(\beta = 113.03(3)°\), \(\gamma = 68.97(3)°\), \(V = 1722.0(6)\) Å³, \(Z = 1\), \(R = 4.89%\).
IR: KBr pressed pellet
**Compound Name:** Ni Trimer \([\text{Ni}_3(\text{hfac})_6(\text{diMeDTANQ•})_2]\)

**MW:** 1943.04 g/mol

**Appearance:**
- green powder (crude)
- brown blocks (subl)

**Lit. and/or notebook # and page:**
- DS03-32 pg 53 (crude)
- DS04-26 pg 27 (subl, passed EA)

**First made on date:**
- June 27/11

**Made by:**
- David Sullivan

**Experimental Data:**

**IR(KBr) \(\nu/\text{cm}^{-1}\):**
- 1643 (s), 1573 (m), 1560 (w), 1532 (w), 1482 (m), 1420 (m), 1331 (w), 1301 (m), 1256 (s), 1198 (s), 1148 (s), 1099 (w), 1043 (w), 951 (w), 907 (w), 844 (w), 799 (s), 770 (w), 744 (w), 734 (w), 675 (s), 648 (w), 589 (s), 530 (w), 503 (w), 469 (w), 425 (w).

**Elemental Anal.**
- Calc. for \(C_{54}H_{22}F_{36}Ni_{3}N_{2}O_{12}S_{4}\): C, 33.38%; H, 1.14; N, 1.44. Found: C, 33.47%; H, 1.14; N, 1.56%.

**Crystal data:**
- collected on a Bruker APEX-II CCD radiation source MoK\(\alpha\), wavelength = 0.71073 Å at University of Toronto, \(T = 150(2)\)K, triclinic group \(P-1\), \(a = 12.1205(11)\), \(b = 12.5589(11)\), \(c = 12.6180(12)\) Å, \(\alpha = 68.686(2)^\circ\), \(\beta = 77.751(2)^\circ\), \(\gamma = 69.302(2)^\circ\), \(V = 1666.1(3)\) Å\(^3\), \(Z = 1\), \(R = 4.17\).
IR: KBr pressed pellet
**Compound Name:** polymeric [Gd(hfac)$_3$(diMeDTAN$^\bullet$)]

**MW:** 1040.73 g/mol

**Appearance:**
blue powder (crude)
orange blocks (subl)

**Lit. and/or notebook # and page:**
DS03-54 pg 79 (crude)
DS03-56 pg 81 (subl, passed EA)

**First made on date:**
Sept 22/11

**Made by:**
David Sullivan

**Experimental Data:**

IR(KBr) $\nu$/cm$^{-1}$: 2963 (w), 2920 (w), 2852 (w), 1686 (w), 1650 (s), 1578 (w), 1561 (w), 1530 (w), 1499 (w), 1492 (w), 1478 (w), 1468 (w), 1451 (w), 1400 (w), 1383 (w), 1356 (w), 1313 (w), 1257 (s), 1209 (s), 1146 (s), 1099 (w), 1045 (w), 951 (w), 906 (w), 864 (w), 801 (m), 741 (w), 695 (w), 661 (m), 586 (m).

**Elemental Anal.**
Calc. for C$_{27}$H$_{11}$F$_{18}$GdNO$_8$S$_2$: C, 31.16; H, 1.07; N, 1.35. Found: C, 30.89; H, 1.41; N, 1.30%.

**Crystal data:** collected on a Bruker APEX-II CCD radiation source CuK$\alpha$, wavelength = 1.54178 Å at University of Toronto, T = 147(2)K, triclinic space group $P-1$, $a = 8.9751(9)$, $b = 16.741(2)$, $c = 24.576(3)$ Å, $\alpha = 80.887(10)^\circ$, $\beta = 84.937(11)^\circ$, $\gamma = 75.917(9)^\circ$, $V = 3531.7(7)$ Å$^3$, $Z = 4$, $R = 7.26\%$. 

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IR: KBr pressed pellet
**Compound Name:** polymeric [Dy(hfac)$_3$(diMeDTAN•)]

**MW:** 1045.98 g/mol

**Appearance:**
- purple powder (crude)
- orange needles (subl)

**Lit. and/or notebook # and page:**
- DS03-66 pg 91 (crude)
- DS04-42 pg 81 (subl, passed EA)

**First made on date:**
Nov 3/11

**Made by:**
David Sullivan

**Experimental Data:**

**IR(KBr) ν/cm$^{-1}$:** 1654 (s), 1580 (m), 1559 (w), 1529 (w), 1500 (m), 1478 (w), 1400 (w), 1341 (w), 1313 (w), 1257 (s), 1254 (s), 1209 (s), 1144 (s), 1101 (w), 1045 (w), 998 (w), 952 (w), 906 (w), 836 (w), 797 (m), 766 (w), 741 (w), 734 (w), 691(w), 661 (m), 586 (m), 528 (w), 496 (w), 467 (w), 434 (w), 424 (w).

**Elemental Anal.** Calc. for C$_{27}$H$_{11}$F$_{18}$DyNO$_8$S$_2$: C, 31.16; H, 1.06; N, 1.34. Found: C, 30.26; H, 0.93; N, 1.28%.

**Crystal data:** collected on a SuperNova Atlas CCD radiation source MoK\(\alpha\), wavelength = 0.71073 Å at University of Guelph, T = 150(2)K, triclinic space group P-1, a = 8.9360(18), b = 12.249(2), c = 16.872(3) Å, \(\alpha = 81.42(3)^\circ\), \(\beta = 75.23(3)^\circ\), \(\gamma = 84.07(3)^\circ\), \(V = 1761.6(6)\) Å$^3$, \(Z = 2\), \(R = 3.91\%\).
IR: KBr pressed pellet
**Compound Name:** polymeric [Nd(hfac)$_3$(diMeDTAN•)]

**MW:** 1027.72 g/mol

**Appearance:**
purple powder (crude)
orange needles (subl)

**Lit. and/or notebook # and page:**
RM01-05 pg 5 (crude and subl. passed EA)

**First made on date:**
May 23/12

**Made by:**
Alex Mayo

**Experimental Data:**

**IR(KBr) \(\text{v/cm}^{-1}\):** 1649 (s), 1611 (w), 1577 (w), 1560 (w), 1534 (w), 1492 (m), 1421 (w), 1353 (w), 1257 (s), 1207 (s), 1146 (s), 1098 (w), 1047 (w), 1021 (w), 996 (w), 950 (w), 900 (w), 864 (m), 806 (s), 762 (w), 741 (w), 694 (w), 685 (w), 660 (s), 641 (w), 585 (s), 528 (w), 463 (w), 421 (w).

**Elemental Anal.** Calc. for C$_{27}$H$_{11}$F$_{18}$NdNO$_8$S$_2$: C, 31.55; H, 1.08; N, 1.36. Found: C, 31.22; H, 1.40; N, 1.36%.

**Crystal data:** collected on a SuperNova Atlas CCD radiation source MoK\(\alpha\), wavelength = 0.71073 Å at University of Guelph, \(T = 150(2)\)K, triclinic space group \(P-1\), \(a = 9.1102(18)\), \(b = 12.498(3)\), \(c = 16.228(3)\) Å, \(\alpha = 76.95(3)^\circ\), \(\beta = 79.51(3)^\circ\), \(\gamma = 86.67(3)^\circ\), \(V = 1769.7(6)\) Å$^3$, \(Z = 2\), \(R = 7.1\)%.
IR: KBr pressed pellet
Compound Name: kinetic product, 4-benzoyl-1,2,3-dithiazolyl-5-one (PODTAO)

MW: 223.28 g/mol

**Synthesis and Structure:**

1. 3.3 S₂Cl₂
2. 5 pyridine
3. 11.4 CHOOH, Δ

**Experimental Data:**

**MP:** 95-97°C; 105-107°C (polymorphism)

**IR(KBr) v/cm⁻¹:** 3257 (w), 3060 (w), 1991 (w), 1910 (w), 1831 (s), 1665 (s), 1603(s), 1595 (m), 1527 (w), 1475 (s), 1445 (m), 1321 (w), 1309 (m), 1292 (s), 1184 (m), 1159 (w), 1149 (m), 1081 (w), 1024 (w), 999 (w), 954 (m), 943 (m), 934 (w), 854 (w), 833 (m), 799 (m), 754 (m), 730 (s), 689 (s), 646 (s), 529 (w), 508(w), 459 (m), 440 (m), 425 (m).

**Elemental Anal.** Calc. for C₉H₅NO₂S₂: C, 48.41; H, 2.26; N, 6.27. Found: C, 48.60; H, 2.37; N, 6.20%.

**Mass Spec** (EI+, r.t., 1.45min); parent ion assigned as m/z 222.99 (M = C₉H₅NO₂S₂)⁺ 12.36%; 194.98 (M – CO)⁺ 33.51%; 105.02 (C₇H₆O)⁺ 100.00%; 76.99 (C₆H₅)⁺ 43.86%; 51.00 (C₄H₃)⁺ 18.98%.

**H NMR** (400MHz, CDCl₃, 25 °C, ppm) δ: 7.954 (2 H, d, CH), 7.651 (1 H, t, CH), 7.503 (1 H, t, CH).

**¹³C NMR** (400MHz, CDCl₃, 25 °C, ppm) δ: 187.84, 185.18 (2 C=O), 152.88, 135.25 (2 sp² quaternary C), 134.66, 130.17, 128.77 (5 CH, Ph).
Crystal data (95-97°C): collected on a Nonius Kappa CCD, radiation source MoK\(\alpha\), wavelength = 0.71073 Å at University of Toronto, T = 150(2)K, orthorhombic space group Pbc\(a\), \(a = 7.1753(14)\) Å, \(b = 11.346(2)\) Å, \(c = 22.898(5)\) Å, \(\alpha = 90^\circ\), \(\beta = 90^\circ\), \(\gamma = 90^\circ\), \(V = 1864.1(6)\) Å\(^3\), \(Z = 8\), \(R = 5.22\%\).

IR: KBr pressed pellet

NMR: \(^1\)H, CDCl\(_3\), 400MHz, 16 Scans
NMR: $^{13}$C Jmod, CDCl$_3$, 400MHz, 4096 Scans

MS: EI+, r.t., 1.45min
**Compound Name:** 4-benzoyl-1,2,3-dithiazolyl-5-thione (PODTAT)

**MW:** 239.34 g/mol

**Appearance:**
red crystalline

**Lit. and/or notebook # and page:**
DS03-02 pg 4 (biprod)
DS04-18 pg 19 (direct)

**First made on date:**
Jan 5/11 (biprod)
Jan 17/12 (direct)

**Made by:**
David Sullivan

**Experimental Data:**

**MP:** 71-73°C

**IR(KBr) ν/cm⁻¹:** 3330 (w), 3082 (w), 3064 (w), 1994 (w), 1973 (w), 1907 (w), 1820 (w), 1774 (w), 1750 (w), 1678 (s), 1593 (m), 1580 (w), 1490 (w), 1474 (w), 1449 (m), 1412 (w), 1341 (w), 1312 (m), 1275 (s), 1199 (s), 1174 (s), 1097 (s), 1070 (w), 1022 (w), 999 (w), 951 (s), 930 (w), 842 (w), 829 (m), 797 (s), 760 (m), 707 (m), 685 (s), 660 (s), 614 (w), 582 (w), 497 (w), 478 (w), 432 (w), 424 (w).

**TOF MS/MS (ESI+, MeOH/H₂O + NH₄CH₃COO, r.t.);** parent ion assigned as m/z 239.97 (M = C₉H₅NOS₃H)⁺ 39.12%; 161.93 (C₉H₆OS)⁺ 69.32%; 105.04 (C₇H₅O)⁺ 100.00%, 101.95 22.89%, 77.05 (C₆H₅)⁺ 7.95%.

**¹H NMR** (400MHz, CDCl₃, 25 °C, ppm) δ: 7.851 (2 H, d, CH), 7.642 (1 H, t, CH), 7.488 (1 H, t, CH).

**¹³C NMR** (400MHz, CDCl₃, 25 °C, ppm) δ: 188.02 (C=O), 205.69, 167.09, 134.60 (3 sp² quaternary C), 134.99, 129.91, 128.98 (5 CH, Ph).
Crystal data: collected on a Nonius Kappa CCD, radiation source MoK\(\alpha\), wavelength = 0.71073 Å at University of Toronto, T = 150(2)K, orthorhombic space group \(P2_12_12_1\), \(a = 8.7510(5)\) Å, \(b = 10.2750(6)\) Å, \(c = 10.9530(6)\) Å, \(\alpha = 90.00^\circ\), \(\beta = 90.00^\circ\), \(\gamma = 90.00^\circ\), \(V = 984.86(10) \text{ Å}^3\), \(Z = 4\), \(R = 3.93\%\).

IR: KBr pressed pellet

NMR: \(^1\text{H}, \text{CDCl}_3, 400\text{MHz, 16 Scans}\)
NMR: $^{13}$C Jmod, CDCl$_3$, 400MHz, 7083 Scans

MS/MS: ESI+, MeOH/H$_2$O + NH$_4$CH$_3$COO, r.t.
APPENDIX B
CRYSTALLOGRAPHIC DATA TABLES
<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>3.15</th>
<th>3.04</th>
<th>4.09</th>
</tr>
</thead>
<tbody>
<tr>
<td>FORMULA</td>
<td>C\textsubscript{12}H\textsubscript{11}BrNO\textsubscript{2.5}</td>
<td>C\textsubscript{12}H\textsubscript{8}NO\textsubscript{2}S\textsubscript{2}</td>
<td>C\textsubscript{54}H\textsubscript{22}F\textsubscript{36}Mn\textsubscript{3}N\textsubscript{2}O\textsubscript{16}S\textsubscript{4}</td>
</tr>
<tr>
<td>M.W.</td>
<td>289.13</td>
<td>262.31</td>
<td>1931.80</td>
</tr>
<tr>
<td>Space Group</td>
<td>C\textsubscript{2}/c</td>
<td>P\textsubscript{2}1/c</td>
<td>P\textsubscript{1}-1</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>V (Å\textsuperscript{3})</td>
<td>2236.83(4)</td>
<td>1073.32(4)</td>
<td>1722.0(6)</td>
</tr>
<tr>
<td>Density (g•cm\textsuperscript{-3})</td>
<td>1.72</td>
<td>1.62</td>
<td>1.86</td>
</tr>
<tr>
<td>R (%)</td>
<td>3.29</td>
<td>4.28</td>
<td>4.89</td>
</tr>
<tr>
<td>a (Å)</td>
<td>7.72070(7)</td>
<td>11.055(2)</td>
<td>12.178(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>13.73969(16)</td>
<td>7.9789(16)</td>
<td>12.716(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>21.1400(2)</td>
<td>13.222(3)</td>
<td>12.809(3)</td>
</tr>
<tr>
<td>α °</td>
<td>90</td>
<td>90</td>
<td>69.55(3)</td>
</tr>
<tr>
<td>β °</td>
<td>94.0880(10)</td>
<td>113.03(3)</td>
<td>76.62(3)</td>
</tr>
<tr>
<td>γ °</td>
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<td>90</td>
<td>68.97(3)</td>
</tr>
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<td>150</td>
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<tr>
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<td>4.11</td>
<td>4.12</td>
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</tr>
<tr>
<td>FORMULA</td>
<td>C_{54}H_{22}F_{36}Ni_{3}N_{2}O_{16}S_{4}</td>
<td>C_{27}H_{11}F_{18}NdNO_{8}S_{2}</td>
<td>C_{27}H_{11}F_{18}GdNO_{8}S_{2}</td>
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</tr>
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<td>P-1</td>
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<td>2</td>
<td>4</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1666.1(3)</td>
<td>1769.7(6)</td>
<td>3531.7(7)</td>
</tr>
<tr>
<td>Density (g·cm⁻³)</td>
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<td>1.93</td>
<td>1.96</td>
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<td>R (%)</td>
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<td>7.1</td>
<td>7.26</td>
</tr>
<tr>
<td>a (Å)</td>
<td>12.1205(11)</td>
<td>9.1102(18)</td>
<td>8.9751(9)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>12.5589(11)</td>
<td>12.498(3)</td>
<td>16.741(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>12.6180(12)</td>
<td>16.228(3)</td>
<td>24.576(3)</td>
</tr>
<tr>
<td>α °</td>
<td>68.686(2)</td>
<td>76.95(3)</td>
<td>80.887(10)</td>
</tr>
<tr>
<td>β °</td>
<td>77.751(2)</td>
<td>79.51(3)</td>
<td>84.937(11)</td>
</tr>
<tr>
<td>γ °</td>
<td>68.302(2)</td>
<td>86.67(3)</td>
<td>75.917(9)</td>
</tr>
<tr>
<td>T (K)</td>
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<td>150</td>
<td>150</td>
</tr>
<tr>
<td>COMPOUND</td>
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<td>5.20</td>
<td>5.21</td>
</tr>
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<td>------</td>
</tr>
<tr>
<td>FORMULA</td>
<td>C_{27}H_{11}F_{18}DyNO_8S_2</td>
<td>C_{9}H_{5}NO_2S_{2}</td>
<td>C_{9}H_{5}NOS_{3}</td>
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<td>M.W.</td>
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<td>Space Group</td>
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<td>Pbca</td>
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</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1761.6(6)</td>
<td>1864.1(6)</td>
<td>984.86(10)</td>
</tr>
<tr>
<td>Density (g·cm⁻³)</td>
<td>1.97</td>
<td>1.59</td>
<td>1.61</td>
</tr>
<tr>
<td>R (%)</td>
<td>3.91</td>
<td>5.22</td>
<td>3.93</td>
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<td>a (Å)</td>
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<td>7.1753(14)</td>
<td>8.7510(5)</td>
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<td>b (Å)</td>
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<td>c (Å)</td>
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<tr>
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