New Paramagnetic Thiazyl Ligands and their Coordination Complexes

by

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ABSTRACT

NEW PARAMAGNETIC THIAZYL RADICAL LIGANDS AND THEIR COORDINATION COMPLEXES

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A series of 1,2,3-dithiazolyl radicals have been prepared as spin-bearing radical ligands for coordination to paramagnetic transition metal and lanthanide ions to afford both interesting magnetic and potential conductive properties. The novel syntheses and full characterization of the ligands are described with the electronic properties investigated by both solution & solid-state EPR and cyclic voltammetry. The ligand structures are characterized by X-ray crystallography and the magnetic properties investigated. The ligands described herein represent the first reported 1,2,3-dithiazolyl radical ligands to coordinate to paramagnetic transition metal or lanthanide ion(s).

The 1,2,3-dithiazoyl ligands described have been used to prepare a number of metal complexes and the structures have been fully characterized by X-ray crystallography. A diverse range of complexes including monomers, trimers and polymers have been synthesized and characterized. The solid-state and solution magnetic properties of the metal complexes have been investigated using a range of appropriate instrumental techniques, and are reported.

The chelating properties of the 1,2,3-dithiazolyl ligands described are via an unprecedented motif. A para-naphthoquinone backbone is utilized with the fused 1,2,3-
dithiazolyl heterocyclic ring. The coordination geometry between the nitrogen atom and
the quinone oxygen(s) allows for the variety of complexes reported, including the design
objective of a polymeric paramagnetic coordination complex.

A series of 1,2,5-thiadiazolyl radical anions have been prepared as spin-bearing
radical ligands for the coordination to paramagnetic transition metal and lanthanide ions
to enable both interesting magnetic and conductive properties. The syntheses and full
characterizations are described with the electronic properties investigated by solution
EPR and cyclic voltammetry. The ligand structures are characterized by X-ray
crystallography and both the magnetic properties and conductivity (including Extended
Hückel Theory calculations) are investigated and reported.

A series of novel fluorinated 1,2,5-thiadiazole closed shell neutral ligands have
been prepared and characterized. The radical anion is studied in situ by EPR. All
materials generated in the synthesis were sent to the National Cancer Institute (USA) for
collaboration involving clinical cancer inhibition studies and the results are reported.
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To be perfectly honest, the graduate student life was not what I had anticipated. There were high times, and many low times, but I quickly realized that this is just academia life in a nutshell. However, throughout these years I met people, both from the chemistry department and beyond, which I could relate to and since have made life-long friendships. First and foremost, I would like to thank these people who took me in, a stranger from N. Ontario, and made me feel comfortable throughout this so-called adventure. I will not name names, but if you are reading this, it is very likely you are one of those people.

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GLOSSARY

A
Electron acceptor

AF
Antiferromagnetic

$a_F$
Hyperfine coupling constant to fluorine

$a_H$
Hyperfine coupling constant to hydrogen

$a_N$
Hyperfine coupling constant to nitrogen

$\vec{B}$
Magnetic induction (vector)

$\beta$
Bohr magneton

$\beta$
Bonding integral

bipy
2,2’-Bipyridine

BTDABQ
Bis-thiadiazole-1,4-benzoquinone

c
Speed of light

Cdc
Cell division cycle

CdK
Cyclin-dependent kinase

CGS
Centimeter-gram-second

Cp
Cyclopentadienyl

Cp*
Pentamethycyclopentadienyl

$\varepsilon_0$
Permittivity of vacuum

Cat
Catecholate

CatH$_2$
Protonated catecholate

CI
Chemical ionization

CO
Crystal orbital

CT
Charge transfer
CV  Cyclic voltammetry
CyHex  Cycohexane
D  Zero-field splitting tensor
D  Axial distortion parameter
D  Electron donor
DA  Dianion
DCM  Dichloromethane
DFT  Density functional theory
DMF  N,N-Dimethylformamide
DMSO  N,N-Dimethylsulphoxide
DRAM  Dynamic random access memory
DTA  1,2,3-,3-Dithiazolyl or 1,3,2-Dithiazolyl
DTANQ  Dithiazolyl-1,4-naphthoquinone
DTDA  1,2,3,5-Dithiadiazolyl
$\Delta E_{pp}$  Peak to peak potential
$\Delta H_{disp}$  Disproportionation enthalpy
E  Rhombic distortion parameter
$E_{1/2}$  Half-peak potential
EA  Electron affinity
$E_{\text{cell}}$  Cell potential
$E_{\text{gap}}$  Energy gap
EHT  Extended Hückel Theory
Emu  Electromagnetic unit
<table>
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<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$E_{\text{eff}}$</td>
<td>Effective Potential</td>
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<tr>
<td>$E_n$</td>
<td>Quantized energy of energy level &quot;n&quot;</td>
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<tr>
<td>$E_p$</td>
<td>Peak potential</td>
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<tr>
<td>EPR</td>
<td>Electron paramagnetic resonance</td>
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<tr>
<td>$f$</td>
<td>Function</td>
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<tr>
<td>$f_{\text{c}}$</td>
<td>Ferrocene</td>
</tr>
<tr>
<td>$f_{\text{c}}^+$</td>
<td>Ferrocenium cation</td>
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<tr>
<td>FM</td>
<td>Ferromagnetic</td>
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<td>$F_4\text{TDNQ}$</td>
<td>$5,6,7,8$-tetrafluoro-thiadiazole-1,4-naphthoquinone</td>
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<tr>
<td>FT-IR</td>
<td>Fourier-transform infrared spectroscopy</td>
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<td>$F_6\text{NQ}$</td>
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<tr>
<td>G</td>
<td>Gauss</td>
</tr>
<tr>
<td>GMR</td>
<td>Giant magneto-resistance</td>
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<tr>
<td>$g$</td>
<td>Electron g-factor or g-value</td>
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<tr>
<td>$\gamma$</td>
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<tr>
<td>$\vec{H}$</td>
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<tr>
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<tr>
<td>$\hat{H}$</td>
<td>Hamiltonian</td>
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<td>HF</td>
<td>Hydrofluoric acid</td>
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<tr>
<td>hfac</td>
<td>$1,1,1,5,5,5$-Hexafluoro-2,4-acetylacetonate</td>
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<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
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<tr>
<td>$\hat{H}_S$</td>
<td>Spin Hamiltonian</td>
</tr>
<tr>
<td>$\hat{H}_{\text{SO}}$</td>
<td>Spin-orbit coupling Hamiltonian</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
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<td>--------</td>
<td>-------------</td>
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<tr>
<td>HS</td>
<td>High spin</td>
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<td>$\hat{H}_{ss}$</td>
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<tr>
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<td>$\hat{H}_{ZFS}$</td>
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<td>IP</td>
<td>Ionization potential</td>
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<td>J or $\mathbf{J}$</td>
<td>Joule</td>
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<td>$\mathbf{J}$</td>
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<td>$k$</td>
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<td>$k_B$ or $k_B$</td>
<td>Boltzmann constant</td>
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<tr>
<td>$\hat{L}$</td>
<td>Angular momentum operator</td>
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<tr>
<td>LS</td>
<td>Low spin</td>
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<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
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<tr>
<td>$\lambda$</td>
<td>Spin-orbit coupling constant</td>
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<td>M</td>
<td>Magnetization (scalar)</td>
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<tr>
<td>mCPBA</td>
<td>meta-chloro-perbenzoic acid</td>
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<tr>
<td>MP</td>
<td>6-Mercaptopurine</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular orbital</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Frequency</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro’s number</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
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<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>NCI</td>
<td>National Cancer Institute</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>NRC</td>
<td>Neutral radical conductor</td>
</tr>
<tr>
<td>Oe</td>
<td>Oersted</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light emitting diode</td>
</tr>
<tr>
<td>Ψ</td>
<td>Wavefunction</td>
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<tr>
<td>Φ</td>
<td>Magnetic flux</td>
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<tr>
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<td>Phthalamido</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
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<tr>
<td>ρ&lt;sub&gt;solution&lt;/sub&gt;</td>
<td>Density of solution (grams solute·mass of solvent&lt;sup&gt;-1&lt;/sup&gt;)</td>
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<tr>
<td>ρ&lt;sub&gt;solvent&lt;/sub&gt;</td>
<td>Solvent density</td>
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<td>Q</td>
<td>Quinone</td>
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<td>RA</td>
<td>Radical anion</td>
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<tr>
<td>RAM</td>
<td>Random access memory</td>
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<tr>
<td>RICs</td>
<td>Radical ion conductor</td>
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<tr>
<td>ROS</td>
<td>Reactive oxygen species</td>
</tr>
<tr>
<td>ˆS</td>
<td>Spin operator</td>
</tr>
<tr>
<td>SCE</td>
<td>Standard calomel electrode</td>
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<tr>
<td>SDNQ</td>
<td>Selenadiazole-1,4-naphthoquinone</td>
</tr>
<tr>
<td>SMM</td>
<td>Single molecule magnet</td>
</tr>
<tr>
<td>SOMO</td>
<td>Singly Occupied Molecular Orbital</td>
</tr>
<tr>
<td>SPS</td>
<td>Solvent purification system</td>
</tr>
<tr>
<td>SQ</td>
<td>Semiquinone</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>SQUID</td>
<td>Superconducting Quantum Interference Device</td>
</tr>
<tr>
<td>TCNE</td>
<td>Tetracyanoethylene</td>
</tr>
<tr>
<td>TCNQ</td>
<td>Tetracyanoquinodimethane</td>
</tr>
<tr>
<td>TDA</td>
<td>Thiadiazole</td>
</tr>
<tr>
<td>TDAE</td>
<td>tetrakis(dimethylamino)ethane</td>
</tr>
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<td>Thiadiazole-1,4-naphthoquinone</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TFA</td>
<td>Trifluoroacetic acid</td>
</tr>
<tr>
<td>TMR</td>
<td>Tunnel magneto-resistance</td>
</tr>
<tr>
<td>TTTA</td>
<td>Trithiatriazapentalyl</td>
</tr>
<tr>
<td>TTF</td>
<td>Tetrathiafulvalene</td>
</tr>
<tr>
<td>$U$</td>
<td>Coulombic repulsion energy</td>
</tr>
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<td>$\mu$</td>
<td>Magnetic permeability</td>
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<tr>
<td>$\mu_B$</td>
<td>Bohr magneton (Electron magnetic moment)</td>
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<td>$W$</td>
<td>Overlap integral</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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<td>Zero-field splitting</td>
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I-4  

I-5  

I-6a  

I-6b  

I-6c  

I-7  

I-8  

I-9  

I-10  

I-11
\[ \text{III-3} \]

\[ \text{[TDNQ]}_3[\text{CoCp}_2]_2 \]

\[ \text{[SDNQ]}_2[\text{CoCp}_2] \]

\[ \text{E = S, Se, O} \]

\[ \text{III-4} \]

\[ \text{III-5} \]

\[ \text{III-6} \]

\[ \text{III-7} \]

\[ \text{III-8} \]

\[ \text{IV-1} \]

\[ \text{IV-1}^- \]

\[ \text{IV-2} \]
Chapter 1

Introduction
Chapter 1 Introduction

1.1 Foreword

As electronic technology continues to advance, the pressure to produce smaller and smaller components increases. However there is a lower limit to the scale on which conventional materials can be used. So-called “molecular materials” may provide a means of breaking that size barrier. Molecular materials, defined as materials composed of individual molecules that impart bulk physical properties, are an important class of materials that is currently at the forefront of research in a number of fields. This recent burst of interest can be attributed to the novel properties that have been reported in nanoscience and nanotechnology. The potential applications of the materials synthesized are quite diverse, ranging from photovoltaic cells (solar energy)\(^1\) to smaller electronic components (high-density random access memory, RAM)\(^2\) to targeted drug delivery systems for specific cell type (e.g. cancer).\(^3\) Of the many molecular material areas, a field that is presently gaining much interest is ‘magnetic molecular materials’.

Molecular magnetic materials arise from the ‘bottom up approach’ concept\(^4\) (as compared to the ‘top down’ concept\(^5\) which includes techniques such as chemical vapour deposition) that utilizes molecular building blocks to generate materials which can exhibit interesting and potentially useful magnetic properties. If the structure is known, the bulk magnetic properties can usually be predicted, and these can also be modified by molecular design. The properties that can occur (such as magnetic hysteresis,\(^6\) ferromagnetism,\(^6,7\) (FM) etc.) are generated either from the bulk properties of the materials through cooperative long-range interactions (e.g. ferrimagnetism\(^8,9\)) or by each
discrete molecule (e.g. single molecule magnet,\textsuperscript{10,11} SMM). The compounds that are researched and subsequently developed for molecular materials vary greatly from transition metal (and lanthanide\textsuperscript{12}) clusters\textsuperscript{13,14} to purely organic molecules,\textsuperscript{15-17} and combinations of both in order to incorporate the advantages of each.\textsuperscript{18-20} However, the inclusion of two different properties (such as magnetism, luminescence, conductivity, etc.) into one material is becoming a key issue in modern materials science. By including two separate properties, the physical size of components can be reduced (e.g. enabling data storage and processing in a single material). A growing field of interest that encompasses both molecular magnetic materials and conductivity simultaneously is \textit{spintronics} (also know as spin-based electronics or magneto-electronics).\textsuperscript{21} This is an example of cooperative interplay between two separate properties to achieve an unprecedented property.

Molecular spintronics is a field devoted the spin transport phenomena in molecule systems. In “traditional” charged based electronics, the transport of the electrons does not take into consideration the associated spin (with equal populations of spin up and spin down charge carriers). However, in molecular spintronic materials, the charge carriers can be induced to undergo a spin preference, resulting in a spin-polarized current. By isolating and switching between spin-polarized currents, the potential applications predicted are quite diverse ranging from magnetic recording, memory storage to data processing.\textsuperscript{2} While this notion has been looming for over 75 years, the progress in scientific research has yet to fully exploit this idea. Mott introduced the thought of “spin up” and “spin down” currents in ferromagnets in 1937\textsuperscript{22,23} which can be treated as two different families, dubbed as the ‘two channel mode’.\textsuperscript{24} The motilities of these two
channels are very different in ferromagnets which led to the discovery of giant magnetoresistance (GMR) in 1988 by Grünberg and Fert by use of an iron/chromium magnetic superlattice.\textsuperscript{25,26} They subsequently shared the Nobel Prize in Physics in 2007. This discovery led to an innovation of data storage and was commercially used in the late 1980’s for roughly a decade.\textsuperscript{27} GMR has now been replaced by more sensitive devices which harness tunnel magnetoresistance (TMR), however it ultimately illustrated that the concept of spintronics is worth pursuing.

Currently the development of spintronic materials is focused on ‘doping’ known semiconducting materials with high spin transition metals to (try and) generate ferromagnetic semiconductors. One such example is doping gallium arsenide (GaAs) with manganese (Mn\textsuperscript{II}), \textit{i.e.} “p-type” doping) to achieve ferromagnetic ordering at ambient temperatures.\textsuperscript{28} There are other doping experiments including manganese doped zinc oxide\textsuperscript{28} and extravagant nitrogen doped diamond\textsuperscript{27} complexes. However, this demonstrates only one approach to synthesizing ferromagnetic semi-conductors and there are alternatives such as using organic materials, which have yet to be exploited.

One such alternative is by use of the metal - radical approach.\textsuperscript{29} Radical organic ligands have been pursued in recent years demonstrating interesting semi-conductive and magnetic properties.\textsuperscript{30-32} These radical ligands (especially with quinone-type moieties\textsuperscript{17,31}) can have multiple oxidation states and thus are redox-active\textsuperscript{34} non-innocent ligands.\textsuperscript{35-38} These redox properties can have a variety of effects on the system allowing for spin crossover\textsuperscript{39} and valence tautomerism\textsuperscript{40-42} to occur. There are also magnetic metallic (and lanthanide) complexes and clusters\textsuperscript{13,14} which have shown interesting magnetic properties. However, by combination of both intramolecular magnetic
coupling between the spin bearing ligand and the metal ion and intermolecular magnetic coupling between complexes in the solid state, this can enhance the overall magnetic interactions of the system. The inclusion of the organic radical ligands not only can direct the exchange coupling between metal centers, but also can act as a pathway for activated conductivity if the complexes pack in a way which allows it. The inclusion of the paramagnetic metal centers can increase the overall spin concentration of the system (and can add magnetoanisotropy), thus making the magnetic moments larger compared to the open shell ligands alone.

The actual synthetic research and knowledge from studied spintronic materials is still in its infancy. In order to understand fully the complex nature of this field, it is easier to do research on simpler systems to help build theoretical models. This thesis discusses the synthesis and characterization of new spin bearing ligands, and their coordination to paramagnetic transition metal and lanthanide ions. This method follows the bottom-up approach for (potential) generation of simple spintronic systems. The ultimate goal would be to synthesize, characterize and fully study a ferromagnetic semiconductor.

This thesis is divided into four chapters. Within this chapter, information necessary for designing, synthesizing and analyzing semi-conductive ferromagnetic materials is discussed. This includes the fundamental principles and physical measurements of magnetism and conductivity. Discussion of previous work performed on thiazyl chemistry, syntheses and reactivity of 1,2,3-dithiazoles (1,2,3-DTA) and 1,2,5-thiadiazoles (1,2,5-TDA) and relevant discussion regarding para-quinones is also provided. This chapter provides the background necessary to understand the design,
synthesis and coordination of the ligands discussed throughout and ultimately the thesis
scope.

Chapter Two covers the synthesis and characterization of two new radical ligands; naphtho[2,3-\textit{d}][1,2,3]dithiazolyl-1,4-dione (DTANQ) and 5,8-dimethyl-naphtho[2,3-
\textit{d}][1,2,3]dithiazolyl-1,4-dione (5,8-Me\textsubscript{2}DTANQ). The synthetic approaches along with
full characterization (FT-IR, NMR, CV, EPR, magnetometry and X-ray crystallography) are
provided in detail. Special attention to crystal packing and solid-state EPR
spectroscopy is discussed. Coordination of these ligands to paramagnetic transition metal
and lanthanide ions including the synthesis and characterization (magnetometry and X-
ray crystallography) of the products is also presented in detail.

Chapter Three covers the synthesis and characterization of three new radical
anion ligands; naphtho[2,3-\textit{c}][1,2,5]thiadiazole-4,9-dione $\textit{\cdot}\cdot$ (TDNQ $\textit{\cdot}\cdot$), naphtho[2,3-\textit{c}]-
[1,2,5]selenadiazole-4,9-dione (SDNQ $\textit{\cdot}\cdot$) and benzo[1,2-\textit{c}:4,5-c']bis([1,2,5]thiadiazole)-
4,8-dione $\textit{\cdot}\cdot$ (BTDABQ $\textit{\cdot}\cdot$). Discussion of the syntheses of all three ligands (including
multiple synthetic routes) along with full characterization (FT-IR, NMR, CV, EPR,
magnetometry, conductivity, DFT and EHT calculations, and X-ray crystallography) is
provided.

Chapter Four is represents a significant tangent from the rest of the thesis. A
novel synthetic route and subsequent modification of the neutral TDNQ is performed to
synthesize the perfluoro-analogue 5,6,7,8-tetrafluoronaphtho[2,3-\textit{c}][1,2,5]thiadiazole-4,9-
dione, ($\textit{F}_4\text{TDNQ}$). Discussion of the synthesis and characterization (FT-IR, NMR, CV,
EPR) is reported. Clinical cancer inhibition studies of all products were performed and
are discussed. This thesis will end with a brief summary of all results and observed trends of chapters two through four.

1.2 Magnetism

In the most general sense, all atom-based matter is ‘magnetic’, that is to say “the material will be attracted to (paramagnetic response) or repelled by (diamagnetic response) a magnetic field”.

These effects arise from the electrons in the materials, regardless of whether they are paired or unpaired. It is the circulation of paired electrons in bonds and lone pairs that generates a magnetic dipole induced by an external magnetic field resulting in diamagnetism. This overall response is weak compared to any system that has other magnetic properties caused by unpaired electrons (i.e. a paramagnetic response is roughly three orders of magnitude larger than diamagnetism). The magnetic data reported throughout this thesis is based upon exchange coupling between the metal centers and the novel radical ligands synthesized, or between two radicals in the solid state, and thus any detailed mathematic discussion of long range ordering phenomena (e.g. ferromagnetism, antiferromagnetism, ferrimagnetism, etc.) will not be discussed. The following discussion is concerned solely with paramagnetic phenomena.

1.2.1 Fundamentals of paramagnetism

Magnetic coupling between individual magnetic moments, (e.g. those arising from an organic radical and a paramagnetic transition metal ion or another organic radical) can either be ferromagnetic (FM) or antiferromagnetic (AF). Molecular orbital (MO) theory can be used to predict the type of magnetic coupling that will occur. Direct exchange coupling refers to the mechanism by which overlap of the magnetic orbitals
determines the ground state spin. Either “Hund’s rule of maximum multiplicity” or the “Pauli exclusion principle” can be invoked. A simple orbital description can illustrate how magnetic coupling occurs and which type, FM or AF, can be predicted. Figure 1.1 portrays an electron in the d orbital of a metal ion (for simplicity, in octahedral symmetry) and an electron in a π system of a weak field ligand. If a d_z^2 orbital interacts with a p_z orbital, Hund’s rule applies, due to the orthogonal overlap (that is, the overlap integral of the two wavefunctions equals zero, \( \int \psi_1 \psi_2 d\tau = 0 \)). The magnetic interaction can be predicted as FM coupling because the lowest energy electronic configuration should have parallel spin alignment, leading to the maximum multiplicity, spin quantum number (\( S = 1 \)). If the same p_z orbital interacts with a d_{x^2-y^2} as can be seen in Figure 1.1, the spatial overlap between the orbitals is non-orthogonal (that is, integration of the two wavefunctions, equals a non-zero value, \( \int \psi_1 \psi_2 d\tau \neq 0 \)) and the Pauli Exclusion Principle results (as no two fermions can have the same set of quantum numbers). Thus, the lowest energy electron configuration is the singlet (\( S = 0 \)) and the electrons are antiparallel, providing AF coupling.

The magnetic coupling term, \( J \), is used to illustrate the magnetic interactions between any two interacting magnetic components. This coupling term is the difference in energy between the two possible states as shown in Figure 1.1.
Figure 1.1 Direct exchange modes: top AFM coupling and bottom FM coupling

The energy units of $J$ are typically expressed as wavenumbers (cm$^{-1}$) or in Kelvin. By fitting a $\chi T$ vs. $T$ plot with a phenomenological Hamiltonian (Figure 1.2), one can retrieve $J$:

$$\hat{H} = -2J \Sigma_{i>j} \left( \hat{S}_i \hat{S}_j \right). \quad \text{(eq 1.1)}$$

where $\hat{S}_i$ and $\hat{S}_j$ are spin operators for spins $S_i$ and $S_j$. It should be noted that there are a variety of conventions how to express this Hamiltonian. The addition of 2 is a convenience factor that allows for simplicity of the equation when expanded. In this case (as expressed in equation 1.1), if the $J$ term is positive, ferromagnetic coupling (spins aligned) occurred when an external magnetic field, $\vec{H}$, was applied. The opposite
scenario, with a negative $J$ term would reflect antiferromagnetic coupling (spins anti-aligned). If $J = 0$, there is no energy difference between the two possible alignments of spins, thus neither coupling scenarios occurs. This ultimately results in a random distribution of spin orientations throughout the system or an equal and opposite amount.

When magnetic data is reported in the literature, the value that is given is the magnetic susceptibility, $\chi$, which indicates the degrees of magnetization, $M$, of the material in response to an externally applied field, $H$. A common representation of magnetization and applied magnetic field is:

$$\frac{\delta M}{\delta H} = \chi(v)$$  \hspace{1cm} \text{(eq 1.2)}

where $\chi(v)$ is the volume magnetic susceptibility, $M$ is the resulting magnetization, and $H$ is the externally applied magnetic field. It should be noted that $\chi_v$ is conventionally expressed in emu/cm$^3$ and since an emu is equal to cm$^3$, the value of $\chi_v$ is dimensionless. If the magnetic field is weak enough, $\chi$ can be related to $H$ by:

$$M = \tilde{H}\chi(v)$$  \hspace{1cm} \text{(eq 1.3)}

The molar magnetic susceptibility ($\chi$) is much more useful for chemical analysis and is related to $\chi(v)$ by:

$$\chi_m = \chi(v) \times MW \div \rho$$  \hspace{1cm} \text{(eq 1.4)}

where $\rho$ is the density and MW is the molecular weight of the material. This provides the magnetic susceptibility per mole of the material. Therefore, the molar magnetic susceptibility in general system can be described as:
\[ \chi_m = \frac{\mathcal{M} N_A}{\mathcal{H}} \]  

(eq 1.5)

where \( N_A \) is Avogadro’s number.

The magnetic susceptibility can also be described as:

\[ \chi = \frac{N_A \mu_{\text{eff}}^2}{3k_B T} = \frac{C}{T} \]  

(eq 1.6)

where \( \mu_{\text{eff}} \) is the effective magnetic moment per paramagnetic ion, \( k_B \) is the Boltzmann constant, \( T \) is temperature and \( C \) is defined as the Curie constant. The Curie law describes the magnetization of ideal paramagnets and illustrates that the magnetic susceptibility, \( \chi \), is inversely proportional to the temperature. It should be noted that \( \mu_{\text{eff}} = g \mu_B \sqrt{J(J + 1)} \), where \( \mu_B \) is the Bohr magneton, \( g \) is the ‘g-factor’, and \( J \) is the total angular momentum quantum number. However when the contributions from orbital angular momentum is small (i.e. orbital angular momentum is quenched) then \( \mu_{\text{eff}} \approx g \mu_B \sqrt{S(S + 1)} \) where \( S \) is the spin quantum number. It should be noted that the Curie Law does not incorporate the exchange coupling term \( J \), or any anisotropic terms.

Typical experimental data are either plotted as \( \chi \) vs. \( T \) (Figure 1.2, left) or, more commonly, by plotting \( \chi^T \) vs. \( T \) (Figure 1.2, right). If \( J = 0 \) there is no energy difference between the two possible alignments of spins (ideal Curie behaviour) and a linear relationship between \( \chi^T \) vs. \( T \) results. If \( J > 0 \) or \( J < 0 \), ferromagnetic coupling or antiferromagnetic coupling occur respectively and the \( \chi^T \) vs. \( T \) and \( \chi \) vs. \( T \) dependences are illustrated in Figure 1.2.
Ideal Curie behaviour rarely occurs in any material because the unpaired electrons are rarely well isolated in the system. Interactions are more apparent at lower temperatures because low lying excited states are thermally depopulated and thus deviation from the Curie law results. A better method of describing these systems is by use of the Curie-Weiss law which incorporates a phenomenological constant, $\Theta$, the Weiss constant:

$$\chi = \frac{C}{(T - \Theta)}$$  \hspace{1cm} (eq 1.7)

The Curie-Weiss equation describes the magnetic susceptibility of a system which shows some magnetic coupling (FM or AF). If $\Theta = 0$, then the material is considered to be an ideal paramagnet. If $\Theta > 0$ then the interaction is ferromagnetic and if $\Theta < 0$ the interaction is antiferromagnetic. However, the Curie-Weiss law does not incorporate the exchange coupling term $J$. Clearly there is a dependence relationship between $J$ and $\Theta$. In mean field theory the two are related by $\Theta = 2zJS(S+1)/3k_B$. 

**Figure 1.2 The comparison of two different plots of magnetic data**
In order to determine $J$, the van Vleck equation\textsuperscript{6} (which was proposed in 1932) is used:

\[ \chi = \frac{N \sum_n \left( \frac{E_n^{(1)}}{k_B T} \right)^2 \exp \left( -\frac{E_n^{(0)}}{k_B T} \right) \exp \left( -\frac{E_n^{(2)}}{k_B T} \right)}{\sum_n \exp \left( -\frac{E_n^{(0)}}{k_B T} \right)} \]  

(eq 1.8)

where $N$ is Avogadro’s number, $k_B$ is the Boltzmann constant. The term $E_n^{(0)}$ represents the ground state energy of the system in absence of any magnetic field and $E_n^{(1)}$ and $E_n^{(2)}$ are first and second order field dependent terms. $E_n^{(0)}$ consists of the exchange coupling (equation 1.1) and any spin-orbit coupling (not applicable to this thesis). $E_n^{(1)}$ is the Zeeman term and $E_n^{(2)}$ consists of the 2\textsuperscript{nd} order Zeeman terms (typically negligible).

1.2.2 Physical methods of measurement

Superconducting Quantum Interference Device (SQUID)

One of the primary methods of acquiring magnetic data of the materials presented in this thesis consists of using a SQUID magnetometer. While the University of Guelph has recently acquired one, Dr. Rodolphe Clérac at the University of Bordeaux performed all experiments throughout this thesis. This device measures magnetic susceptibility, $\chi$, of the material as a function of temperature and applied field, $H$. The experimental value of $\chi$ is the sum of the independent contributions. These include the diamagnetic susceptibility $\chi_{(\text{dia})}$, paramagnetic susceptibility $\chi_{(\text{para})}$ and other forms of magnetic responses such as temperature independent susceptibility (not covered further as not relevant to this thesis).
\[ \chi_{\text{exp}} = \chi_{\text{dia}} + \chi_{\text{para}} \]  

(eq 1.8)

Diamagnetism is a property of all matter having electron pairs and manifests as repulsion from a magnetic field. In order to properly determine the correct \( \chi_{\text{para}} \) value, \( \chi_{\text{dia}} \) must be accounted for. Since experimental diamagnetic susceptibilities of many compounds have already been determined, the elemental contributions can be calculated and tabulated (including various hybridizations, oxidation states and coordination numbers). By applying a linear sum of these ‘Pascal’s’ constants, the diamagnetic susceptibility for any unknown species can be calculated. The error associated with this approach is typically negligible. The value of \( \chi_{\text{dia}} \) is always < 0 and typically on the order of magnitude of \( \sim 10^{-6} \) emu/mol. A rough approximation can also be made using:

\[ \chi_{\text{dia}} = k \times MW \times 10^{-6} \]  

(eq 1.9)

where \( k \) is a weighing factor between 0.4 and 0.5.

To extract \( \chi_{\text{para}} \) from the experimental data, one must also correct for the sample holder (which will be diamagnetic). This can be done easily by measuring the sample holder empty.

In order to avoid any possible interference from ferromagnetic impurities, measurement of magnetization as a function of the applied field at 100 K is performed. For paramagnetic or diamagnetic systems, a linear response in the \( M \) vs. \( H \) data that extrapolates to \( M = 0 \ H = 0 \) is expected (Figure 1.3). It should be noted that compounds with ferromagnetic ordering would show a spontaneous magnetization and not
extrapolate to zero. Any trace of ferromagnetic impurities will be seen in this measurement since magnetic susceptibility is extremely sensitive.

![Figure 1.3 Generic M vs. H plot illustrating a perfectly linear response](image)

If the solid state structure of the material is known, and prediction of the magnetic data can usually occur (e.g. diamagnetic dimers), thus this quick experiment is performed to ensure the sample is pure. It should also be noted that even though a sample could be pure by elemental analysis, any trace of ferromagnetic impurity (even a ppm amount) will be seen and can be potentially problematic for magnetic measurements.

Another experiment performed prior to obtaining $\chi$ is a saturation experiment, $M$ vs. $H$, typically performed between 1 - 4 K. This is performed in order to choose an appropriate field for the variable temperature measurements. This is also to determine the saturation magnetization of the sample, which can confirm the number of unpaired electrons per molecular unit. Having the correct applied field is critical; the field has to be large enough to generate a response from the material being measured, but small enough that the magnetization has a linear relationship and the $\chi = M/H$ approximation is
valid. If the applied field is too strong, the magnetic moment of any paramagnetic centers will align with the field. This will conceal any weak intramolecular magnetic coupling of the material.

Other concerns prior to measuring the sample include desolvation of the material. If a material is crystallized with inclusion of solvent molecules in the solid state, loss of these solvent molecules could change the intermolecular interactions and/or mass of the sample and/or the molecular weight of the compound. If the sample becomes amorphous as a result, this would produce data that cannot be interpreted as a function of the structure. A crystal structure of the material must be produced without the solvent molecules present or thermogravimetric experiments must be performed to identify solvent loss at higher temperatures.

**Electron Paramagnetic Resonance (EPR)**

Another method of examining magnetic behaviour of the materials presented in this thesis consists of using Electron Paramagnetic Resonance (also known as Electron Spin Resonance (ESR)).\(^{50}\) This technique is known as the ‘electron equivalent’ of \(^1\)H NMR. Systems with a non-zero spin will experience splitting of microstates (*i.e.* lift the degeneracy of \(m_s\) energy levels) when placed in an applied magnetic field (the Zeeman effect). For a system with one unpaired electron (\(m_s = \pm \frac{1}{2}\)), the splitting would yield two spin states. The EPR instrument sweeps the magnetic field while irradiating with a constant microwave frequency.
Figure 1.4 Fundamental principle of EPR spectroscopy illustrating a $S = 1/2$ system

An unpaired electron can move between the two energy levels by absorbing/emitting electromagnetic radiation ($\epsilon = h\nu$) when the conditions are obeyed ($\Delta E = \epsilon$), therefore when:

$$h\nu = g\beta H$$ \hspace{1cm} (eq 1.10)

The constants are the same as previously mentioned; $\beta$ is the Bohr magneton, $H$ is the field strength and $g$ is the $g$-factor. The value of the $g$-factor has a similar meaning comparable to chemical shift in NMR spectroscopy.

EPR is a useful spectroscopic tool for observing the coupling distribution (spin density) in species with atoms having non-zero nuclear spin. If there are locations of spin density on atoms with non-zero nuclear spin, hyperfine coupling interactions occur, splitting the EPR signal. The splitting pattern can be determined using:

$$2nl + 1$$ \hspace{1cm} (eq 1.11)

where $n$ is the number of atoms and $I$ is the nuclear spin.
In solution EPR spectroscopy, the molecules being probed are tumbling rapidly enough in solution that an average of all three spatial directions is usually observed and an isotropic value of the g-factor is seen. However, in solid state EPR spectroscopy, typically the molecule is magnetically anisotropic and individual values of $g_x$, $g_y$, and $g_z$, must be found in order to simulate the data. The simulation of a solid state EPR signal (triplet, $S = 1$) is not a trivial task; one has to include possible $S = \frac{1}{2}$ defects in the crystal lattice, all three g-factor values (for the spatial directions) and both zero-field splitting parameters, $D$ (axial magnetooanisotropy) and $E$ (tetragonal/rhombic magnetooanisotropy), to model the data. $D$ is a measure of the delocalization of the molecular orbitals involved in the triplet state and is inversely proportional to the cube of the distance between the unpaired electrons, and $E$ is attributed to the extent of distortion from axial symmetry and is in the range $0 \leq 3 (|E|/|D|) \leq 1$.51

1.3 Fundamentals of conductivity

Conduction properties of a solid-state material are often described in terms of its band structure. This is a good starting point for the explanation of electrical conductivity. The electronic band structure of a material describes the energy bands (the allowed ranges of energy) that an electron within a solid may have, and band gaps (the forbidden ranges of energy) it may not have. A metallic conductor is a partially filled band (with no band gap) and the occupying electrons are able to move relatively freely within the band. A true metallic conductor is described an increase of conductivity with a decrease in temperature.
Both insulators and semiconductors have completely filled bands with empty bands lying higher in energy. The difference between them is the distance between these two bands, known as the band gap. The smaller the band gap, the smaller the thermal (or other) activation energy required for conduction to occur. For these materials to allow conduction, an activation energy is required to move the electrons from the valence band to the conduction band. This activation energy is proportional to the width of the band gap. If $E_{\text{gap}}$ is very large, the material is considered to be an insulator. Some typical generic bands are shown below in Figure 1.5.

![Band Structures](image)

**Figure 1.5 Several types of generic band structures**

Another useful tool for the explanation of experimental conductivity measurements is a dispersion curve. In a hypothetical dispersion curve (Figure 1.6), there are a continuous set of $n$ states, beginning from $k = 0$, where all crystal orbitals (COs, which derive from a linear combination of atomic orbitals, AOs) are in the same phase and ending with $k = \pi/a$ where all crystal orbitals now have phase alternation at every atomic site (reversing the bonding properties in the COs).
Band theory and dispersion curves are directly related. The bands are actually generic density of states (DOS) drawings, which arise from dispersion curves. The transition from dispersion curves to the bands of band theory is fairly simple as illustrated below (Figure 1.7).
The bandwidth of a system, \( W \), is expressed in terms of the dispersion, \( W = |\Delta E_k| = [E(k = \pi/a) - E(k = 0)] \) of the crystal orbitals. In order to have a metallic ground state in a partially filled band, \( W > U \), where \( U \) is the Coulombic repulsion energy. In order to understand the Coulombic barrier, another model, ‘the Hopping’ model is shown below.

In a \( \frac{1}{2} \) filled band, the electron ‘hops’ from one site to the next (Figure 1.8). However, during this hopping, the electron is experiencing repulsion from the electron that is currently at that site. The energy that is required to force an electron from one radical site to another is equivalent to the Coulombic Barrier \( (U) \) which is approximately equal to the gas phase disproportionation enthalpy \( (\Delta H_{\text{disp}}) \). This enthalpy is equal to the ionization potential (IP) minus the electron affinity (EA) for a neutral species. For other systems, such as radical anions, the difference between the first electron affinity \( (EA_1) \) and the second electron affinity \( (EA_2) \) would equal \( \Delta H_{\text{disp}} \).

1.3.1 Neutral radical conductors (NRCs)

In 1975, Haddon proposed the use of odd alternant hydrocarbons (OAHs) as candidates for building blocks of 1-D molecular metals. If a 1-D \( \pi \)-stacked array of planar radical molecules formed, with strong orbital overlap between the singly occupied molecular orbitals (SOMO), band theory would predict that it would develop a half filled energy band, thus being an organic metal (Figure 1.9).
As a consequence of this proposal, Haddon favoured planar organic radicals, such as phenalenyl (PLY). While this theory is completely valid for generation of a half-filled band using organic radicals, in practice there are other issues that prevent real materials from easily attaining this type of electronic structure. Firstly, any partially filled band will be vulnerable to Peierls distortion (vide infra), thus disrupting the perfectly uniform lattice and ultimately removing the potential for conductivity. However, since we use the ‘bottom up’ approach, we are able to design our ligands in such a fashion that should discourage this distortion. Ultimately, our goal structure aims to minimize the propensity for a Peierls distortion to occur and is discussed in further detail in section 1.6 of this chapter. Secondly, since the band is predicted to be half filled, the on-site Coulomb repulsion energy will be very large and could (potentially) generate a Mott insulating state (vide infra) if the bandwidth is too small. If metallic conductivity should not occur,
however, Mott-type activated conductivity is possible. Our target structure actually counts on this Mott type behaviour to give rise to the desired activated conductivity.

1.3.2 Charge transfer salts and radical ion conductors

A charge transfer (CT) salt is composed of two (or more) molecules, wherein one is a $\pi$-molecular electron donor (D) and the other is a $\pi$-molecular electron acceptor (A). When both of these components are present in a material (e.g. co-crystallized), the donor is oxidized and the acceptor is reduced by electron transfer. However, the highest occupied molecular orbital (HOMO) must be close in energy to the lowest unoccupied molecular orbital (LUMO) for this to occur. The overall degree of electron transfer is described by:

$$\Delta E = EA - IP + J$$  \hspace{1cm} (eq 1.12)

where $J$ is the electrostatic Coulomb interactions within the ionic material.$^{54}$

The most famous CT salt is that of the co-crystallization of tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) in 1973.$^{55}$ It exhibits very high conductivity ($\sim 10^4$ S cm$^{-1}$) at room temperature and was the first discovered purely organic metallic conductor. Within the solid state structure, the TTF and TCNQ molecules are arranged in separate parallel stacks such that electron transfer can occur between stacks. The electrons and the holes are separated in each independent stack. When an electric potential is applied, these electrons (and holes) can move in a one-dimensional direction along each respective stack.
Radical ion conductors (RICs) are closely related to CT salts. In comparison to CT salts, RICs incorporate a simple inorganic counter ion instead of either the donor or the acceptor component of the system. This system potentially forms a highly conductive radical ion salt (D$^+$ X$^-$ or X$^+$ A$^-$) by the oxidation of a $\pi$-molecular donor or the reduction of a strong $\pi$-molecular acceptor. Complete electron transfer is not necessary (and may be unfavourable due to Coulombic repulsion interactions in the solid state). The conductivities of [TTF][Br] and [TTF][Br]$^{0.7}$ are $10^{-4}$ and $10^{2}$ s cm$^{-1}$ respectively.$^{56}$

**1.3.3 Insulating states**

Using the terminology of physics, any material that demonstrates activated conductivity (*i.e.* a band gap) is classified as an insulator. Therefore all semiconductors are insulators by this definition. There are four major insulating states: a) a band theory insulator (as mentioned above) b) an Anderson insulator$^{57}$ caused by impurities and/or disorder in the crystal lattice c) a Mott insulator and d) a Peierls insulator. The last two will be described below, as they are most relevant to this thesis.

**Mott insulators**
Systems that should behave as metallic conductors (i.e. partially filled bands) but are insulators when measured, are called Mott insulators. This is very common for species in which there is a lone electron on each site (i.e. a $\frac{1}{2}$ filled band). Since there is a high Coulombic repulsion, there is an energy barrier to charge transfer. If the orbital overlap of atomic sites ($\beta$) is very small, then the probability density is not very high between atomic sites (i.e. the spatial part of the wavefunction makes it unlikely that the electron will be in the interatomic space). If the Coulombic repulsion is too large, it will prevent conduction. As $\beta$ increases, there comes a point in which a half filled band best describes the system because the Coulombic repulsion to orbital overlap is now optimal. This transition from an insulator to metal system is the Mott-Hubbard transition (Figure 1.11). It should be noted that this transition is less likely to occur when the system is not exactly $\frac{1}{2}$ filled.

\[ \text{Figure 1.10 Mott-Hubbard transition when the } \beta \text{ is increased going from an insulating to metallic state} \]
Peierls distortion\textsuperscript{58} lowers the energy of systems with partially filled bands (\textit{e.g.} \(1/2\) filled) by disrupting the regular array of sites giving alternation of intersite distances (\textit{e.g.} dimerization). This transition is purely thermodynamically driven. The resulting periodicity creates a band gap, which was not present prior to distortion. It should be noted that Peierls distortion could occur with any degree of filling however it is convenient and more relevant to this thesis to use the concept with one unpaired electron per site. A classic example is a uniform one-dimensional chain with one unpaired electron per site (\textit{e.g.} a 1-D array of hydrogen atoms) shown below. After distortion, the new lattice consists of alternating long and short distances between each atomic site. The overall result is the bottom half of the band is lowered in energy while the upper half is raised in energy. This then separates the two bands with a band gap that is proportional to the size of the distortion in the system.\textsuperscript{50}

\textbf{Figure 1.11} Visual representation between Peierls distortion in a lattice and the corresponding splitting of the band, generating a band gap
1.3.4 Physical methods of measurement

Conductivity measurements reported in this thesis were generated using a crude pressed pellet conductivity cell. This cell is composed of two conductive plates that are separated by an insulating material. A small amount of finely ground sample (< ~3 mg) is placed in the middle of an insulating cylinder held in place by two conductive screws, attached to each plate. A multimeter is attached to both plates, allowing for the only conductive pathway to be through the sample. This apparatus allows for crude conductivity measurements and can be performed under inert atmosphere if the sample is air or moisture sensitive. This system also allows for crude pressure tests to be performed as pressure can influence the conductivity of the sample. A more accurate and sensitive approach is to perform a four-point single crystal measurement. However, this cumbersome method does not allow for air and moisture sensitive experiments and very large single crystals are needed.
1.4 Spin bearing ligands

Organic radicals are typically thought to be highly reactive and rapidly decompose via a number of routes such as dimerization, hydrogen abstraction, etc.\textsuperscript{61} However, stable free radicals have been studied for over 100 years\textsuperscript{61} and continue to be studied in part because of their interesting solid state properties. The term ‘stable’ is relative and should be more thoroughly defined. When referring to a stable radical molecule, it is a material that can be isolated and stored as a pure substance for a prolonged period of time.\textsuperscript{61} A persistent radical is a compound that survives long enough to be spectroscopically observed but not isolated.\textsuperscript{61} This concept of stability is especially important in this thesis, as the radicals ligands synthesized must be stable to undergo transition metal (and lanthanide) coordination chemistry. Within the past 15 years,
research on the coordination of radical ligands to impart interesting magnetic (and now conductive) properties has grown and there have been some important contributions in this field.

There are three common and important concepts to the design of stable radicals throughout the literature:

a) incorporate bulky substituents on the molecule to add steric hindrance to prevent close contacts between molecules, and position these substituents around reactive sites to impede irreversible dimerization, b) the higher the delocalization of the spin density the more stable the radicals, and c) incorporation of electronegative heteroatoms with lone pairs makes the radicals less reactive to molecular oxygen and also helps prevent any possible thermodynamic energy gain from σ bond formation.

Although there exist many different types of radical systems in the literature, only a few are reported as being ligands (i.e. coordinated to a metal). This niche is still in its infancy of generating magnetic and (potentially) conductive materials. Prior to our research, there were few known examples of magnetic complexes with spin bearing ligands published in the literature. Some of these ligands are semiquinones I-1, nitroxyI29 and nitronyl nitroxides I-2, verdazyls I-3, azaphenylenyls I-4, tetracyanoquinodimethane I-5, and thiazyls I-6a,b,c. Examples of these are illustrated below.
However, even with all these radical ligand designs, many of them have one or more of the following issues: a) unavailable coordination site, b) coordination site(s) present but without any remarkable spin density for significant magnetic coupling with the metal, c) steric bulk on the ligands prevents coordination and/or any type of π stacking (for conductivity), and d) difficult to synthesize (and possibly dangerous) and/or purify to allow for coordination attempts to occur. As can be seen in Figure 1.14, most of the reported coordinated spin bearing ligands have a bidentate (or bis-bidentate) coordination pocket. As mentioned above in the magnetic section, the nature of magnetic coupling will be dictated by the relative symmetries of the interacting orbitals *(i.e.* the
degree of overlap and orthogonality). If there is free rotation around the metal-radical bond (as with a nitroxide (I-2) radical), the magnetic interaction is completely unpredictable as the orientation of the relevant magnetic orbitals have the possibility of changing, thus the magnetic interactions change. It should be noted that the energy required allowing for various conformations of coordinations are typically quite small. However, recent development in new thiazyl radical ligands has had a significant impact on this narrow field of magnetism.

### 1.4.1 General review of thiazyl chemistry

The molecular building block of thiazyl molecules is the SN fragment. In the early 1970s, poly(sulfur-nitride), ([SN]ₙ), was synthesized and its interesting metallic and superconducting properties were discovered. This behaviour arises from its polymeric nature that has extensive π-delocalization of electrons within each S-N-S chain. In the crystal structure, there are one-dimensional chains which have S--S interactions between them. This results in a partially filled band and was the first conducting inorganic polymer reported. Thus began the rapid interest in thiazyl chemistry in the 1970s, however the majority of the interest was to modify the (SN)ₙ polymer. Multiple fragments of the SN unit can be combined to produce a variety of cyclic structures (Figure 1.15). Many of these compounds by nature are highly explosive depending on the purity. For example tetrasulfur tetranitride is highly shock sensitive, to decomposing exothermically into elemental sulfur and gaseous nitrogen: 2 S₄N₄(s) → S₈(s) + 4 N₂(g)
The SN fragment is most closely related to its isoelectronic NO fragment, however the chemistry is not the same at all. Despite this, both molecules do share one important quality: they are both building blocks to the generation of stable radical molecules. Like the chemistry between each building block is different, the chemistry of each independent radical species is different. Typically, thiazyl radicals tend to be susceptible to oxidation by molecular oxygen and hydrolysis, thus being unsuitable for any chemistry in air and/or aqueous media. In comparison, nitrooxide radicals tend to be stable enough for spin labeling experiments of biological molecules such as proteins (monitored by EPR).

Although there is a large number of thiazyl radicals reported in the literature, a review of all thiazyls would be beyond the scope of this thesis and not necessary for this introduction. Therefore, discussion only about the five-membered organothiazyl radicals is included. A large variety of 5-membered ring thiazyl radicals are known. All are planar, and resonance stabilized with $7\pi$ electrons. The first to be isolated was the 1,2,4,3,5-trithiadiazolyl radical cation ($\text{S}_2\text{N}_2^+$) and since then, many of the other radicals have been synthesized related to this cation, as seen in Figure 1.16.
Figure 1.15 Some examples of known five-membered ring thiazyl radicals and the structural relationship to the 1,2,4,3,5-trithiadiazolyl radical cation

Of the five related species shown above, much work in the development of radical ligands in the last decade on thiazyls has been directed at the dithiadiazole (DTDAs) (I-7) moiety. Resonance structures can be drawn on either the nitrogen or sulfur atoms, and density functional calculations (DFT) illustrate that the singly occupied molecular orbital (SOMO), is of $\pi^*$-type symmetry. The electron density of the SOMO is restricted to the DTDA ring, as the SOMO is nodal on the carbon. Therefore any substituent as the R group has little effect on the nature of the radical.
The chemistry behind the synthesis of DTDAs is well known and a large variety of R groups have been reported. Not surprisingly, electrochemical studies suggest that the cell window is typically 1.4 - 1.5 V regardless of the substituent used. Interestingly, since the electron density of the SOMO is isolated to the DTDA ring, DTDA biradicals (I-6c) have been synthesized as seen in Figure 1.1. It has been found that DTDA radicals can coordinate to metals in three different known modes: a) metal insertion into the DTDA sulfur-sulfur bond b) side-on coordination to the sulfur-sulfur bond in an $\eta^2$ type fashion and c) end-on coordination to the DTDA nitrogen atoms. Recent work within our group has seen very interesting magnetic properties from coordination of DTDAs to a variety of paramagnetic transition (and lanthanide) metal ions resulting in monomeric species, dimeric species and polymeric species. The structure of the 1,3,2,4-DTDA isomer, I-8, is also known, however there are no reported coordination attempts reported in the literature. This might be due as the 1,3,2,4-DTDA readily converts to the 1,2,3,5-DTDA in solution and the solid state.

Dimerization in the solid state is a typical occurrence with 1,2,3,5-DTDA systems even when coordinated to transition metal centers. There are multiple modes that have been identified for dimerization and although these are reported for DTDAs, the same terminology will be used for other reported thiazyl radicals in this thesis for simplicity.
Another extensively studied thiazyl radical is the 1,3,2-dithiazolyl (DTA) (I-9). Unlike that of the DTDAs, this 1,3,2-DTA can have a fused carbon backbone. The SOMO of a generic 1,3,2-DTA demonstrates electron density on the carbon atoms, allowing for delocalization throughout the backbone of the molecule. This delocalization allows for ‘tuning’ of their properties, by variation of the R substituents.

These 1,3,2-DTAs are extremely stable in the solid state, however are quite air sensitive in solution. Strong π-dimerization in the solid state is not uncommon, however there are examples in the literature which are monomeric, thus being paramagnetic in the solid state.\textsuperscript{75} Also, there are recent examples of weaker π-dimers which exhibit a triplet excited state in the solid state detectable via EPR and demonstrate interesting properties, including magnetic hysteresis.\textsuperscript{76} A structural isomer, the 1,2,3-DTA (I-10), is one of the main interests in this thesis and is more thoroughly discussed below.
1.4.2 Focused review of 1,2,3-DTAs

A common preparation of 1,2,3-DTA salts is via the Herz reaction. In 1922, aniline hydrochloride was reacted with excess sulfur monochloride (S$_2$Cl$_2$) and a fused 1,2,3-DTA ring system resulted. It is assumed that the Herz reaction conditions are selected to ensure that only 5 equivalents of S$_2$Cl$_2$ are used. Although the reaction appears relatively simple, no mechanism is known for how this system actually functions. If the carbon atom directly adjacent (para) to the nitrogen atom is not substituted (e.g. a C-H), chlorination readily occurs. There are many other reported para-substituents, which are also displaced besides hydrogen, which include nitro, carboxyl, and sulfoxyl (all deactivating groups). However, not all substituents under the Herz reaction conditions are substituted, including bromo, dimethylamino, ethoyl, methoxyl, and methyl.

The dithiazolium chloride salt produced can be hydrolysed to generate the 1,2,3-DTA-2-oxide. However, if sodium sulphite is present in the hydrolysis reaction, the amino-thiol product is isolated which can only be convert back to the halogenated salt via reproduction of the Herz reaction or by an alternative synthesis by use of thionyl chloride (SOCl$_2$). Interestingly the 1,2,3-DTA-2-oxide can be converted to its corresponding radical species with heat, although if excess heat is allowed, decomposition occurs.
Figure 1.20 Reactions of a dithiazolium chloride salt

The re-conversion to the 1,2,3-DTA heterocyclic ring by reaction of SOCl₂ and a
amino-thiol starting material is typically milder and does not lead to chlorination of the
system. The heterocyclic ring can also be closed by use of selenium oxychloride
(SeOCl₂) with an amino-thiol starting material, and selenium is inserted into the 2-
position of the heterocyclic ring.⁸⁰

The electrochemical behaviour of 1,2,3-DTAs is fairly well known.⁷⁹ These
molecules can theoretically exist in three different oxidation states (Figure 1.23). However, the closed shell anion of any 1,2,3-DTA has never been isolated, only
electrochemically seen.⁸¹ The SOMO is very similar to its stereoisomer, the 1,3,2-DTA,
having 7π electrons and is a π antibonding orbital with significant coefficients on the
heterocyclic ring. Comparable to the DTDA SOMO, there is no electron density at C4,
which has no coefficient present.
Some early work with 1,2,3-DTAs involved only the 5 member skeleton ring (no fused organic rings) and when the radical was synthesized, dimerization in the solid state occurred.\textsuperscript{82} This dimerization was completely irreversible as the dimers formed a new $\sigma$ C-C bond via the C5 position.\textsuperscript{82} The addition of steric bulk to the C5 position (C$_6$F$_5$) prevented this,\textsuperscript{83} however the addition of a fused benzo-ring would ultimately be the key to delocalization of the spin density.\textsuperscript{80,84}

This addition of a planar, aromatic ring, fused to the 1,2,3-DTA (as in the Herz reaction mentioned above) allows for spin density to be delocalized throughout the system. While this delocalization inhibits irreversible C-C bond formation, dimerization in the solid state via S--S close contacts, as mentioned for DTDAs (cis-cофacial, trans- cofacial, \textit{etc.}), generating a singlet ground state (\textit{i.e.} diamagnetism) can still occur. In solution, the dimers dissociate and EPR signals are easily detectable (although there is likely a dimer-monomer equilibrium in solution\textsuperscript{85}).

Much work on 1,2,3-DTAs has been focused on developing neutral radical conductors (NRCs). Several radicals have been synthesized but when isolated, they
formed π dimers in the solid state. This dimerization quenches any potential magnetic properties and also generates a band gap, disposing of any conductivity that could occur. The inclusion of an additional 1,2,3-DTA ring fused onto a ring system, which allowed resonance from the open shell and the closed shell ring through a fused aromatic system prevented π-dimerization. These bis-dithiazoly1 radicals have become of recent interest due to their conductive and magnetic properties. The SOMO is completely delocalized throughout the system and the lone electron can be on either of the DTA rings, ultimately lowering the Coulombic repulsion between molecules.

![Figure 1.22 (top) A resonance stabilized bis-DTA (bottom) A generic SOMO of a bis-DTA](image)

It should be noted that throughout the literature, many 1,2,3-DTA radical compounds have been isolated and characterized, however, there is not one published report of any 1,2,3-DTA radical coordination attempt. While these systems exhibit interesting magnetic properties themselves, interaction with a paramagnetic center could potentially provide interesting magnetic results. This narrow niche directed my research goals and thus the design, synthesis, and the first reported coordination attempts of new 1,2,3-DTA radicals are discussed in the ‘thesis scope’ section of this chapter.
1.4.3 Focused review of 1,2,5-TDAs

The synthesis, isolation and characterization of 1,2,5-thiadiazole was performed in the 1960s\textsuperscript{87} and since then there have been numerous reported preparations of 1,2,5-TDA molecules throughout the literature.\textsuperscript{88} The most common is similar to the Herz reaction mentioned above, however utilizing a \textit{ortho}-diamino- substituted molecule.\textsuperscript{89} Using an excess of thionyl chloride (typically a minimum of 5 equivalents) generation of 1,2,5-TDA heterocyclic rings occurs readily. As with the Herz reaction, the use of thionyl chloride (or selenium oxychloride to produce the selenazyl analogue) allows for milder reaction conditions and any substituents are typically unmodified.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.23.png}
\caption{The typical formation of a 1,2,5-TDA}
\end{figure}

However, synthesis of these diamino- starting materials can be tedious and/or impossible. It usually involves the use of the Gabriel synthesis\textsuperscript{90} followed by the Ing-Manske procedure\textsuperscript{91} to generate the diamino-product as seen in Figure 1.26.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.24.png}
\caption{Hypothetical Gabriel synthesis and Ing-Manske procedure to produce diamino-starting material}
\end{figure}
There are other reported one-pot methods to synthesize the heterocyclic ring by use of thiazyl chlorides (SₓNᵧClₓ), ethyl carbamates, etc. with varying yields and purity.

The recovered compounds are typically closed shell, neutral, 6 π electron species, many of which possess positive electron affinities (EA). This results in their corresponding radical anions to be more thermodynamically stable than the neutral molecules themselves. The electrochemical behaviour of these systems should be noted. 1,2,5-TDAs can theoretically exist in three different oxidation states (Figure 1.27). The one-electron reduction from the neutral species affords the open shell radical anion (RA) and a successive one-electron reduction produces the closed shell dianinon (DA). The SOMO of the radical anion species is similar to that of 1,2,3-DTAs but with a slightly higher coefficient of electron density on the nitrogen atoms. As with the 1,2,3-DTAs, the spin density on the carbon atoms allows for delocalization, which helps prevent irreversible dimerization (i.e. bond formation).

![Figure 1.25](image)

**Figure 1.25** a) Accessible redox states of a 1,2,5-TDA b) The SOMO of a 1,2,5-TDA and c) The numbering scheme of a 1,2,5-TDA

Much work on 1,2,5-TDAs has been focused on synthesizing various molecules with the 1,2,5-TDA structure for organic light emitting diodes and low-band gap
polymers for photovoltaic applications. However, the 1,2,5-TDAs were, and are still, pursued in these fields due to their interesting redox potentials. Until recently, many RAs of 1,2,5-TDA compounds were only seen spectroscopically as their alkali metal salts and never isolated. New research in isolating the RAs involved reducing the neutral species with organometallic sandwiches (cobaltocene, decamethylchromocene and decamethylcobaltocene), tetrakis(dimethylamino)ethane (TDAE) and chalcogenolates (PhX) to generate their respective RA salts. The magnetic exchange interactions were not all diamagnetic π dimers and led to some interesting magnetic interactions in the solid state. This is likely due to the fact that the species are charged, and electrostatic repulsion helps prevents dimerization in the solid state.

As with the synthesis of 1,2,5-TDA RAs, coordination attempts to paramagnetic transition metal ions of these RAs have been reported in the literature, but have only been seen spectroscopically. The attempts usually involve a redox active starting material (e.g. Cr(CO)_6) and the EPR spectrum is reported. The metal coordination is not clearly identified, isolated or characterized. Some of the 1,2,5-TDA reported work mentioned above for OLEDs utilized 2nd row transition metals (Pd). Also, recently reported 1,2,5-TDA complexes with 3rd row transition metals (Ir) have been synthesized and are currently being pursued for interesting luminescent studies.

The only reported coordination of an open shell DTA or TDA ligand to a paramagnetic transition metal was that of 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA) (IUPAC [1,2,5]thiadiazolo[3,4-d][1,3,2]dithiazole (Figure 1.28) by Awaga et. al in 2001. The ligand itself exhibited interesting magnetic properties (such as a large thermal bistability) but when coordinated to bis(hexafluoroacetylacetonato)copper(II) a
coordination polymer formed (Figure 1.28) which had weak ferromagnetic coupling. Ferromagnetic coupling between the metal and one of the open shell ligands (TTTA$^A$) dominates the high temperature range (300 K - 30 K) until antiferromagnetic coupling dominates. This antiferromagnetic response was reported likely between the metal and the other open shell ligand coordinated (TTTA$^B$) or from coupling between chains.

![Coordination polymer diagram](image)

**Figure 1.26 The copper coordination polymer of TTTA**

This lack of reported attempts at 1,2,5-TDA coordination attempts directed my research goals and thus the design and synthesis of new 1,2,5-TDA radicals will be illustrated and further discussed in the ‘thesis scope’ section of this chapter.

### 1.5 Quinone chemistry

An organic cyclic compound containing two exocyclic moieties is referred to as a quinoid. Quinoidal compounds can contain oxygen (O), nitrogen (as NH), sulfur (S) and carbon (as CH$_2$) as the exocyclic moieties. The more electronegative substituents tend to
increase the stability of quinoidal compounds, thus oxygen and nitrogen are more stable compared to the sulfur and carbon analogues. Quinodal compounds do not have to have the same two exocyclic moieties, as seen in Figure 1.29.

![Diagram of quinoidal compounds]

Figure 1.27 Examples of a variety of simple quinoidal compounds

The most common quinodal compound is when both exocyclic atoms are oxygen, also referred to as quinones. These quinones can be either para- or ortho- to one another as in I-11 and I-12. This thesis involves the synthesis of novel radical ligands that use a para-quinone backbone, thus further discussion will be restricted to $p$-quinones. However, it should be noted that the remainder of this section on general quinone information is also applicable to ortho-quinones.

The electrochemical behaviour of quinones should be noted. Quinones have three possible oxidation states: a) the fully oxidized quinone (Q), b) a one electron reduction to the semiquinone (SQ), and c) the fully reduced catecholate (Cat) (Figure 1.30) The catecholate can then accept one or two protons to generate the hydroquinone (CatH$_2$, also
known as a diol). In a typical cyclic voltammetry experiment, all three oxidation states of a select quinone would be illustrated in two successive one-electron steps with complete reversibility (in an aprotic solvent, under standard conditions.).

\[
\text{Q} \quad \overset{+e^-}{\rightleftharpoons} \quad \text{SQ} \quad \overset{+e^-}{\rightleftharpoons} \quad \text{Cat}
\]

**Figure 1.28 The accessible redox states of para-quinones**

The addition of electron donating substituents (*e.g.* OR, NR₂, Ph) on the quinone structure shifts the oxidation potential toward the reductive direction, and *vice versa* for electron withdrawing groups (*e.g.* Cl, F, NO₂). The oxidized quinone is a conjugated π system. This conjugation allows for simple nucleophilic addition reactions to occur readily. Any increase in conjugation increases resonance stabilization (of SQs and Cats) and results in lower \( E_{\text{cell}} \) values.

### 1.5.1 Synthesis of para-quinones

There are numerous syntheses of \( p \)-quinones reported in the literature and thus an extensive discussion regarding every type of approach and mechanism would be too exhaustive and unrelated to this thesis. This section only touches on a few synthetic methods for the generation of \( p \)-quinones. A typical synthesis for the generation of a quinone species from a condensed aromatic system is by use of a strong oxidizing agent.
Various oxidizing agents are reported\textsuperscript{108}, such as CrO\textsubscript{3}, and (NH\textsubscript{4})\textsubscript{4}Ce(SO\textsubscript{4})\textsubscript{4}, which produce the \textit{p}-quinones in high yields.

![Figure 1.29 Oxidation of an aromatic system to its corresponding quinone](image)

The most common methods of synthesis are typically \textit{via} oxidation of the corresponding diol. These catechols are easily oxidized with inexpensive reagents such as Ag\textsubscript{2}O, Ag\textsubscript{2}CO\textsubscript{3}, MnO\textsubscript{2} and Pb(C\textsubscript{2}H\textsubscript{3}O\textsubscript{2})\textsubscript{4}.\textsuperscript{109} The standard procedure is to mix/shake the reagents in a dry solution (usually ether) and filter off the metal reagents through a bed of celite. If only substituted diols are available \textit{(e.g.} methoxy\textit{)}, these have been shown to be oxidized with an excess of CoF\textsubscript{3} in a mixture of water and dioxane in high yields.\textsuperscript{110}

![Figure 1.30 An example of an oxidation of a hydroquinone to quinone](image)

A very effective and well studied reagent for systems with only one OH group is the use of the stable radical [K\textsubscript{2}(ON(SO\textsubscript{3})\textsubscript{2})] (IUPAC potassium nitrosodisulfonate) also known as ‘Fremy’s Salt’. However, Fremy’s salt is difficult to use. It is stored under oil as it rapidly decomposes in air exothermically and is only soluble in aqueous media.
Therefore, any reactions must be completely degassed and have some sort of aqueous media (e.g. aqueous alcohols, aqueous acetone, etc.) for the reaction to occur. In the solid state, the compound is dimerized, but dissociates into its stable radical form in solution. The selected phenol is then oxidized in solution via a radical pathway to its corresponding quinone (Figure 1.33).

![Figure 1.31 Mechanism to produce a quinone from an alcohol via Fremy's Salt.]

While it has been hypothesized that the second oxidation might occur by a solvation effect (i.e. any water present), $^{17}$O labeled studies have shown that the introduced oxygen is indeed from the nitroxide, and not the solvent.$^{111}$

For an extensive, in depth review of the syntheses and reactivity of quinones, the reader is encouraged to begin with these selected books and articles.$^{109,112-114}$
1.5.2 Quinones as spin bearing ligands

Quinones, in a variety of oxidation states, have been reported throughout the literature since the 1900s, however, there was only one structural report on a quinone chelate complex prior to 1975. The structure was in its dianionic oxidation state (Cat), coordinated to molybdenum and thus no interesting magnetic properties were present. The majority of the work with quinones as spin bearing ligands involves \( o \)-quinones as opposed to \( p \)-quinones. The bidentate coordination pocket allows for better chelation to metal centers when reduced, however there are reports of \( p \)-semiquinone coordination complexes. Quinone molecules tend to be a ‘non-innocent’ ligands (\( i.e. \) the ability to be redox active) when coordinated to transition metal centers. The energy of the quinone \( \pi \)-orbital is fairly close to many energies of transition metal \( d \)-orbitals, thus electrochemical redox reactions can readily occur. The energy difference is often small, in the near-infrared. The electronic structure of a metal-quinone complex can be viewed in three isoelectronic forms:

![Figure 1.32 Three possible redox coordination species for a MQ complex](image)

While there are reported M(Q) complexes, quinone compounds in their fully oxidized state are poor donors and are readily displaced. The most common oxidation states of quinones in their coordination complexes are the catecholate and semiquinone. Catecholates and semiquinones bond both as strong \( \sigma \) and \( \pi \) donors, especially with high
oxidation state metals, however SQs have the unique unpaired electron, allowing for interesting magnetic properties to arise. Magnetic coupling can either be from M-SQ or SQ-SQ depending on how many semiquinones are coordinated in any given complex. Identifying the oxidation state of these quinone complexes is no trivial matter. The typical techniques of identifying the oxidation states are by IR spectroscopy, EPR (for paramagnetic complexes), $^{13}$C NMR spectroscopy (for diamagnetic complexes) and X-ray crystallography.

Most quinones exhibit strong and sharp $\nu$(C=O) bands at 1800-1600 cm$^{-1}$.$^{119}$ However, when coordinated, the typical $\nu$(C=O) of a M(Q) is $\sim$1650 cm$^{-1}$ whereas M(Cat) is 1300 cm$^{-1}$ and M(SQ) is in between.$^{120}$ Since M(SQ) is paramagnetic, $^{13}$C is not an option, however for M(Cat) and M(Q) it can be an useful tool. The $^{13}$C of the carbon atom of the C=O for a M(Q) is $\sim$180 ppm compared to M(Cat) where it shifts upfield to $\sim$150 ppm. EPR spectroscopy can be used to characterized M(SQ) species, either in solution or the solid-state for determining the oxidation state of both the quinone and the metal (diamagnetic vs. paramagnetic). Lastly, X-ray crystallography is very important and the most critical parameter is that of the C–O bond lengths, which like IR, distinguishes unambiguously between the three oxidation states. A typical C–O bond length for M(Q), M(SQ) and M(Cat) are 1.20, 1.29 and 1.35 Å respectively. Comparatively, other changes of bond distances of neutral non-coordinated quinones reduced to semiquinones, such as chloranil, increase from 1.211 to 1.248 Å.$^{121}$ Other consistent characteristics can be seen by use of X-ray crystallography. The bite angle of O-M-O species consistently differs between M(SQ) and M(Cat) by approximately 2°.
Also, the C--C bond length changes with oxidation state where M(Q), M(SQ) and M(Cat) have 1.53, 1.44 and 1.40 Å respectively.\textsuperscript{118}

Depending on the metal (and quinone), a variety of redox reactions can occur and there is a trend in the d-block. The general trend going down a row results in first row metals (due to a higher IE) forming complexes with partially reduced SQ ligands while second and third row metals form Cat complexes. The higher oxidation state metals are stabilized by strong $\pi$ donation from the ligands.\textsuperscript{122} Trends from left to right also occur resulting in metals left of Fe tend to be in higher oxidation states than metals to the right in the second and third row of the d-block. This results in a typical complexes such as $\text{M}^{\text{VI}}\text{(Cat)}_3$ compared to $\text{M}^{\text{II}}\text{(SQ)}_2$ respectively.\textsuperscript{123}

Valence tautomerism is a common occurrence with these systems (M(Q)$_{2/3}$). Two conditions of these systems must be met in order to characterize a complex as a valence tautomer; a) the energy of the frontier orbitals of the bonding components must be similar, and b) the degree of covalency in the interactions between the acceptor and donor must be low. It should be noted that there is a possibility of the existence of isomers with different charge distribution. However, if the energy difference between two electronic tautomers is small, intramolecular electron transfer between the metal and the ligand may occur, resulting in a valence tautomeric equilibrium.\textsuperscript{124} The first reported valence tautomeric interconversion in a transitional metal was by Pierpont \textit{et.al} in 1980 (Figure 1.35).\textsuperscript{125} This valence tautomerism interconversion was between (HS) $\text{Co}^{\text{II}}\text{(SQ)}_2\text{(Bipy)}$ and (LS) $\text{Co}^{\text{III}}\text{(SQ)}\text{(Cat)}\text{(Bipy)}$ (where HS denotes high-spin, LS low- spin and Bipy is 2,2'$\prime$-bipyridine). At temperatures below 250 K the LS-Co$^{\text{III}}$ species predominates and above 250 K the thermally driven HS-Co$^{\text{II}}$ species predominates.
Figure 1.33 Intramolecular electron transfer of Pierponts reported valence tautomer

Much work has been performed on this system because of its interesting electronic properties. These cobalt valence tautomeric complexes can be interconverted by use of external stimuli. These stimuli include temperature pressure and irradiation with light. It is also possible to electrochemically reduce/oxidize to yield ‘dual-mode’ valence tautomerism. It should be noted that all the complexes shown were with cobalt as the metal center, however, there are reports of other metals being used, such as manganese.
Valence tautomers are of research interest for their molecular ‘switching’ abilities and properties. These include magnetic switches where the magnetization of the system and thus the material, that can be altered from HS to LS. Optical switches are also an interest, as can be seen of the colour changes in Figure 1.34.

Figure 1.34 Dual-mode switching array via external stimulus. Interconversion between valence tautomers is obtained reversibly by a one electron reduction.
1.6 Thesis Scope

My graduate project concept began with one reported crystal structure in 1988.\textsuperscript{126} The antitumor drug 6-mecaptopurine when coordinated to cadmium ions results in a very interesting coordination polymer (Figure 1.37).

![Figure 1.35 Crystal structure of [Cd(6-MP)$_2$]$_n$ with the atomic numbering scheme (printed with permission)\textsuperscript{127}](image)

The ligand is a closed shell anion and the metal center is diamagnetic, thus no interesting magnetic properties were reported. However, in 2007, Zamora et al. performed a computational experiment with the same structure [M(6-MP)$_2$]$_n$ but where M = Mn$^{\text{II}}$, Fe$^{\text{II}}$, Co$^{\text{II}}$, Ni$^{\text{II}}$, Cu$^{\text{II}}$ and predicted that Fe$^{\text{II}}$, Co$^{\text{II}}$ and Ni$^{\text{II}}$ would exhibit ferromagnetism via superexchange and simultaneously act as semiconductors.\textsuperscript{127} However, only the Ni$^{\text{II}}$ species could be synthesized and isolated.\textsuperscript{128} Upon characterization, it was found that the isolated crystals were indeed semiconductive (\textasciitilde 10$^{-4}$ S cm$^{-1}$) however the magnetic properties were not investigated. Since then, similar structures have been reported using other paramagnetic transition metals and similar closed shell anionic ligands, resulting in
similar properties.\textsuperscript{129,130} These findings are encouraging in synthesizing a similar structure with paramagnetic transition metal (or lanthanide) ions however, with an open shell, spin bearing ligand. This would allow for direct magnetic coupling between the ligand and the metal ions, resulting overall in either bulk ferromagnetism or ferrimagnetism. The open shell ligand would also allow for the possibility of a $\frac{1}{2}$ filled band, so long as the molecular overlap between single chains is significant. Therefore my ultimate project goal was to mimic this system. The work included designing, synthesizing, isolating and characterizing the new thiazyl radical ligands, followed by coordination to paramagnetic transition (and lanthanide) metals with full characterization of the complexes recovered.

The Preuss group focuses on the development of thiazyl radicals and coordination of these ligands to paramagnetic transition metals. Much work had revolved around the DTDA structure, leading to many publications.\textsuperscript{19,20,48,131-133} However, our interest was to diversify our thiazyl chemistry and attempt to mimic the $[M(6\text{-MP})_2]_n$ structure via an unprecedented approach. By use of a 1,2,3-DTA or a 1,2,5-TDA heterocycle fused to a quinone moiety, the same coordination environment as of 6-mercaptopurinate ligand can be achieved:
These concepts led to the synthesis, isolation and full characterization of two new neutral 1,2,3-DTAs as discussed in **Chapter 2**. Coordination attempts of both ligands, the isolation of metal complexes and full characterization are also discussed in the chapter. In case the ligands were poor donors and thus unsuitable for coordination, three new radical anionic ligands were synthesized, isolated and characterized in **Chapter 3**, leading to interesting magnetic and conductive properties in the solid state. Significant modification of the RAs led to a completely novel molecule, which, including all its preceding starting materials, led to interesting cancer inhibition studies which are discussed in relative detail in **Chapter 4**.
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Chapter 2

Synthesis, characterization and coordination of quinone-based 1,2,3-dithiazolyl neutral radicals
Chapter 2  Synthesis, characterization & coordination of quinone-based 1,2,3-dithiazolyl neutral radical

2.1  General

The key compound in this thesis is the naphtho[2,3-\(d\)][1,2,3]dithiazolyl-1,4-dione (DTANQ) radical II-1 and the subsequent modification of the original ligand design to generate the 5,8-dimethyl-naphtho[2,3-\(d\)][1,2,3]dithiazolyl-1,4-dione (5,8-Me\(_2\)DTANQ) radical II-2 (Figure 2.1). These ligands were designed to mimic the mercaptopurinate ligand mentioned in chapter 1 by the coordination geometry.\(^1\) Although II-1 was known previously,\(^2\) only solution EPR data were reported and the radical was never isolated nor fully characterized. The modification of II-1 to II-2 was completely unknown prior to our research. Prior to my research in the Preuss group, coordination attempts using 1,2,3-dithiazole (DTA) radicals were also unknown.

![II-1 and II-2 radicals](image)

**Figure 2.1** The two project compounds, II-1 & II-2 radicals

The skeletal structure of these ligands utilizes the para-naphthoquinone backbone, which allows for a bidentate coordination pocket between the oxygen and nitrogen atoms. The quinodal portion draws some \(\alpha\)-spin density away from the DTA heterocycle and the
naphthalene portion allows for resonance throughout the ligand, decreasing the propensity for dimerization of the ligand via S--S contacts.

The majority of reported 1,2,3-DTA radicals have been synthesized for their magnetic and conductive properties. These radicals can also be modified, either by insertion of selenium into the heterocycle or by modification of the backbone structure, which can tune certain desirable material properties. Coordination of these open shell species to paramagnetic transition metal ions may allow for the same interesting type of magnetic and conductive properties, albeit enhanced by the magnetic coupling between the radical(s) and/or metal ion(s).

The syntheses of 1,2,3-DTAs is often performed by using a Herz type ring closure from the corresponding primary amine and S₂Cl₂. This produces the dithiazolium cation chloride in quantitative yields, however the reaction produces a large amount of byproducts such as elemental sulfur. If the ring closure cannot be performed from the primary amine, substitution at the neighbouring carbon atom with either a thiol or protected thiol can allow for full ring closure of the heterocycle in a milder reaction by use of thionyl chloride. The result is the same and produces the dithiazolium cation chloride. The chloride can be purified by anion metathesis using one of many reagents such as silver triflate (AgOTf), gallium trichloride (GaCl₃), nitrosonium hexafluoroantimonate (NOSbF₆) and nitrosonium hexafluorophosphate (NOPF₆) followed by recrystallization of the now soluble salt. These purification steps are normally used only if the reduction to the radical does not proceed clearly enough that either recrystallization or sublimation generates the ligand in high purity. The generation
of good quality single crystals may also require these extra steps. The reduction from the
dithiazolium chloride to the radical can be achieved using Zn dust, Zn-Cu couple or with
SbPh$_3$.$^{12}$

2.2 Synthetic Approach to the DTA Radicals

The main difficulty encountered with this project was dealing with insolubility of
II-1 when attempting coordination, thus modification to II-2 was pursued. However, II-2
is not found in the literature and the starting materials were very expensive if purchased
from commercial sources. The literature methods of synthesizing the necessary starting
materials for II-2 provided poor yields with multiple by-products. Therefore, the
preparation of II-2 is a new procedure. Conveniently, this procedure can be easily
modified to generate a multitude of similar ligands, perhaps with different properties (see
future work section).

2.2.1 Synthesis of 5,8-dimethyl-1,4-naphthoquinone (II-3)

There are commercial sources of 5,8-dimethyl-1,4-naphthoquinone however the
quantities available are very small and the cost is very high. Therefore, synthesis of this
material was undertaken. Although there are preparations for II-3,$^{13}$ they utilize 1,2,4,5-
hexatetrene which is not commercially available and difficult to synthesize. Therefore,
another route was sought to produce the compound of interest. 1,1’-Thiophene dioxides
have been used in Diels-Alder reactions as the diene with 1,4-benzoquinone as the
dienophile.$^{14-17}$ Although these reactions produce the desired product, the yields are poor,
with a mixture of products, as the dienophile can re-attack the diene still present in
solution to form the anthraquinone as seen in Figure 2.2. Therefore, this procedure was modified (vide infra) to only produce the desired product, resulting in very high yield and purity.

![Generic scheme for generation of substituted quinones with byproducts](image)

Substituted 1,1'-thiophene dioxides cannot be purchased, however, they can be synthesized from peroxybenzoic acid in relatively high yields and purity. The in situ synthesis of peroxybenzoic acid is dangerous to it being a strong oxidizer. Furthermore, the oxidations using peroxybenzoic acid, especially those of the 3,4-disubstituted thiophenes afford the corresponding sulfones in high yields, however, the oxidations of 2,5-disubstituted do not. Fortunately, other alternatives exist, such as meta-chloroperoxybenzoic acid (m-CPBA) which is more stable, easier to handle and can be purchased commercially. Preparation with dialkyl-substituted thiophenes in the 2,5 positions are typically done with m-CPBA.

To produce the desired di-substituted naphthoquinone, the oxidized di-substituted thiophene was reacted with purified 1,4-benzoquinone. This is typically performed
throughout the literature in a variety of refluxing solvents such as toluene\textsuperscript{14} and acetic acid.\textsuperscript{17} However, the sulfone bridge in the naphthalene backbone is unstable with temperatures exceeding 70 °C. Sulfur dioxide (SO\textsubscript{2(g)}) is released as a gas and the resulting naphthoquinone can re-attack the remaining thiophene dioxides to produce a mixture of starting materials, substituted naphthoquinone, and substituted anthraquinone. To avoid this issue, we used refluxing chloroform (~62 °C) to generate the sulfur dioxide bridged naphthoquinone, which does not re-attack the remaining thiophene dioxide in solution. This reaction was monitored \textit{via} \textsuperscript{1}H NMR until completion, usually between 5-7 days.

Once the reaction to the sulfur dioxide bridged species has gone to completion, the solvent is removed \textit{via} flash distillation and dry toluene is added to the resulting yellow oil. The temperature of refluxing toluene is higher than needed to remove the SO\textsubscript{2} bridge, however, aromatization of the naphthalene backbone is still needed. It has been shown that manganese dioxide (MnO\textsubscript{2}) in refluxing dry toluene can afford the desired products in very high yields,\textsuperscript{21,22} thus aromatization and removal of the sulfur dioxide bridge can occur in one-pot synthesis. After 24 h the reaction is complete and the resulting mixture is filtered through a bed of Celite, washed with toluene and rotary evaporated to give the yellow crystalline \textbf{II-3}. The product does not have to be purified further before subsequent use.
2.2.2 Synthesis of 2,3-substituted-5,8-dimethyl-1,4-naphthoquinones (II-4 & II-5)

In order to synthesize the DTA ring, a primary amine in the 2-position must be present. However, unlike many reactions with both para- and ortho-quinones, sodium azide (NaN₃) in an acidic environment does not produce the desired amino product. Bromination has been shown to occur with these type of systems, substituting in the 3,4-positions. A modification of the literature procedure using methylene chloride as the solvent was employed in the bromination of II-2. This generated II-4 in high yield and purity.

It has been shown that one bromine atom can be substituted for a primary amine using ammonium hydroxide (NH₄OH) and gaseous ammonia in refluxing dry nitrobenzene. Not only is nitrobenzene highly toxic and readily absorbed through the skin, when dried it is potentially explosive. Therefore modification of the procedure was
necessary. The same procedure was followed, except using refluxing ethanol with constant $^1$H NMR monitoring until completion. The reaction does go to completion, however it takes much longer than when using nitrobenzene as the solvent. Nonetheless, after 24 h, 2-amino-3-bromo-5,8-dimethyl-1,4-naphthoquinone, II-5, is successfully generated.

![Synthetic route to II-5](image)

**Figure 2.4 Synthetic route to II-5**

### 2.2.3 Ring closure attempts to generate II-1$^+$ & II-2$^+$ via the Herz reaction

The Herz reaction to generate a thiazyl heterocycle is typically performed with excess (∼5-10 depending on the stoichiometry) sulfur monochloride, $S_2Cl_2$, which generates the desired DTA ring. This procedure is typically done in a solvent that will not be chlorinated (*e.g.* CH$_3$CN) and temperatures vary according to the starting materials used. However, it has never been shown in the literature that if there is a substituted carbon beside the primary amine, the ring can close. In order to test this reaction, 2-amino-3-bromo-1,4-naphthoquinone, which is commercially available and inexpensive, was used as the starting material. After refluxing for 6 h in acetonitrile, the crude product was hot filtered to minimize elemental sulfur and other impurities that co-precipitate upon cooling and washed with acetonitrile. The bright orange powder that was obtained was dried under reduced pressure. The ring closure worked as intended generating the
desired chloride salt, $\text{II-}1^+\text{Cl}^-$ confirmed by FT-IR. The product is pure enough for further use, however an anion metathesis reaction was performed with silver triflate to generate the bright yellow triflate salt in higher purity (by mass spectrometry).

Synthesis of $\text{II-}2^+\text{Cl}^-$ via the same procedure using the dimethyl analogue, $\text{II-}5$, did not yield satisfactory results. The resulting greyish precipitate could not be identified, however, *in situ* EPR reactions with the filtrate illustrated the expected 3-line pattern of the radical. Unfortunately, the filtrate is very acidic, ‘tacky’ and rapidly decomposes under inert atmosphere. Therefore, modification of the standard Herz reaction was necessary. Having a thiol group present beside the primary amine allows for milder reaction conditions. The substitution of the bromine atom to afford a thiol can be achieved by a variety of methods. These include the use of thiocyanates followed by reduction to the thiol,$^{25}$ and nucleophilic substitutions *via* alkaline sulfides.$^{26}$ The latter was used to generate the 2-amino-3-thiol substituted naphthoquinone. In this typical procedure, sodium sulfide nonahydrate was reacted in water with the 2-amino-3-bromo naphthoquinone at 80 °C. The solution was cooled and the thiol generated by acidification with acetic acid. FT-IR and $^1$H NMR suggest that the thiol was made, however ring closure attempts using sulfur monochloride or the more mild thionyl chloride reactions failed to generate any of the desired product. It was later found that the unprotected thiol was very air and moisture sensitive, decomposing rapidly. Therefore the protected thiol was synthesized. The synthesis of the S-acetate protected thiol was performed in degassed deionized water, ethanol and acetic anhydride under argon. Confirmation by $^1$H NMR, FT-IR and MS showed the successful synthesis. The attempts at ring closure using sulfur monochloride and thionyl chloride using the conditions
generally reported for this type of reaction, once again failed to produce the desired chloride salt. The reactions were then performed with temperatures not exceeding 40 °C for only 3 h. The dense dull orange powder was filtered, washed with acetonitrile and dried *in vacuo*. The FT-IR and *in situ* EPR suggested that under these very mild conditions, the desired chloride salt, \( \text{II}-2^+ \text{Cl}^- \) was generated in high yield. The material was used without any further purification.

![Reaction Scheme](image)

**Figure 2.5 Herz reactions to generate the chloride salts of II-1 & II-2**

### 2.2.4 Synthesis of the DTANQ radicals, II-1 & II-2

Reductions of the DTANQ\(^+\) chlorides were performed with triphenyl antimony. This reaction is a simple and effective way to generate the desired radicals, **II-1** and **II-2**. The orange starting material chloride and a half molar equivalent of recrystallized SbPh\(_3\) were placed in a Schlenk flask which is then charged with dry acetonitrile. Visibly, the
reaction occurred immediately, changing from a bright orange slurry to a blue-purple slurry, however the reaction takes approximately 30 minutes to go to completion. Afterwards, the slurry was cooled to 0 °C and filtered in vacuo. The collected precipitate was washed with cold acetonitrile and dried under reduced pressure. The reaction byproduct, triphenyl antimony dichloride, SbPh₃Cl₂, is soluble in acetonitrile whereas the radical is not, allowing for a relatively high purity product.

![Chemical Structures](image)

**Figure 2.6 Reduction of the DTANQ chloride salts to II-1 & II-2**

Analytically pure II-1 and II-2 radicals were obtained by sublimation in a variable temperature furnace under reduced pressure (ca. 10⁻² – 10⁻⁵ torr) as described in Appendix B. Any excess SbPh₃ starting material sublimes at 80 °C, followed by the SbPh₃Cl₂ byproduct between 85-95 °C. This allows for easy separation of the desired radicals as they both sublimes ~135 °C. After sublimation, the crystalline radicals were quite air and moisture stable and could be manipulated outside of the glove box. Crystalline material of II-1 has been stored outside of the glove box for up to 2 months without evidence of any decomposition remaining analytically pure. Pure
microcrystalline radical can also be obtained *via* recrystallization in dichloroethane and toluene for II-1 and II-2 respectively.

### 2.3 Physical Properties of DTANQ radicals II-1 & II-2

#### 2.3.1 FT-IR

**DTANQ (II-1)**

All samples for FT-IR were prepared as KBr pellets and IR spectra were measured on a Nicolet 4700FT-IR. The FT-IR spectra of the 2-amino-3-bromo-1,4-naphthoquinone starting material, II-1\(^+\) and II-1 are shown in Figure 2.7.

![FT-IR spectra](image)

**Figure 2.7** FT-IR spectra of the products to form II-1 in the region 4000-400 cm\(^{-1}\). (*) marks the \(\nu(C=O)\) stretches and (S) marks the \(\nu(N-H)\) stretches

Most quinones exhibit strong and sharp \(\nu(C=O)\) bands at 1800-1600 cm\(^{-1}\).\(^{27}\) Since the LUMO of the C=O bond is a \(\pi\) anti-bonding orbital, any electron density donated to or withdrawn will either shift the energy lower or higher respectively. This is shown in
Figure 2.7. The strong carbonyl stretch of the amino starting material is at 1690 cm\(^{-1}\), the chloride salt (II-1\(^+\)) at 1710 cm\(^{-1}\) and the radical at 1685 cm\(^{-1}\). Also, the strong amine stretches in the starting material are not present in the others, as the ring has fully closed without any hydrogen atoms still bonded to the nitrogen atom which would afford a noticeable imine stretch.

**5,8-Me\(_2\)DTANQ (II-2)**

All samples for FT-IR were prepared as KBr pellets and IR spectra were measured on a Nicolet 4700FT-IR.

![FT-IR spectra]

**Figure 2.8 FT-IR spectra of the products to form II-2 in the region 4000-400 cm\(^{-1}\). (\(^{*}\)) marks the \(\nu(C=O)\) stretches and (S) marks the \(\nu(N-H)\) stretches**

The FT-IR spectra of the amino-bromo precursor, II-5, the protected thiol precursor, II-6\(^+\), and the radical, II-2 are shown in Figure 2.8. The strong carbonyl stretch of the amino-bromo precursor (II-5) is at 1690 cm\(^{-1}\), the thioacetetate (II-6) at
1706 cm\(^{-1}\) (quinone) and 1677 cm\(^{-1}\) (acetate) and the radical (II-2) at 1685 cm\(^{-1}\). The methyl stretch does not shift at all, remaining at 2926 and 2974 cm\(^{-1}\) throughout.

### 2.3.2 NMR

\(^1\)H NMR spectra were recorded on a Brüker Avance-300 at ambient temperature. For the synthesis of II-2, \(^1\)H NMR was a key monitoring tool for the generation of the starting materials.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(^1)H NMR (300MHz, CDCl(_3), 25 °C, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,5-Dimethyl-thiophene-1,1'-dioxide</td>
<td>6.267 (s, 2H) 2.101 (s, 6H)</td>
</tr>
<tr>
<td>5,8-Dimethyl-1,4-naphthoquinone</td>
<td>7.378 (s 1H) 6.820 (s, 1H) 2.686 (s, 3H)</td>
</tr>
<tr>
<td>2,3-Dibromo-5,8-dimethyl-1,4-naphthoquinone</td>
<td>7.376 (s, 2H) 2.684 (s, 6H)</td>
</tr>
<tr>
<td>2-Amino-3-bromo-5,8-dimethylnaphthalene-1,4-dione</td>
<td>7.315 (d, 1H) 7.245 (d, 1H) 5.419 (br s, 1H) 2.676 (s, 3H) 2.631 (s, 3H)</td>
</tr>
</tbody>
</table>
2.3.3 Cyclic voltammetry

**DTANQ (II-1)**

Cyclic voltammetry measurements of **II-1** (Figure 2.10) were performed in dry DCM under argon atmosphere at ambient temperature with 0.05 M $^{n}$Bu$_4$NPF$_6$ as supporting electrolyte, with substrate concentrations *ca.* 1.0 mM and a sweep rate of 100mv/s. A three-electrode glass cell was used with platinum wire for all three electrodes. The ferrocene/ferrocenium (fc/fc+) redox couple was used as the internal reference for $E^\circ$(fc/fc+) = +0.48 V in CH$_2$Cl$_2$. All potentials are thus reported *vs.* SCE. The ferrocene was sublimed before use.

In Figure 2.10 a reversible oxidation wave with $E_{1/2}(0/+1) = 0.75$ V and a reversible reduction wave was $E_{1/2}(-1/0) = -0.49$ V are observed. The former is the oxidation of the neutral radical **II-1** to a cation and the latter is the reduction of **II-1** to its corresponding anion. The window potential is 1.24 V, and the $\Delta E_{pp}$'s are 130 mV and 129 mV (oxidation and reduction waves respectively); these values are within the guidelines for electrochemical reversibility in aprotic solutions.$^{28,29}$

![Chemical structure of DTANQ (II-1)](image)

*Figure 2.9 The neutral radical II-1 and the related oxidation and reduction products*
Figure 2.10 The cyclic voltammogram for II-1 in CH$_2$Cl$_2$ solution vs. SCE (1mM substrate, 0.05M nBu$_4$PF$_6$, scan rate of 100 mV/s)

Me$_2$DTANQ (II-2)

Cyclic voltammetry measurements of II-2 (Figure 2.11) were performed in the same manner as described for II-1. In Figure 2.11 a reversible oxidation wave with $E_{1/2}(0/+1) = 0.77$ V and a reversible reduction wave with $E_{1/2}(-1/0) = -0.48$ V are observed. The window potential ($E_{\text{cell}}$) is 1.25 V, and the $\Delta E_{\text{pp}}$’s are 218 mV and 350 mV (oxidation and reductive waves respectively). The larger $\Delta E_{\text{pp}}$ of the reductive wave could be due to impurities in the solvent, glassware, etc. However, the window potentials and the $E_{1/2}$ values of II-2 in comparison with both DTANQ and the 6,7-Me$_2$DTANQ$^{30}$ analogue are values within the trend. The electron donating methyl groups increase the oxidation potential and decrease the reduction potential in comparison to DTANQ. The
half-wave potentials of select related compounds are also found in Table 2.2. The 6,7-dimethyl analogue also prepared in our lab displays the same trend as the 5,8-dimethyl.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>$E_{1/2(ox)}$ (V)</th>
<th>$E_{1/2(red)}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-DTANQ (II-1)$^a$</td>
<td></td>
<td>0.752</td>
<td>-0.488</td>
</tr>
<tr>
<td>5,8-Dimethyl-DTANQ (II-2)$^a$</td>
<td></td>
<td>0.770</td>
<td>-0.483</td>
</tr>
<tr>
<td>6,7-Dimethyl-DTANQ$^b$</td>
<td></td>
<td>0.811</td>
<td>-0.410</td>
</tr>
<tr>
<td>$o$-DTANQ$^c$</td>
<td></td>
<td>0.207</td>
<td>-0.910</td>
</tr>
<tr>
<td>1,2,3-DTA-naphthalene$^d$</td>
<td></td>
<td>0.790</td>
<td>-0.300</td>
</tr>
</tbody>
</table>

$^a$ = values described in this thesis, $^b$ = values described in David Sullivan’s M. Sc. thesis, $^c$ = values described in Chad Smithson’s M. Sc. thesis, $^d$ = values described from Kathryn Preuss’ thesis.
2.3.4 X-ray crystallography

DTANQ

From the reaction and the subsequent sublimation, a large, dark green block-like crystal of II-1 was mounted on a thin glass fibre, coated with epoxy and examined at Western University (UWO). Data were collected at low temperature (150 K) on a Nonius Kappa-CCD area diffractometer with COLLECT (Nonius BV., 1997-2002). The unit cell parameters were determined and refined from the full data set. The asymmetric unit is shown in Figure 2.12. Selected crystal data of the radical II-1 are listed in Table 2.3.
The most important feature within the crystal packing of II-1 is the unprecedented dimerization mode. The typical motif for dimerization throughout the literature for thiazyl radicals involves a short S--S contact which, generally results in diamagnetism. These short S--S contacts occur from π stacking of the heterocyclic rings (with the 1,3,2-DTA isomer) in the solid state. The close contacts in this structure are shown in Figure 2.13. Rather than close S--S contacts, the structure dimerizes via close S--O contacts (3.024 Å).
This dimerization mode can be rationalized by looking at the radical resonance forms (Figure 2.15).

![Figure 2.14 The resonance forms of II-1: N-radical (left) and the O-radical (right)](image)

As the electron density increases at O, the C—O bond length should increase. The typical C=O double bond in benzoquinone is 1.220 Å compared to the C9—O2 bond length of 1.245 Å, suggesting an increase in electron density. Lastly, in the computational section of this chapter, there is a large amount of spin density on the oxygen, nitrogen and sulfur atoms in the singly occupied molecular orbital (SOMO). This adds additional support for this type of dimerization motif.

Interestingly, upon sublimation, this molecule produces two distinct polymorphs. The structure shown in Figure 2.12 is the α-phase, which has a green block habit. The second polymorph (β-phase) has a red needle habit. The asymmetric unit for both polymorphs is the same, as shown in Figure 2.12. However, the crystal packing is completely different and dimerizes via the typical S--S short contacts (3.53 Å).

The molecular packing within this crystal structure is worth noting. Throughout the structure there are slipped π-stacks. There is disorder in the structure, such that it there is dimerization of the molecules in the stacks. These systems tend to have Peirels distortion of short-long-short-long contacts as mentioned in chapter 1. This is illustrated
in Figure 2.16 below. This dimerization is consistent with the solid state EPR studies, illustrating no triplet state.

**Figure 2.15** Dimerization via S–S contacts of II-1 (red needle habit) within the crystal structure (full molecule disorder shown)

**Figure 2.16** Uneven dispersed radical II-1(red) via close S–S contacts down the a-axis (left) and the slipped π stacks down the c-axis (left)
Table 2.3 Crystal data and selected C—O (Å) distances of the two polymorphs of DTANQ, II-1

<table>
<thead>
<tr>
<th></th>
<th>DTANQ (green blocks, S–O dimers)</th>
<th></th>
<th>DTANQ (red needles, S–S dimers)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>$C_{10}H_4O_2NS_2$</td>
<td><strong>Density</strong></td>
<td>1.781</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>234.26</td>
<td><strong>Unit cell volume</strong></td>
<td>873.912</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
<td><strong>Space group</strong></td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td><strong>a</strong></td>
<td>11.569(2)</td>
<td><strong>α</strong></td>
<td>90°</td>
</tr>
<tr>
<td><strong>b</strong></td>
<td>8.8345(18)</td>
<td><strong>β</strong></td>
<td>103.61(3)°</td>
</tr>
<tr>
<td><strong>c</strong></td>
<td>8.7975(18)</td>
<td><strong>γ</strong></td>
<td>90°</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td><strong>Temperature</strong></td>
<td>100 K</td>
</tr>
<tr>
<td><strong>Bond Length (Å)</strong></td>
<td></td>
<td><strong>Bond Length (Å)</strong></td>
<td></td>
</tr>
<tr>
<td>C9—O10</td>
<td>1.245(2)</td>
<td>C5—O6</td>
<td>1.221(2)</td>
</tr>
<tr>
<td>O—S</td>
<td>3.024</td>
<td></td>
<td>R1 = 3.68%</td>
</tr>
<tr>
<td><strong>Formula</strong></td>
<td>$C_{10}H_4O_2NS_2$</td>
<td><strong>Density</strong></td>
<td>1.81</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>234.26</td>
<td><strong>Unit cell volume</strong></td>
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</tr>
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<td><strong>Crystal system</strong></td>
<td>Orthorhombic</td>
<td><strong>Space group</strong></td>
<td>$Pnna2_1$</td>
</tr>
<tr>
<td><strong>a</strong></td>
<td>30.37(2)</td>
<td><strong>α</strong></td>
<td>90°</td>
</tr>
<tr>
<td><strong>b</strong></td>
<td>7.997(6)</td>
<td><strong>β</strong></td>
<td>90°</td>
</tr>
<tr>
<td><strong>c</strong></td>
<td>3.531(2)</td>
<td><strong>γ</strong></td>
<td>90°</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td><strong>Temperature</strong></td>
<td>100 K</td>
</tr>
<tr>
<td><strong>Bond Length (Å)</strong></td>
<td></td>
<td><strong>Bond Length (Å)</strong></td>
<td></td>
</tr>
<tr>
<td>C8—O7</td>
<td>1.238(3)</td>
<td>C9—O1</td>
<td>1.209(3)</td>
</tr>
<tr>
<td>S—S</td>
<td>3.531</td>
<td></td>
<td>R1 = 6.52</td>
</tr>
</tbody>
</table>
Me$_2$DTANQ (II-2)

From the reduction of the chloride salt and subsequent slow evaporation to grow crystalline material, a large, red needle-like crystal of II-2 was mounted on a thin glass fibre, coated with epoxy and the XRD experiment was run on-site with a SuperNova Dual diffractometer with Atlas CCD system. The unit cell parameters were calculated and refined from the full data set. The asymmetric unit is shown in Figure 2.17. Selected crystal data of the radical II-2 are listed in Table 2.4.

Figure 2.17 An ORTEP drawing of the asymmetric unit of II-2 (ellipsoids at 50% and H atoms excluded)

Unlike the previous two structures, this material appears to dimerize via close S--N & S--S contacts. This slipped co-facial arrangement is not typical for 1,2,3-DTAs but common for other thiazyl systems such as DTDAs.$^{31}$ These close contacts appear to
direct the herringbone arrangement seen in Figure 2.18 below. Close S--O contacts (2.933 Å) also aid in the herringbone packing.

![Diagram showing the unit cell of II-2 illustrating the herringbone motif](image)

**Figure 2.18 The unit cell of II-2 illustrating the herringbone motif**

Another polymorph of II-2 were observed upon dynamic vacuum sublimation. Purple clusters of blocks were collected from sublimation at 135°C or 120°C for 10^2 and 10^-5 torr respectively. A small, redish-purple prism-like crystal of II-2 was mounted on a thin glass fibre, coated with epoxy and the XRD experiment was run on-site with a SuperNova Dual diffractometer with Atlas CCD system. The unit cell parameters were calculated and refined from the full data set. The asymmetric unit is shown in Figure 2.19. Selected crystal data of this polymorph of radical II-2 are listed in Table 2.4.

The packing in the crystal structure is unique in that there are 12 independent molecules in the asymmetric unit. This structure was examined, and re-examined to ensure that the space group was correct and no other symmetry was present which could afford a lower Z value. As with II-1, II-2 clearly has two distinct polymorphs, which appear to be dimerized in different ways. In this phase, the dimerization mode is the more common S--S close contacts motif (cis-cofacial). This is seen for each dimer pair
and for the ‘column’ of two pairs of dimers. Interestingly, the S--S distances vary from dimer to dimer. The range of these close contacts is between 3.048 to 3.252 Å throughout the structure. The closest distance between dimer pairs is 3.636 Å, which is outside of the sum of the Van der Waals radii for two sulfur atoms.

Figure 2.19 An ORTEP drawing of the asymmetric unit of I1-2 (ellipsoids at 50% and H atoms and labels excluded for clarity)
Table 2.4 Crystal data and selected short contacts (Å) distances of the two polymorphs of Me₂DTANQ, II-2

**Me₂DTANQ (red needles, grown by recrystallization)**

<table>
<thead>
<tr>
<th>Formula</th>
<th>C₁₂H₈O₂NS₂</th>
<th>Density</th>
<th>1.60</th>
</tr>
</thead>
<tbody>
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<td>Formula weight</td>
<td>262.33</td>
<td>Unit cell volume</td>
<td>2179.37</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Space group</td>
<td>P 2₁/c</td>
</tr>
<tr>
<td>a</td>
<td>8.0663(16)</td>
<td>α</td>
<td>90°</td>
</tr>
<tr>
<td>b</td>
<td>7.8899(16)</td>
<td>β</td>
<td>100.20(3)°</td>
</tr>
<tr>
<td>c</td>
<td>34.794(7)</td>
<td>γ</td>
<td>90°</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>Temperature</td>
<td>298 K</td>
</tr>
<tr>
<td>Bond</td>
<td>Length (Å)</td>
<td>Bond</td>
<td>Length (Å)</td>
</tr>
<tr>
<td>C8—O7</td>
<td>1.215(2)</td>
<td>C9—O1</td>
<td>1.228(3)</td>
</tr>
<tr>
<td>S--S</td>
<td>3.252</td>
<td>S--N</td>
<td>3.252</td>
</tr>
<tr>
<td>R¹ = 4.96 %</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Me₂DTANQ (red blocks, grown by sublimation)**

<table>
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<tr>
<th>Formula</th>
<th>C₁₂H₈O₂NS₂</th>
<th>Density</th>
<th>1.59</th>
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</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Space group</td>
<td>P -1</td>
</tr>
<tr>
<td>a</td>
<td>16.9485(3)</td>
<td>α</td>
<td>86.653(2)°</td>
</tr>
<tr>
<td>b</td>
<td>17.0034(4)</td>
<td>β</td>
<td>81.895(2)°</td>
</tr>
<tr>
<td>c</td>
<td>23.4658(5)</td>
<td>γ</td>
<td>78.748(2)°</td>
</tr>
<tr>
<td>Z</td>
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<td>Temperature</td>
<td>298 K</td>
</tr>
<tr>
<td>Bond</td>
<td>Length (Å)</td>
<td>Bond</td>
<td>Length (Å)</td>
</tr>
<tr>
<td>R¹ = 5.46 %</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**2.3.5 EPR**

**DTANQ (solution)**
The solution EPR spectrum of \textbf{II-1} in deoxygenated methylene chloride shows a strong signal (Figure 2.12). The best-fit parameters are $g = 2.0094$, $a_N = 4.409$ G for one nitrogen atom. The EPR spectrum was simulated using the Public EPR Software Tools (Winsim) software.\textsuperscript{34} The hyperfine coupling constants found are comparable to the previously studied EPR\textsuperscript{2} and computational studies of \textbf{II-1} predict similar values, as discussed later in this chapter (\textit{vide infra}).

![EPR spectrum of the II-1 in CH\textsubscript{2}Cl\textsubscript{2} (top) and simulation (bottom)](image)

\textbf{Figure 2.20} EPR spectrum of the II-1 in CH\textsubscript{2}Cl\textsubscript{2} (top) and simulation (bottom)

Typically, these radicals dimerize in the solid state, essentially quenching their paramagnetism making them diamagnetic species. However, there have been instances with other thiazyl radicals (both 1,3,2-DTAs and 1,2,3,5-DTDAs) in which dimerization could be suppressed leading to interesting long range magnetic ordering in the solid state.\textsuperscript{35-37} Therefore, the solid-state signals of both polymorphs of \textbf{II-1} were taken, and yielded interesting triplet excited state properties.
DTANQ (II-1) red needles (solid state)

A room temperature solid-state EPR experiment was performed on ~80 % red needles sample sealed in a capillary tube under inert atmosphere. The resulting spectrum is shown below (Figure 2.21). The spectrum suggests that the compound is completely dimerized (i.e. singlet, S = 0). It should be noted that the spectrum is composed of $S = \frac{1}{2}$ spins resulting from defects in the crystal lattice. There was no evidence for any triplet excited state (S = 1) at centerfield or half-field. The sample was probed at low temperature (~200 K) with the same result.

DTANQ (II-1) green blocks (solid state)

A room temperature solid-state EPR experiment was performed on 100 % green block sample (confirmed by PXRD) sealed in a capillary tube under inert atmosphere. The resulting spectrum is shown below (Figure 2.22). The spectral features are indicative
of a triplet state, which is confirmed by the presence of the half-field signal (inlay of Figure 2.22). Simulation of the solid-state signal is not trivial and the best fit-parameters are show in Table 2.5.\textsuperscript{38,39}

![Solid state EPR spectrum of II-1 (green) at 298K. The inlay is the half-field signal.](image)

**Figure 2.22** Solid state EPR spectrum of II-1 (green) at 298K. The inlay is the half-field signal.

<table>
<thead>
<tr>
<th></th>
<th>Triplet (S = 1) signal parameters (with weight = 1000)</th>
<th>Singlet (S = 0) signal parameters (with weight = 3000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_x$ = 2.026, $\Delta H_{pp}$ = 2</td>
<td>$g_y$ = 2.026, $\Delta H_{pp}$ = 6</td>
<td>$g_x$ = 2.046, $\Delta H_{pp}$ = 10</td>
</tr>
<tr>
<td>$D = 0.0155$ cm$^{-1}$</td>
<td>$E = 0.0014$ cm$^{-1}$</td>
<td>$g = 2.026$, $\Delta H_{pp}$ = 6</td>
</tr>
</tbody>
</table>
In order to properly probe the singlet-triplet character of this material, collaboration with Dr. Stephen Hill at the National High Magnetic Field Laboratory in Tallahassee, Florida was established and samples were run with varying temperatures from 288 K to 5 K. The EPR spectra at selected temperatures are illustrated in Figure 2.23. The intensity of the triplet state (side features) decrease below 100 K and are almost completely absent below 50 K.

![EPR spectra](image)

**Figure 2.23** The variable temperature EPR data (run in Tallahassee) from 288 K to 5 K.

The double integral of the EPR data is proportional to the magnetic susceptibility, $\chi$. As discussed in chapter 1, the $\chi$ vs. $T$ plot for an antiferromagnetic species initially increases, and then decreases upon cooling. Therefore, the double integral of the EPR
intensity vs. T should reflect this and ultimately result in a Curie-type plot (above $\chi_{\text{max}}$). The double integral was performed and plotted as a function of temperature (Figure 2.25). The intensities increase from 288 K until roughly 125 K when there is a large, significant decrease until below 50 K which is clear evidence for a thermal depopulation of the triplet. This data can be roughly modeled using temperature dependence from 300 K - 100 K and a Boltzmann distribution below 100 K. This data is currently being attempted at being reproduced by variable temperature single crystal EPR studies. A ‘crude’ best fit parameter predicts $J = -235$ K; this being the smallest singlet-triplet gap for any reported thiazyl radical.

![Figure 2.24 The double integrated intensities of the variable temperature EPR data (Tallahassee) plotted against temperature](image)

**Me$_2$DTANQ (II-2) (solution)**
The solution EPR spectrum of II-2 in deoxygenated methylene chloride shows a strong EPR signal (Figure 2.26). The best-fit parameters are $g = 2.0093$, $a_N = 4.836$ G for one nitrogen atom. As expected, the coupling constant on the nitrogen atom is higher than II-1 due to the electron donating properties of the two methyl groups, however the coupling constants are still consistent with this type of system.

2.4 Molecular orbital studies

The quantum-mechanical calculations on the electronic structures of the II-1 and II-2 were performed using the Gaussian 09 Rev.A.02 package for Mac OSX. The method and basis set, B3LYP and 6311-G(d) respectively, were chosen as they are known to be compatible with our systems and provide data that can be compared to
literature results. The open shell species were calculated using unrestricted methods and calculations used the gas phase optimized geometry.

**DTANQ (II-1)**

The singly occupied molecular orbital (SOMO) of II-1 (geometry optimized, gas phase structure) is a $\pi^*$ orbital and is delocalized throughout the naphthalene framework. It also has significant coefficients on the quinone backbone and the DTA heterocycle (Figure 2.27). A Mulliken spin density of 25.0% is calculated for N3 compared to 13.7% for O10 as seen in Figure 2.27. This provides further evidence of the O-radical form as shown in Figure 2.14.

![Figure 2.26 Pictorial representation of the SOMO (right) and spin density distribution (left) of the geometry optimized gas phase structure of II-1 (DTANQ)](image)

**Me₂DTANQ (II-2)**

Similar to II-1, the singly occupied molecular orbital (SOMO) of II-2 (geometry optimized, gas phase structure) is a $\pi^*$ orbital and is delocalized throughout the naphthalene framework. Again, it also has significant coefficient on the quinone backbone and the DTA heterocycle (Figure 2.28). A Mulliken spin density of 26.9% is
calculated for N3 compared to 12.7% for O10 as illustrated in Figure 2.28. This increase of spin density on the nitrogen atom is expected due to the electron $\sigma$-donation properties of the two methyl groups on the naphthalene backbone.

![Figure 2.27 Pictorial representation of the SOMO (right) and spin density distribution (left) of the geometry optimized gas phase structure of II-2 (Me$_2$DTANQ)](image)

### 2.6 Magnetometry

All data were collected by Rodolphe Clérac at Centre de Recherche Paul Pascal CRPP-CNRS UPR 8641, where the magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 K and 400 K for DC applied fields ranging from -7 to 7 T.

**DTANQ (II-1) (green blocks; S--O dimers)**

To check for interference from ferromagnetic impurities, the measurement of magnetization as a function of the applied field was performed at 100 K, as described in Chapter 1. For paramagnetic or diamagnetic systems, a perfectly linear response that extrapolates to $M = 0$ at 100 K is expected. Unfortunately, the material was contaminated with a ferromagnetic impurity (ppm amount), which cannot be detected via elemental
analysis. However, the data was acquired in spite of this. Although it is difficult to correct for a ferromagnetic impurity when the bulk sample of interest is diamagnetic, after a rough correction factor of the $\chi T$ vs $T$ plot, the $\chi T$ product was essentially zero. This confirms the diamagnetic behaviour of this compound. The magnetometry was performed four times on fresh, pure samples, each time having a small ferromagnetic impurity. However, the $\chi T$ product (after correction) was essentially zero each time. In a related material, 6,7-dimethyl-dithiazole-1,4-naphthoquinone, the dimerization motif is exactly the same with very similar contacts (S--O). The magnetometry of this related species indicates it is indeed diamagnetic, and thus the results for II-1 are likely correct.

**DTANQ (II-1) (red needles; co-facial dimers with π stacking)**

Separation of the green blocks and red needles could only be performed by hand with the use of a microscope in the air. However, both polymorphs as crystalline material are quite robust (with respect to) decomposition in air. After separation, powder XRD was performed to determine the exact ratio of the two. A 60 : 40 mix of red needles : green blocks was sent for magnetometry. Unfortunately, as with the green blocks, a ferromagnetic impurity undetectable by elemental analysis was present. However, our collaborator is certain that the $\chi T$ product is essentially zero after correction and thus the material is very likely diamagnetic. This is consistent with the solid state EPR results discussed vide supra.
2.6 Quinone backbone modification attempts

Protonation of the oxygen atom of II-1 and subsequent reactions to modify the quinone backbone have proven successful within our laboratory. The ortho-quinone isomer of II-1 illustrated stability when protonated and could successfully be isolated in high yields and purity. The same reactions were performed in an attempt to duplicate the results with the para-quinone backbone. DTANQ, II-1, was added to a mixture of THF and water (5 : 1) and the solution was stirred for 18 hours, over which time a red product formed. The precipitate was filtered, washed with water and dried in air. Recrystallization from MeCN resulted in red crystalline needles, unsuitable for X-ray crystallography. Crystallography quality crystals of II-7 were grown from slow evaporation from a dilute solution of MeCN over two weeks.

2.6.1 X-ray crystallography

From the reaction and the subsequent recrystallization, a small, dark red needle-like crystal of II-7 was mounted on a thin glass fibre, coated with epoxy and examined at McMaster University. Data were collected at low temperature (150K) on a Bruker APEX II CCD detector. The unit cell parameters were calculated and refined from the full data set. The asymmetric unit is shown in Figure 2.29. Selected crystal data of II-7 are listed in Table 2.5.

Unlike the o-DTANQ isomer, the modification to generate the hydroxy-closed shell, II-7, predictably did not occur. Thiazyl radicals in general are relatively sensitive
to air and moisture. For more information regarding the $o$-DTANQ synthesis and characterization, see Chad Smithson’s M.Sc. thesis.

![Figure 2.28 The resulting asymmetric unit of the crystal structure from the modification attempt of to generate II-7](image)

<table>
<thead>
<tr>
<th>II-7 (red needles, grown by slow evaporation)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
</tr>
<tr>
<td><strong>a</strong></td>
</tr>
<tr>
<td><strong>b</strong></td>
</tr>
<tr>
<td><strong>c</strong></td>
</tr>
<tr>
<td><strong>Z</strong></td>
</tr>
</tbody>
</table>
### 2.7 Metal coordination

Once characterization of the two ligands was completed, attempts to coordinate these paramagnetic ligands to paramagnetic transition metal and lanthanide ions and investigate the magnetic exchange interaction between the spin on the radical and the spins on the metal/lanthanide ions was pursued. As mentioned above, the ligands were designed to coordinate via a N-coordination mode with the possibility of chelation through the oxygen atom. In this section, we demonstrate methods of preparing a series of complexes with both II-1 and II-2 and the subsequent characterization of the complexes.

As seen with other work within our lab,\(^\text{44-46}\) bis(hfac)-metal (hfac = hexafluoroacetylacetonato) starting materials are utilized because the materials: a) are inexpensive, b) allow for the anhydrous conditions required and are very soluble in organic solvents, c) can provide intramolecular magnetic interactions \textit{i.e.} magnetic exchange interactions, with the ligands, d) provides two independent coordination sites for either bidentate chelation or two monodentate coordinations, and e) resulting in complexes that are very easily separated and purified. However, recent discoveries within our lab (private communications - Elisa Fatila) now allow for tris(hfac)-lanthanide metal starting materials which also have the same properties as mentioned above.
2.7.1 General synthesis of metal complexes

The bis(hexafluoroacetylacetonato) metal complexes were prepared by known literature procedures. The commercial hexafluoroacetylacetone is deprotonated in a basic aqueous solution (typically sodium or potassium hydroxide) and an aqueous solution of the desired metal (II) chloride salt is added. The precipitate is recovered yielding the bis(hexafluoroacetylacetonato)metal aqua complex. The complex can be dehydrated in THF and Na$_2$SO$_4$ to yield the bis(THF) adduct, M(hfac)$_2$•2THF, where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II). The corresponding lanthanide analogues are made in a similar fashion, however dimethoxyethane must be used to yield Ln(hfac)$_3$•(DME)$_x$ (DME = dimethoxyethane or monoglyme) as the THF adducts are unstable. The absence of any O-H stretches in the IR spectra indicates the dehydration of the starting material.

Once the metal starting materials are synthesized, generation of the desired metal complex is fairly straightforward. Equimolar amounts (for generation of a 1:1 complex) of the metal/lanthanide starting material and desired radical (II-1 or II-2) were added to a Schlenk flask and either dry DCE or toluene (for II-1 and II-2 respectively) were added. For II-1, the solution was gently refluxed for 18 hours whereas II-2 was stirred at room temperature for 3 hours. The reaction mixture is cooled to room temperature, filtered and the solvent is removed in vacuo. The crude product was purified by sublimation (ca. 10$^{-2}$ - 10$^{-5}$ torr) and single crystals suitable for X-ray crystallography can be grown either by dynamic or static vacuum sublimation. Crystals were brought either to University of
Western, University of Toronto, McMaster University or performed on-site at the University of Guelph.

2.7.2 Characterization

2.7.2.1 X-ray crystallography

DTANQ, II-1, Complexes

\[ [\text{Mn(hfac)}]_3[\text{DTANQ}]_2 \]

The first coordination attempts were performed with Mn(II)(hfac)₂•2THF and II-1 in DCE. The resulting blue material was sublimed on the dynamic vacuum furnace, and resublimed on a static vacuum furnace to yield large brown needles. A large, dark, brown needle-like crystal was mounted on a thin glass fibre, coated with epoxy and examined at Western University (UWO). Data were collected at low temperature (150 K) on a Nonius Kappa-CCD area diffractometer with COLLECT (Nonius BV., 1997-2002). The unit cell parameters were calculated and refined from the full data set. Selected crystal data are listed in Table 2.6. The resulting crystal structure was the Mn trimer species shown below (Figure 2.30).
Figure 2.29 ORTEP representation of the solid state structure of [Mn(hfac)$_2$]$_3$[DTANQ]$_2$ at 150 K. (H and F atoms removed for clarity)

The Mn2 atom is located on an inversion centre and therefore Figure 2.30 is a representation of two asymmetric units combined. The radicals coordinate in a monodentate fashion (O6 to Mn2), resulting in almost an 180° angle and in a bidentate fashion (N3 & O10 to Mn1). The coordination geometry about the Mn2 atom is near octahedral whereas the geometry about the Mn1 atoms is distorted octahedral. As with many metal-hfac species, the fluorine atoms have disorder.

Within the packing of the structure, there are S--O close contacts of 2.968 Å between trimer units. These close contacts are now known to direct FM coupling between neighbouring dithiadiazyl Mn(II) complexes$^{49}$ which will be described later. However, there are also close S--S contacts of 3.394 Å between trimers as well, which could direct AFM coupling. These contacts are illustrated in Figure 2.31.
Figure 2.30 Close contacts between trimer units of S–O and S–S

| Table 2.7 Crystallographic data and selected bond lengths for [Mn(hfac)$_2$]$_3$[DTANQ]$_2$ |
|---|---|---|---|
| [Mn(hfac)$_2$]$_3$[DTANQ]$_2$ (brown needles, grown by sublimation) |
| **Formula** | C$_{50}$H$_{14}$F$_{36}$Mn$_3$N$_2$O$_{16}$S$_4$ | **Density** | 1.89 |
| **Formula weight** | 1875.67 | **Unit cell volume** | 1645.47 |
| **Crystal system** | Triclinic | **Space group** | P -1 |
| **a** | 11.1494(15) | **α** | 116.267(2)$^\circ$ |
| **b** | 12.9941(16) | **β** | 109.368(2)$^\circ$ |
| **c** | 13.6531(18) | **γ** | 90.408(2)$^\circ$ |
| **Z** | 1 | **Temperature** | 150 K |
| **Bond** | **Length (Å)** | **Coordination angles($^\circ$)** |
| Mn1—N3 | 2.320(2) | N3-Mn1-O6 | 70.86(9) |
| Mn1—O6 | 2.319(3) | O10-Mn2-O10 | 170.5(9) |
| Mn2—O10 | 2.172(2) | R1 = 4.62% |
**Ni(hfac)$_2$(DTANQ)**

Due to the success of the coordination with Mn(II), coordination with Ni(II)(hfac)$_2$•2THF was attempted. The resulting blue material was sublimed on the dynamic vacuum furnace, and resublimed on the static vacuum furnace to yield large brown needles. Interestingly, the brown crystalline material that was obtained initially from the dynamic vacuum furnace is extremely moisture sensitive and rapidly turns dark blue upon exposure to very small amount of water vapour (air). A large, dark, brown needle-like crystal was mounted on a thin glass fibre, coated with epoxy and examined at Western University (UWO). Data were collected at low temperature (150 K) on a Nonius Kappa-CCD area diffractometer with COLLECT (Nonius BV., 1997-2002). The unit cell parameters were calculated and refined from the full data set. Selected crystal data are listed in Table 2.7. The resulting crystal structure reveals the Ni monomer species shown below (Figure 2.32).

Within the crystal structure, there are close contacts between complexes via S--O of the ligands. However, these close contacts are not pi in nature, but are lateral contacts, and therefore unlikely to resulted in diamagnetic dimers. There are also S--O lateral contacts between the radical ligand and the auxiliary ligand, hfac.
Figure 2.31 ORTEP representation of the solid state structure of Ni(hfac)$_2$(DTANQ) at 150 K. H atoms and F atoms removed for clarity.

Figure 2.32 Close S–O and C–C contacts between complexes of Ni(hfac)$_2$(DTANQ).
Table 2.8 Crystallographic data and selected bond lengths for Ni(hfac)(DTANQ)  

| Ni(hfac)$_2$(DTANQ) (brown needles, grown by sublimation) |
|---------------------------------|------------------|-----------------|----------------|
| Formula                        | C$_{20}$H$_6$F$_{12}$NiNO$_6$S$_2$ | Density | 1.94 |
| Formula weight                 | 707.07           | Unit cell volume | 1211.58 |
| Crystal system                 | Triclinic        | Space group     | P - 1 |
| a                              | 7.2162(14)       | α               | 88.96(3) |
| b                              | 12.947(3)        | β               | 81.96(3) |
| c                              | 13.162(3)        | γ               | 84.30(3) |
| Z                              | 2                | Temperature     | 150 K |
| Bond                           | Length (Å)       | Coordination angles (°) |
| Ni-O6                          | 2.161(3)         | N3-Ni-O6        | 77.6(1) |
| Ni-N3                          | 2.108(4)         | R1 = 5.47 %     |

[Gd(hfac)$_3$(DTANQ)]$_x$

The final metal coordination with DTANQ (II-1) was attempted with the recently synthesized and published, Gd(hfac)$_3$•DME starting material. The resulting blue material was sublimed on the dynamic vacuum furnace, and resublimed on the static vacuum furnace to yield large orange blocks. A large, orange, block-like crystal was mounted on a thin glass fibre, coated with epoxy and examined at McMaster University. Data were collected at low temperature (150 K) on a Brüker APEX II CCD detector. The unit cell parameters were calculated and refined from the full data set. Selected crystal data are listed in Table 2.8. The resulting crystal structure was the Gd$^{III}$ polymeric species seen below (Figure 2.34).
Figure 2.33 ORTEP representation of the solid state structure of [Gd(hfac)$_3$(DTANQ)]$_x$ at 150 K. a) asymmetric unit b) expansion of one chain (H and F atoms removed for clarity)

Table 2.9 Crystallographic data and selected bond lengths for Gd(hfac)$_3$(DTANQ)

| Gd(hfac)$_3$(DTANQ) (brown needles, grown by sublimation) |
|-----------------|-----------------|-----------------|-----------------|
| Formula         | C$_{25}$H$_{7}$F$_{18}$GdNO$_8$S$_2$ | Density        | 2.07            |
| Formula weight  | 1012.68          | Unit cell volume| 6481.93         |
Crystal system | Monoclinic | Space group | P 2_1/c |
---|---|---|---|
a | 20.0514(17) | α | 90 |
b | 16.2128(14) | β | 108.981(2) |
c | 21.0854(18) | γ | 90 |
Z | 8 | Temperature | 150 K |

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Coordination angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd—N3</td>
<td>2.621(6)</td>
<td>N3-Gd-O6</td>
</tr>
<tr>
<td>Gd—O6</td>
<td>2.609(7)</td>
<td>O10-Gd-N3</td>
</tr>
<tr>
<td>Gd—O10</td>
<td>2.401(6)</td>
<td>R1 = 6.50 %</td>
</tr>
</tbody>
</table>

Unlike the two transition metal complexes, no short S--O contacts between polymeric chains is seen in the crystal structure. Interestingly, there are also no short S--S contacts between radical ligands, suggesting the compound is likely not dimerized.

**Me_2DTANQ, II-2, Complexes**

**[Mn(hfac)_2][Me_2DTANQ]_2**

The first coordination attempt of II-2 was performed with Mn(II)(hfac)_2•2THF in toluene. The resulting blue material was sublimed on the dynamic vacuum furnace, and resublimed on the static vacuum furnace to yield large brown plates. A large, dark, brown plate-like crystal was mounted on a thin glass fibre, coated with epoxy and the XRD experiment was run on-site with a SuperNova Dual diffractometer with Atlas CCD system. The unit cell parameters were calculated and refined from the full data set. Selected crystal data are listed in Table 2.9. The resulting crystal structure was very similar to the Mn trimer species as shown above for DTANQ, II-1.
The differences from the methyl groups result in longer S--S contacts (3.536 Å) and shorter S--O contacts (2.947 Å). The longer S--S contacts are on the pinnacle of dimerization (sum of vDW radii for $S^2 = 3.6$ Å) whereas the S--O contacts are quite short (sum of vDW radii = 3.2 Å). However, this data was collected at room temperature (298 K), whereas the previous data for the Mn trimer with II-1 was collected at 150 K. This difference in temperature could result in the different short contacts, and lowering the temperature could result in compression of the species in the solid state, thus having very similar close S--S contacts to that of the complex with II-1. Investigation of this phenomenon is ongoing.

| Table 2.10 Crystallographic data and selected bond lengths for [Mn(hfac)$_2$][Me$_2$DTANQ] |
|-----------------------------------------------|-----------------------------------------------|
| [Mn(hfac)$_2$][Me$_2$DTANQ]$_2$ (brown plates, grown by sublimation) | |
| **Formula** | **C$_{54}$H$_{22}$F$_{36}$Mn$_3$N$_2$O$_{16}$S$_4$** | **Density** | **1.76** |
| **Formula weight** | 1931.77 | **Unit cell volume** | 1821.5 |
| **Crystal system** | Triclinic | **Space group** | P -1 |
| **a** | 11.5566(9) | **α** | 115.306(7) |
| **b** | 12.9756(9) | **β** | 92.468(6) |
| **c** | 13.5080(10) | **γ** | 93.764(6) |
| **Z** | 1 | **Temperature** | 298 K |
| **Bond** | **Length (Å)** | **Coordination angles(°)** |
| Mn1—N3 | 3.091(3) | N3-Mn1-O6 | 70.1(1) |
| Mn1—O6 | 2.307(3) | O10-Mn2-O10 | 180.0(1) |
| Mn2—O10 | 2.188(3) | | R1 = 5.89 % |
[Co(hfac)$_2$][Me$_2$DTANQ]$_2$

The second coordination attempt of II-2 was performed with Co(II)(hfac)$_2$•2THF in toluene. The resulting blue material was sublimed on the dynamic vacuum furnace, and resublimed on the static vacuum furnace to yield two different crystal species; the majority were large brown plates and with a minority of small bright red prisms. A large, dark, brown plate-like crystal was mounted on a thin glass fibre, coated with epoxy and the XRD experiment was run on-site with a SuperNova Dual diffractometer with Atlas CCD system. The unit cell parameters were determined and refined from the full data set. Selected crystal data are listed in Table 2.11. The resulting crystal structure was isomorphous with the Mn trimer species as seen above for DTANQ, II-1.

| Table 2.11 Crystallographic data and selected bond lengths for [Co(hfac)$_2$][Me$_2$DTANQ] |
|---------------------------------|-----------------|-----------------|-------------------|
| [Co(hfac)$_2$][Me$_2$DTANQ]$_2$ (brown plates, grown by sublimation) | Formula | C$_{54}$H$_{22}$F$_{36}$Co$_3$N$_2$O$_{16}$S$_4$ | Density | 1.81 |
| Formula weight | 1943.76 | Unit cell volume | 1783.63 |
| Crystal system | Triclinic | Space group | P -1 |
| a | 11.672(2) | α | 115.26(3) |
| b | 12.934(3) | β | 101.25(3) |
| c | 13.517(3) | γ | 93.88(3) |
| Z | 1 | Temperature | 298 K |
| Bond | Length (Å) | Coordination angles(°) |
| Co1—N3 | 2.160(2) | N3-Co1-O6 | 74.67(1) |
| Co1—O6 | 2.189(2) | O10-Co2-O10 | 180.0(1) |
| Co2—O10 | 2.172(2) | R1 = 3.88 % |
A small, bright red prism-like crystal was mounted on a thin glass fibre, coated with epoxy and the XRD experiment was run on-site with a SuperNova Dual diffractometer with Atlas CCD system. However, the crystal decomposed prior to collection of the full data set. The resulting unit cell was not triclinic (as seen for all trimer species) but monoclinic. The sensitivity to air/moisture could reflect the nature of the species. The Ni(hfac)$_2$(DTANQ) was the only other synthesized complex that was extremely air and moisture sensitive. This could arise from the packing of the structure. Further investigation of this phenomenon is ongoing.

2.7.2.1 Magnetometry of complexes

All the metal complexes using DTANQ, II-1, as the radical ligand were produced in very small yields and did not provide satisfactory elemental analyses. During the course of the synthesis, the ligand rapidly precipitates out of solution when cooled to room temperature. Clearly it is not a very good ligand. However, the crystal structures obtained suggest that these 1,4-naphthoquinone DTA radical ligands can be used in coordination complexes. As a result, we modified the structure to become more soluble and a better $\sigma$-donor by the addition of methyl groups in the naphthalene backbone. This gave rise to II-2 as a ligand.

At the time of writing, the [Mn(hfac)$_2$]$_3$[Me$_2$DTANQ]$_2$ has passed elemental analysis and has been sent for magnetometry. However, the 6,7-dimethyl variation of DTANQ coordinated to the Mn(hfac)$_2$ material produces a very similar trimer structure and may lend some insight into what may be expected. The $\chi T$ value initially decreases but increases to 15.6 cm$^3$Kmol$^{-1}$ at 15 K which is expected for a $S_T = 13/2$ ground state.
This thermal behaviour is consistent with AF coupling between radical ligand and the metal ion spins (leading to an overall ferromagnetic arrangement). Below 15 K, the $\chi T$ product rapidly decreases to 4.7 cm$^3$Kmol$^{-1}$, an indication of additional AF intermolecular interactions. Although there are S--O contacts which could direct FM coupling between trimer units, the competing S--S contacts ultimately establish the mechanism for the intermolecular AF coupling.\textsuperscript{33} However, in the 5,8-dimethyl variation (II-2), the close S--O contacts are still present but the closest S--S contact is 3.544Å, which may be far enough removed to direct the FM coupling between trimer units.

The 6,7-dimethyl analogue was also coordinated to Gd(hfac)$_3$•DME and resulted in a very similar crystal structure to Gd(hfac)$_3$(DTANQ) and may lend some insight into what may be expected for the Gd(hfac)$_3$(DTANQ) complex. At room temperature, the $\chi T$ product is 8.75 cm$^3$Kmol$^{-1}$ which is in agreement with an $S = 7/2$ species (Gd$^{\text{III}}$) and $S = 1/2$ (the radical ligand). Upon cooling, the $\chi T$ product decreases until a minimum of 1.97 cm$^3$Kmol$^{-1}$ at 1.8 K. This decrease is indicative of AF interactions between the lanthanide and radical. Although there are contacts between polymeric chains, they ultimately direct further AF coupling (for further information see David Sullivan's M.Sc. thesis).

At the time of writing, [Co(hfac)$_2$]$_3$[Me$_2$DTANQ]$_2$ had just been recently synthesized, crystallized and characterized. Samples were packed and sent for elemental analysis and magnetometry.
2.8 Summary

The main intention of this chapter was to synthesize an open shell ligand and coordinate it to a paramagnetic metal containing fragment, allowing for magnetic coupling to occur. The ultimate goal was to produce a metal complex, which also potentially could allow for activated conductivity to occur simultaneously. The synthesis and full characterization of II-1, has led to interesting singlet-triplet interactions in the solid state. As seen in the EPR section, there is clear evidence of the triplet state of the radical II-1 and with collaboration from Dr. Stephen Hill the complete thermal depopulation is seen below 50 K.

DTANQ (II-1) was designed to act as a ligand, however, its ligand properties turned out to be rather poor. The metal complexes were never recovered in amounts that allowed for magnetometry experiments. Nevertheless, coordination attempts produced crystallographic quality crystals of a variety of complexes (e.g. monomer, trimer and polymer) spurring development of 1,2,3-DTAs with improved ligand properties. Synthesis of a polymeric species, \([\text{Gd(hfac)}_3(\text{DTANQ})]_x\) was obtained as per the stated concept of the thesis. This offers the opportunity to redesign the ligands to generate conductive and polymeric species including lanthanide ions.

The promising coordination results of DTANQ paved the way for modification to the development of the 6,7-dimethyl analogue. This simple modification proved to be the key, as it has the solubility and donation properties that DTANQ lacked. In order to study different donation and steric effects, the 5,8-dimethyl version was produced. The known procedures to generate the 6,7-dimethyl analogue could not be adapted to
synthesize II-2, and new techniques had to be generated. Ultimately, II-2 was made in high purity and coordination to paramagnetic transition metals resulted in similar coordination motifs as seen previously. The intermolecular distances of II-2 complexes are slightly different when compared to the 6,7-analogue complexes, which could allow for interesting magnetic interactions. The magnetic measurements of the Mn and Co trimer complexes are currently being performed.

**2.9 Future work**

The potential future work of this chapter is two-fold: a) continuation of the modification of II-1 to generate smaller singlet-triplet gaps in the solid state, and b) continuation of the modification of II-1 to generate different ligands with different properties for coordination to paramagnetic transition metal and lanthanide ions. Regardless of which is to be followed, the largest issue is the synthesis of these new proposed ligands. As seen within this chapter, very recent developments in our lab allow for substitution throughout the naphthalene backbone in relatively high yields by utilizing a Diels-Alder type reaction with substituted 1,1’-thiophene dioxides. This allows for a diverse selection of substitution throughout the naphthalene backbone, which can greatly affect the properties of the material.

![Figure 2.34 General scheme for developing substituted 1,4-naphthoquinones](image-url)
For further pursuing these interesting singlet-triplet properties in the solid state, modification of the ligand could be performed to have electron-withdrawing substituents on the naphthalene backbone. Since the singlet-triplet properties arise from weakly bonding dimers, the withdrawing of more electron density should allow for even weaker dimers, making the singlet-triplet gap even smaller. This can be achieved via the 1,1’-thiophene-dioxide route with a variety of substituents such as Br, Cl, CF₃ and CN.

For further pursuing the development of new ligands, completion of the ‘methyl trend’ should be performed first. The 6,7- and 5,8-dimethyl analogues have been completed, and the 5,6,7,8-tetramethyl analogue was also partially synthesized, however not fully characterized due to the same issues (solubility and thermal instability) that II-2 had. However, now that the conditions for synthesis of II-2 have been determined, the synthesis of the tetramethyl analogue should be fairly straightforward. There is also a 6-methyl and 7-methyl which could be generated, however, due to the asymmetry of the molecule, is slightly more synthetically challenging. These different analogues should result in different coupling of the radical to the metal center and perhaps different structural packing in the solid state. Molecular orbital calculation studies were performed to determine the difference in spin density and are shown in Table 2.11 below.
Table 2.12 Calculated\(^\text{48}\) Mulliken spin densities for various analogues of II-1

<table>
<thead>
<tr>
<th>Substituted DTANQ</th>
<th>Structure</th>
<th>Mulliken spin densities</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTANQ (II-1)</td>
<td><img src="image" alt="Structure" /></td>
<td>N3 = 25.0%, O10 = 13.7%</td>
</tr>
<tr>
<td>6-methyl</td>
<td><img src="image" alt="Structure" /></td>
<td>N3 = 25.5%, O10 = 13.2%</td>
</tr>
<tr>
<td>7-methyl</td>
<td><img src="image" alt="Structure" /></td>
<td>N3 = 25.0%, O10 = 13.7%</td>
</tr>
<tr>
<td>6,7-dimethyl</td>
<td><img src="image" alt="Structure" /></td>
<td>N3 = 25.4%, O10 = 13.1%</td>
</tr>
<tr>
<td>5,8-dimethyl (II-2)</td>
<td><img src="image" alt="Structure" /></td>
<td>N3 = 26.9%, O10 = 12.7%</td>
</tr>
<tr>
<td>5,6,7,8-dimethyl</td>
<td><img src="image" alt="Structure" /></td>
<td>N3 = 27.4%, O10 = 12.1%</td>
</tr>
</tbody>
</table>

Also, sterically bulky substituents such as tert-butyl can also be synthesized\(^{15,20,56}\). This may allow for disruption of the generation of the typical metal-trimer complex as seen with the 5,8-dimethyl and lead to other interesting magnetic and conductive properties. Also, convenient syntheses of other substituents, such as a cyano,\(^{55}\) could yield interesting magnetic properties through close contacts within the solid-state packing. This has been seen to occur with other thiazyl systems\(^{57-59}\).
2.10 Experimental

**DTANQ, II-1**

1,4-Dioxo-naphtho[2,3-d][1,2,3]dithiazol-2-i um chloride (II-1\(^+\) Cl\(^-\)):

MeCN (100 mL) was added to 4.38 g (21.2 mmol) of 2-amino-3-chloro-1,4-naphthoquinone. An excess of S\(_2\)Cl\(_2\) (14.3 mL, 106 mmol) was added to the solution, which was then refluxed for 6 hours. The resulting slurry was hot filtered isolating the product as an orange powder. The solid was washed with 2 x 50 mL of MeCN and dried under vacuum; 3.805 g (67% crude mass yield). The crude product was used in the next step without further purification. **IR(KBr)** \(\nu/cm\(^{-1}\): 1699 (s), 1668 (s), 1580 (m), 1418 (w), 1318 (w), 1292 (s), 1260 (s), 1144 (w), 1052 (w), 1024 (w), 977 (w), 907 (s), 874 (m), 824 (m), 789 (m), 701 (s), 686 (m), 660 (w), 621 (w), 538 (w), 470 (w), 443 (w), 419 (w).

**Naphtho[2,3-d][1,2,3]dithiazoyl-1,4-dione, II-1**:

MeCN (60 mL) was added to a solid mixture of triphenylantimony (0.519 g, 1.47 mmol) and p-DTANQ\(^+\)Cl\(^-\) (0.791 g, 2.93 mmol). The slurry was stirred for 3 hours, over which time it changed colour from orange to black. The black solid was filtered *in vacuo* and washed 3 x 5 mL MeCN yielding a black solid 0.653 g (2.27 mmol, 77% crude yield). Sublimation of 0.330 g (1.41 mmol) under dynamic vacuum (10\(^{-5}\) Torr) using a 3 stage gradient tube furnace 145, 95, 45°C, produced two distinct polymorphs - green crystalline blocks and red crystalline needles of 1 0.279 g (1.19 mmol, 84% ~ 80 : 20 ratio respectively) **Elemental Anal.** Calc for C\(_{10}\)H\(_4\)NO\(_2\)S\(_2\): C, 51.27; H, 1.72; N, 5.98. Found C, 51.21; H, 1.96; N, 6.01%. **IR(KBr) v/cm\(^{-1}\): 1671 (s), 1590 (m), 1575 (m), 1543 (s), 1475 (w), 1416 (m), 1361 (m), 1322 (m), 1305 (m), 1252 (s), 1215 (s), 1161 (m), 1043 (w), 1017 (w), 995 (w), 895 (w), 824 (m), 789 (m), 701 (s), 686 (m), 660 (w), 621 (w), 538 (w), 470 (w), 443 (w), 419 (w).
861 (w), 801 (m), 774 (s), 728 (w), 708 (m), 683 (w), 669 (w), 658 (w), 557 (w), 523 (w), 484 (w).

**Me<sub>2</sub>DTANQ, II-2**

**2,5-Dimethyl-thiophene-1,1′-dioxide:** mCPBA (28.66 g, 0.1658 mol) was slowly added to 2,5-dimethyl thiophene (8.086 g, 0.0727 mol) in DCM (250 mL) at 0 °C and stirred for 6h and then at RT for 3 days. Excess mCPBA was filtered off and the burgundy filtrate was cooled with an EtOH/CO<sub>2</sub>(s) bath and filtered. Excess A21 resin base was added to the filtrate and stirred until the solution became yellow. The resin was filtered off and the yellow filtrate was evaporated. The resulting orange/yellow solid was recrystallized in MeOH and dried in vacuo, (2.084 g, 0.0145 mol, 20 % yield). $^1$HNMR (300 MHz, CD<sub>3</sub>Cl, 25 °C, ppm) δ: 6.267 (s, 2H), 2.101 (s, 6H). Pure in comparison to previously published.<sup>20</sup>

**5,8-Dimethylnaphthalene-1,4-dione:** 2,5-Dimethylthiophenesulfone (1.56 g, 10.4 mmol) was added to a 100 mL round bottom flask with 45mL of chloroform. Freshly sublimed 1,4-benzoquinone (1.13 g, 10.4 mmol) was added and the mixture was refluxed for 7 days until the intermediate was 100 % converted by $^1$H NMR. The solution was flash distilled and dry toluene (50 mL) was added. Activated MnO<sub>2</sub> (9.04 g, 0.104 mol) was added slowly over a period of 30 minutes. The solution was refluxed overnight, cooled to room temperature and filtered through a plug of celite to remove the MnO<sub>2</sub>. The solids were washed with toluene until the filtrate was colourless. The resulting bright yellow filtrate was flash distilled to provide a yellow crystalline product; 1.36 g (70 % yield). The product was used without further purification. IR(KBr) v/cm<sup>−1</sup>:
3075.0 (w), 3017.8 (w), 2963.3 (w), 2924.2 (w), 1961.3 (w), 1657.9 (s), 1618.4 (m), 1555.2 (m), 1458.0 (w), 1438.2 (w), 1382.5 (w), 1370.9 (w), 1328.7 (m), 1260.6 (m), 1104.1 (s), 1020.1 (m), 853.4 (w), 821.0 (m), 800.7 (m), 718.0 (w), 594.5 (w), 466.2 (w), 438.2 (w). ¹H NMR (300 MHz, CDCl₃, 25 °C, ppm) δ: 7.378 (s, 1H), 6.820 (s, 1H), 2.686 (s, 3H).

2,3-Dibromo-5,8-dimethyl-1,4-naphthoquinone: A solution of Br₂ (2.743 g, 0.0177 mol) and DCM (~10 mL) was prepared and poured into a dropping funnel. 5,8-Dimethyl-1,4-naphthoquinone (1.598 g, 0.00858 mol) was added to a 3 neck round bottom flask with 10 mL DCM under argon. The Br₂/DCM mixture was added dropwise to the orange solution in darkness and was allowed to stir in the dark for 3 days. Ar(g) was bubbled through the resulting red/brown solution where a white gas evolved and a yellow precipitate occurred. After the evolution of white gas ceased, the slurry was poured into a beaker and bubbling with Ar(g) continued. At a minimum of CH₂Cl₂, the resulting yellow slurry was filtered, rinsed with a small amount of CH₂Cl₂, and the filtrate was returned to the beaker and bubbling continued. This step was repeated until a yellow/orange paste remained in the beaker, which was rinsed with EtOH and filtered. All filtration residues were combined in a vial and dried in vacuo overnight leaving a bright yellow crystalline material. (2.516 g, 7.311 mmol, yield: 85 %). ¹H NMR (300MHz, CDCl₃, 25 °C, ppm) δ: 7.376 (s, 2H), 2.684 (s, 3H). The product was pure compared to previously published.⁶⁰

2-Amino-3-bromo-5,8-dimethylnaphthalene-1,4-dione: 2,3-Dibromo-5,8-dimethyl-1,4-naphthoquinone (1.823 g, 5.3 mmol) was added to a dry 250 mL three neck flask
with 130 mL of anhydrous ethanol. To the yellow slurry was added ammonium hydroxide (2.65 mL, 37.1 mmol) and a reflux condenser attached. A balloon of ammonia gas was added and the apparatus was refluxed. Refilling of the ammonia occurred whenever needed and the solution was refluxed for up to 24 hours with $^1$H NMR monitoring the progress of conversion. The red/orange solution was cooled to room temperature and argon was bubbled through for 30 minutes. The solution was filtered to provide an orange precipitate, and washed copiously with water. The resulting filtrate was evaporated and recrystallized from ethanol to give a total 1.430 g (96 % yield). The product was used without further purification. IR(KBr) $\nu$/cm$^{-1}$: 3495.6 (m), 3382.1 (m), 2965.7 (w), 2923.9 (w), 1659.4 (m), 1639.4 (s), 1618.1 (s), 1589.0 (s), 1547.9 (m), 1455.4 (w), 1430.9 (w), 1384.6 (m), 1366.2 (m), 1328.1 (w), 1235.8 (s), 1123.0 (w), 1070.4 (m), 996.2 (w), 826.3 (w), 784.7 (w), 755.0 (w), 743.3 (w), 693.0 (w), 582.0 (w), 512.9 (w). $^1$H NMR (300 MHz, CDCl$_3$, 25 °C, ppm) $\delta$: 7.315 (d, 1H), 7.245 (d, 1H), 5.419 (br s, 2H), 2.676 (s, 3H), 2.631 (s, 3H).

2-Amino-3-thioacetate-5,8-dimethyl-1,4-naphthoquinone: Sodium sulphide nonahydrate (0.453 g, 18.8 mmol) was added to a solution of 25 mL water and 5 mL ethanol and was degassed with argon for 15 minutes. 2-Amino-3-bromo-5,8-dimethylnaphthalene-1,4-dione (0.264 g, 9.43 mmol) was added and the solution was warmed to approximately 70 °C for 2 hours. The resulting deep purple solution was cooled to room temperature and excess acetic anhydride was added until a pH of 5. The solution quickly turned from transparent purple to an opaque orange and was stirred for 30 minutes at 0 °C. The resulting orange precipitate was filtered in air and washed with copious amounts of water. The precipitate was then dried, and stored under vacuum until
used. 0.242 g (93 %) crude yield. The product was used without further purification.

**IR(KBr) v/cm⁻¹:** 3490.0 (w), 3368.2 (s), 2967.0 (w), 2925.5 (w), 1701.7 (w), 1671.6 (w), 1607.1 (s), 1577.8 (m), 1540.3 (m), 1378.4 (m), 1328.4 (m), 1237.8 (m), 1198.4 (w), 11191.1(w), 1068.4 (w), 1036.4 (w), 992.9 (w), 949.0 (w), 824.9 (w), 797.9 (w), 763.1 (w), 699.9 (w), 616.5 (w), 593.8 (w).

**5,8-Dimethyl-1,4-dioxo-naphtho[2,3-d][1,2,3]dithiazol-2-ium chloride, II-2⁺Cl⁻:** 2-Amino-3-thioacetate-5,8-dimethyl-1,4-naphthoquinone (0.420 g, 1.53 mmol) was added to a dry 150 mL round bottom flask with 20 mL of acetonitrile under argon. Sulfur monochloride (1.03 g, 7.63 mmol) was added slowly to the orange slurry. The solution was very gently warmed (< 40 °C) for 2 hours, cooled to room temperature and filtered. The resulting orange precipitate was washed with cold acetonitrile (2 x 5 mL) and dried *in vacuo.* 0.387 g (85 %) crude yield. The product was used without further purification.

**IR(KBr) v/cm⁻¹:** 2963.0 (w), 2917.3 (w), 2848.9 (w), 1685.2 (m), 1654.6 (m), 1647.9 (w), 1637.6 (w), 1617.9 (w), 1609.1 (w), 1544.7 (w), 1375.7 (m), 1318.4 (m), 1263.1 (w), 1222.3 (s), 1171.1 (w), 1101.3 (m), 1031.6 (w), 950.7 (w), 921.5 (w), 859.7 (w), 811.8 (m), 800.1 (m), 744.9 (w).

**5,8-Dimethyl-naphtho[2,3-d][1,2,3]dithiazolyl-1,4-dione, II-2:** 5,8-Dimethyl-1,4-dioxo-naphtho[2,3-d][1,2,3]dithiazol-2-ium chloride (0.180 g, 0.604 mmol) was added to a round bottom under argon with 12 mL of acetonitrile. Triphenylantimony (0.106 g, 0.301 mmol) was added to a separate round bottom flask with 10 mL of acetonitrile. The triphenylantimony solution was slowly added via cannula into the orange slurry that quickly became a dark green/blue colour. The solution was stirred for 3 hours, filtered, washed with cold acetonitrile and dried *in vacuo.* The resulting blue precipitate (0.117 g,
0.445 mmol, 75 % crude yield) was sublimed in a gradient vacuum furnace at $10^{-5}$ torr (145 °C, 95 °C, 70 °C, 30 °C) to give dark purple/black needles (~35 % sublimation yield:) IR(KBr) $\nu$/cm$^{-1}$: 2969.1 (m), 2925.7 (s), 2851.8 (m), 1675.1 (s), 1655.1 (sh, w), 1603.3 (s), 1577.4 (w), 1571.3 (w), 1560.3 (w), 1550.3 (m), 1419.6 (m), 1375.7 (sh, m), 1368.5 (m), 1328.1 (m), 1292.4 (w), 1262.5 (w), 1222.5 (s), 1187.4 (sh, w), 1177.6 (w), 1106.1 (m), 1033.3 (w), 1004.3 (w), 939.1 (w), 909.7 (w), 827.2 (w), 813.9 (w), 771.0 (w), 744.8 (w), 629.4 (w), 526.4 (w), 497.4 (w). Elemental Anal. Calc: C: 54.94 H: 3.07 N: 5.34 Found: C: 54.78 H: 3.23 N: 5.21 %.

Generic metal coordination example

$[\text{Mn(hfac)}_2]_3[5,8-\text{Me}_2\text{DTANQ}]_2$: 5,8- Me$_2$-DTANQ (II-2) (61.0 mg, 0.233 mmol) and Mn(hfac)$_2$·2THF (142 mg, 0.233 mmol) were added to a Schlenk flask under inert atmosphere. Toluene (350 mL) was added and the solution was stirred for 24 hours initially generating a bright green solution followed by a bright orange solution. The solvent was evaporated leaving a purple/blue residue. Crude: (0.170 g, 0.233 mmol, yield: 100 %). The material purified by sublimation on a three-stage dynamic vacuum-gradient tube furnace and at $10^{-5}$ Torr, (115/90/60 °C). Light brown microcrystalline material was recovered. (46.5 mg, 6.35 mmol mol, yield: 25 %) Crystallographic quality crystals were grown by static sublimation. IR(KBr) $\nu$/cm$^{-1}$: 3142.1 (w), 2963.3 (w), 2917.3 (w), 2849.1 (w), 1647.5 (s), 1602.0 (m), 1560.2 (m), 1541.5 (m), 1482.9 (s), 1465.8 (m), 1449.7 (w), 1396.3 (w), 1382.5 (w), 1368.2 (w), 1341.4 (w), 1259.7 (s), 1203.8 (s), 1148.6 (s), 1095.6 (w), 1032.9 (w), 948.6 (w), 922.3 (w), 847.0 (w), 803.5 (s), 781.9 (sh, m), 742.3 (w), 665.4 (s), 585.5 (m), 528.4 (w). Elemental Anal. Calc: C: 33.57 H: 1.15 N: 1.45 Found: C: 33.41 H: 1.20 N: 1.43 %.
[Co(hfac)$_2$][5,8-Me$_2$DTANQ]; Data:

IR(KBr) $\nu$/cm$^{-1}$: 3142.1 (w), 2963.3 (w), 2917.3 (w), 2849.1 (w), 1647.5 (s), 1602.0 (m), 1560.2 (m), 1541.5 (m), 1482.9 (s), 1465.8 (m), 1449.7 (w), 1396.3 (w), 1382.5 (w), 1368.2 (w), 1341.4 (w), 1259.7 (s), 1203.8 (s), 1148.6 (s), 1095.6 (w), 1032.9 (w), 948.6 (w), 922.3 (w), 847.0 (w), 803.5 (s), 781.9 (sh, m), 742.3 (w), 665.4 (s), 585.5 (m), 528.4 (w). Elemental Anal. Calc: C: 33.36 H: 1.14 N: 1.44 Found: C: 33.38 H: 1.12 N: 1.46 %.

[Gd(hfac)$_3$(DTANQ)]$_x$

IR(KBr) $\nu$/cm$^{-1}$: 1649.7(s), 1611.1(w), 1560.7(m), 1535.0(m), 1498.8(m), 1257.8(s), 1209.7(s), 1145.6(s), 1100.8(m), 1046.3(m), 1021.4(w), 867.2(w), 804.6(s), 741.5(w), 708.0(w), 660.4(m), 586.3(m), 528.1(w), 468.9(w).

Ni(hfac)$_2$(DTANQ)

IR(KBr) $\nu$/cm$^{-1}$: 1649.4(s), 1558.2(w), 1532.3(w), 1484.0(m), 1257.9(s), 1206.2(s), 1184.9(s), 799.4(w), 715.4(w), 675.0(m), 588.9(w).

[Mn(hfac)$_2$]$_3$[DTANQ]$_2$

IR(KBr) $\nu$/cm$^{-1}$: 1647.5(s), 1602.0(w), 1560.2(m), 1541.2(w), 1482.9(w), 1465.8, 1449.7(w), 1382.5(m), 1368.2(m) 1341.4(w), 1259.7(s), 1203.8 (s), 1184.2(s) 1095.6(m), 803.5(w), 781.0(w), 665.4(w), 585.5(w).
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Chapter 3

Synthesis & characterization of quinone-based 1,2,5-thiadiazolyl radical anions
Chapter 3  
Synthesis & characterization of quinone-based 1,2,5-thiadiazolyl radical anions

3.1 General

The main focus of this chapter is the development of [1,2,5]thiadiazolyl radical anions, which are fused to a para-quinoid backbone as seen in Figure 3.1.

![Figure 3.1 The three studied and synthesized thiadiazolyl radical anions](image)

These three ligands have similar structured features and that is of no accident as the intelligent design of these ligands focuses on a variety of valuable physical properties. The coordination pocket between the oxygen(s) and nitrogen(s) is of importance as it provides dual functionality; the bidentate coordination angle is similar to that of bipyridine and also the mercaptand mentioned in chapter 1, which should allow for similar coordination environment. The other is to allow for magnetic coupling between the open shell ligand and the paramagnetic transition metal. The quinoidal backbone of the ligands allows for stability through a variety of oxidation states and thus would be a better ligand for coordination to a positively charge transition metal ion as a radical anion. The quinone would also draw electron density away from the thiadiazole (TDA) heterocycle to diminish the tendency of dimerization in the solid state. The naphthalene
backbone allows for resonance delocalization throughout and should also provide assistance to preventing dimerization. The anionic charge would generate electrostatic repulsion between systems, also diminishing the tendency for dimerization.

3.2 Synthetic Approach

3.2.1.1 Thiadiazole 1,4-naphthoquinone, III-1 (TDNQ)

Naphtho[2,3-c][1,2,5]thiadiazole-4,9-dione (TDNQ) is a well known molecule which has been synthesized by many different methods. The most common is by using the Gabriel synthesis to convert primary alkyl halides into primary amines by the use of potassium phthalimide. The substituted phthalimido-product can then be subjected to the Ing-Manske procedure which uses ethanolic hydrazine hydrate to generate the primary amine and the phthalhydrazide byproduct as shown in Figure 3.2. The ring closure to the 1,2,5-TDA heterocycle is well known and is typically performed by a neat reaction in refluxing thionyl chloride. The golden product after flash distillation can be purified by recrystallization in chlorobenzene and activated decolourizing charcoal. The resulting product is extremely pure and ready for use. Other one-pot methods are illustrated in Figure 3.2 and were also attempted to prepare III-1. The second route using thionyl chloride and urethane was completely unpredictable and yields varied between 0 % to 80 %. The third, which used tetrasulfur tetrinitride, was an easy to perform reaction resulting in high yields but the generation and subsequent use of a shock-sensitive explosive was unnerving and unsafe (in my honest opinion). Thus the well studied Gabriel synthesis and Ing-Manske procedure were utilized to generate the closed shell species, III-1.
3.2.1.2 Syntheses of thia-diazole 1,4-naphthoquinone radical anion (TDNQ $^-$)

The formation of the TDNQ $^-$ was reported in 1982 by the electrochemical observation of a reversible reduction process via a cyclic voltammogram however the reduced product was not reported nor isolated. Although there is a plethora of literature in which the interest of III-1 is a starting material for the synthesis of larger molecules to generate extended π systems, there is only one example of an attempt to generate and isolate the radical anion itself. Within this article the authors claim to have generated the radical anion by a co-crystallization of TDNQ with tetrathiafulvalene (TTF), a well known donor for charge transfer systems. However, upon closer inspection of the crystals structures reported, both molecules remain independent, neutral, closed shell species, which have co-crystallized.
The reduction potential of III-1 is quite large thus a strong reducing agent must be used in order to generate the radical anion. A large variety of reducing agents were used in order to try and isolate the radical anion. The first attempted generation of TDNQ$^-\cdot$ was by using an alkaline thiophenolate (either sodium or potassium) in a variety of solvents by following a known procedure for reducing these type of systems.$^{13,14}$ The obtained green amorphous product was completely insoluble and could not be purified nor crystallized, however shift in the infrared spectrum provided evidence of reduction. Countless crystallization attempts by slow diffusion utilizing both H-cells and a D-cell and slow evaporation by vial-in-vial (see Appendix B for procedures) using many different solvent mixtures did not lead to crystallization. The elemental analysis was impure which was assumed to be the generation of diphenyl disulfide \textit{in situ} and likely could not be removed.

Since the product was completely insoluble, efforts shifted to try and encapsulate the counter cation to provide some solubility in common organic solvents typically used with crystallization techniques. Crown ethers (18-crown-6, 15-crown-5, and 12-crown-4 for the potassium and sodium and lithium salts respectively) were used. The exact same results were obtained as above. Other uncommon encapsulating agents were used, such as benzo-15-crown-5, however none lead to a soluble product. Therefore another procedure was to be followed.$^{15}$

The expensive 2.2.2 cryptand (IUPAC 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)*, which captures a cation in a three dimensional cage as opposed to a two dimensional crown ether, along with using elemental potassium as the reducing agent, allowed for the desired soluble radical anion. However, although the
radical anion was soluble, it would not crystallize and was extremely air and moisture sensitive whereas the insoluble materials appeared to be relatively inert. Due to its now high solubility, EPR spectroscopy was able to confirm the species in solution. However, the lack of crystallinity and therefore the unknown crystal packing was problematic for probing the magnetic properties of the compound.

Ultimately, cobaltocene was used as the reducing agent in an equimolar ratio with III-1, as it has been used to produce a variety of thiazyl radicals.\textsuperscript{16} An H-cell was used to allow for slow diffusion of the two reagents in methylene chloride. Surprisingly, the resulting crystals that were formed were not of the expected product, but of a species with a 3 : 2 TDNQ : Co(Cp)$_2$ ratio as shown in Figure 3.3. Although the product crystallizes in methylene chloride, the material is completely insoluble in other low dielectric constant (low polarity) organic solvents suitable for EPR spectroscopy. Since the crystal structure was determined, measurements such as magnetometry and conductivity could now be performed. Ultimately the lack of solubility of III-1$^-$ led us to believe that changing the counter cation would allow for greater solubility.
There are few strong reducing agents reported in the literature that can also provide the solubility properties needed for this system. As with cobaltocene, thiazyl radicals have been generated with both Co(Cp*)₂ and Cr(Cp*)₂. Reduction of TDNQ using Co(Cp*)₂ in methylene chloride produced a soluble radical anion, which crystallized upon slow evaporation of the solvent and passed elemental analysis for a 1 : 1 species. Unfortunately, the crystals were too small for single crystal XRD. Recrystallization from a mixture of methylene chloride and cyclohexane at -20 °C to generate crystallography quality crystals solvated with 3 molecules of CH₂Cl₂ per asymmetric unit, produced [TDNQ ••][Co(Cp*)₂]·3CH₂Cl₂.

3.2.2.1 Syntheses of selenadiazole 1,4-naphthoquinone radical anion (SDNQ ••)

The selenium analogue of III-1, naphtho[2,3-ε][1,2,5]selenadiazole-4,9-dione, SNDQ, has also been studied extensively for the same reasons mentioned in chapter 1. As with TNDQ, the only reduction to the radical anion was reported by a cyclic voltammogram. SDNQ can be synthesized in the same manner as seen in Figure 3.1 but by replacing thionyl chloride with selenium oxychloride. Again, the highest yielding
synthesis utilized the Gabriel synthesis/Ing-Manske procedure to generate the diamino product following ring closure with SeOCl_2. The product was recrystallized with dry chlorobenzene and activated charcoal to produce a shiny golden material. However, unlike TDNQ, the closed shell selenium analogue is air sensitive and must be stored under argon.

The reductions of SDNQ to III-2\(^{-}\) were performed in parallel with TDNQ. Many of the procedures and attempts to reduce and crystallize respectively, mentioned above were also performed with SDNQ and yielded similar results. The elemental potassium and [2.2.2] cryptand synthesis was not attempted due to the extreme cost of the starting material. The solubility of the neutral SDNQ species was less than that of TDNQ, and any procedure that yielded an insoluble product for TDNQ was ultimately worse for SDNQ. Therefore, the reduction with cobaltocene was not performed in the same manner. Three solvent-layered vial crystallization reactions (see Appendix B for procedure) were performed with a varying ratio of the dimethyl formamide and methylene chloride. Golden brown crystals of III-2\(^{-}\)·Co(Cp)_2\(^{+}\) were slowly grown from the 2.5 mL : 0.5 mL and 2.5 mL : 1 mL ratios and sent for single crystal XRD. Interestingly, the material did not crystallize as a 1 : 1 salt, nor the 3 : 2 salt like TDNQ, but as a 2 : 1 SNDQ\(^{-}\)·(CoCp)_2\(^{+}\) as shown in Figure 3.3. Conductivity measurements were performed on the crystalline material. Amorphous brown material produced in separately a Schlenk flask passed elemental analysis for the 2 : 1 salt and sent for magnetometry.
3.2.3.1 bis-Thiadiazole 1,4-benzoquinone (BTDABQ)

Benzo[1,2-c:4,5-c′]bis([1,2,5]thiadiazole)-4,8-dione, BTDABQ, is a known closed shell neutral species and can be synthesized via a variety of methods.²
However, there are one-pot synthetic procedures involving 1,4-benzoquinone and sulfur tetranitride, which also give high yields and purity. Both syntheses were performed however the prior was favoured, as the synthesis, storage and use of $\text{S}_4\text{N}_4$ is not a safe practice when other alternatives exist. The product is very insoluble except in solvents of high polarity such as DMF, from which it is recrystallized.

### 3.2.3.2 Synthesis of bis-thiadiazole 1,4-benzoquinone radical anion (BTDABQ $\cdot \cdot$)

As with TDNQ and SDNQ, isolation of the radical anion was not previously attempted but cyclic voltammetry experiments indicated that it could be generated electrochemically.\(^7\) Due to its lack of solubility, the preparation of the radical anion was only attempted by layered vial experiments as described above for SDNQ. Large blue/black needles were grown from the ratio of 2.5 mL : 1 mL DMF/DCM and sent for single crystal XRD. The remainder of the crystalline product was used for conductivity measurements. Unfortunately, repeated attempts failed to produce material that was pure by elemental analysis and fit for further characterization such as magnetometry.

### 3.3.1 Physical Properties

All four isolated radical anion products mentioned above will be compared in the following section in the following order: $\text{III-1} \cdot \cdot \cdot \text{Co(Cp)}_2^+$, $\text{III-1} \ \text{Co(Cp*})_2^+$, $\text{III-2} \cdot \cdot \cdot \text{Co(Cp)}_2^+$ and $\text{III-3} \cdot \cdot \cdot \text{Co(Cp)}_2^+$. Since all of the neutral species and intermediates are reported and fully characterized, they will not be mentioned further except for comparison to the reduced species.
3.3.1.1 FT-IR

All samples for FT-IR were prepared as KBr pellets and IR spectra were measured on a Nicolet 4700FT-IR. The FT-IR spectra of the neutral TDNQ, [TDNQ]$_3$: [Co(Cp)$_2$]$_2$ and [TDNQ$^-$][Co(Cp*)$_2$] are shown in Figure 3.6. The finger print region is shown.

![FT-IR spectra of TDNQ, [TDNQ]$_3$: [Co(Cp)$_2$]$_2$, and [TDNQ$^-$][Co(Cp*)$_2$]](image)

**Figure 3.6** FT-IR spectra of TDNQ (top), [TDNQ]$_3$: [Co(Cp)$_2$]$_2$ (middle) and TDNQ$^-$[Co(Cp*)$_2$] (bottom) in the region from 1800-700 cm$^{-1}$ (* marks the $\nu$(C=O) stretches

Most quinones exhibit strong and sharp $\nu$(C=O) bands at 1800-1600 cm$^{-1}$. Since the LUMO of TDNQ is a $\pi$ anti-bonding orbital with respect to the C=O bond, any donated or withdrawn electron density will either shift the frequency lower or higher respectively. This expected lengthening of the carbon-oxygen bond, accompanying the reduction of the quinone to semiquinone is shown in Figure 3.5. Both ionic species, Co(Cp)$_2^+$ and Co(Cp*)$_2^+$, have a fully reduced semiquinone molecule in the crystal structure and its corresponding stretch is seen at 1496 cm$^{-1}$. Interestingly, since the reduction using Co(Cp)$_2^+$ is incomplete, there are more carbonyl stretches at 1605 and
1580 cm$^{-1}$. These stretches relate to the partially reduced species having slightly shorter carbon-oxygen bonds than the fully reduced species but longer bonds than the closed shell TDNQ.

The selenium analogue of III-1 has the expected quinone stretches and the corresponding shifting to a lower frequency when reduced to the semiquinone as seen in Figure 3.7. The shift is not as pronounced as the 1:1 TDNQ:Co(Cp*)$_2^+$ salt because the reduction is incomplete providing a 2:1 SDNQ:Co(Cp)$_2^+$ salt.

The same trend is observed when comparing the neutral BTDABQ species to its reduced species. Since there is only one fully reduced species (as it is a 1:1 ionic species with complete charge transfer), the FT-IR illustrates a large shifting of the $\nu$(C=O) peak as seen in Figure 3.8 comparable to the TDNQ Co(Cp*)$_2$ quinone shift.
3.3.1.2 Cyclic Voltammetry

The solution electrochemical behavior of III-1 has been reported in DMF as -0.66 V. However, since the reduction of this molecule with Co(Cp)$_2$ and with Co(Cp$^*$)$_2$ was performed in DCM, and the former, does not generate a 1:1 salt, it is worth determining whether this is in part a function of the reduction potential of III-1 in this particular solvent.

Cyclic voltammetry measurements of III-1 (Figure 3.9) were performed in dry DCM under argon atmosphere at ambient temperature with 0.05 M nBu$_4$NPF$_6$ as supporting electrolyte, with substrate concentrations ca. 2.0 mM and a sweep rate of 100 mV/s. The ferrocene/ferrocenium (fc/fc$^+$) redox couple was used as the internal standard with $E^o$(fc/fc$^+$) = +0.48 V vs. SCE in CH$_2$Cl$_2$. All potentials are thus reported vs. SCE. The ferrocene was sublimed before use.
The first reduction of $\text{III-1}$ to $\text{III-1}^-$ occurs at $E_{1/2} = -0.85$ V vs. SCE ($\Delta E_{pp} = 210$ mV) with complete chemical reversibility as seen in Figure 3.8. There is a second reduction presumably to the closed shell dianion, which appears to have incomplete chemical reversibility at $E_{1/2} = -1.49$ V vs. SCE ($\Delta E_{pp} = 210$ mV). The oxidative wave peak area is much smaller than that of the reductive wave, possibly due to comproportionation between the generated dianion and bulk solution of the neutral species, $\text{III-1}$ or decomposition of the thiadiazole ring.

The reduction potential of Co(Cp)$_2$ and Co(Cp*)$_2$ in DCM has been reported as 1.33 V and 1.94 V vs. ferrocene respectively.$^{19}$ The first reduction wave of $\text{III-1}$ is measured to be -1.27 V vs. ferrocene under the same conditions. Thus by applying the Nernst equation, reduction of $\text{III-1}$ with Co(Cp)$_2$ at room temperature results in an approximate 4 : 1 ratio of products : reagents in solution.$^{19}$ Therefore, it is not a surprise
that the reaction does not go to completion and generates a 3 : 2 species. However, with Co(Cp\(\ast\))\(_2\) when the same conditions are used, the ratio is \(10^6 : 1\) products : reagents in solution indicating that the reaction should proceed to completion. Since the Co(Cp\(\ast\))\(_2\)\(^+\) salt is completely soluble in DCM and the Co(Cp)\(_2\)\(^+\) salt crystallizes very slowly out of solution, the Nernst equation should remain valid for these systems.

The electrochemical potential of III-2 has been reported in DMF as -0.76 V.\(^7\) However, unlike III-1, SDNQ is not soluble in DCM, hence the reduction reaction occurs in a mixture of DMF/DCM. The reported reduction potential is larger than that of III-1 thus it would also be expected not to go to completion for the same reasons *vide supra*.

Interestingly, the electrochemical potential of III-3 has been reported in DMF as -0.54 V\(^7\) which is the lowest of the three molecules studied. As with III-2, BTDABQ is completely insoluble in DCM and a mixture of DMF/DCM was used for the reduction to generate the radical anion. Since the reported reduction potential is the lowest, it would be reasonable to assume that Co(Cp)\(_2\) would yield a larger product : reagent ratio in solution, and a complete reaction would occur. This is confirmed by single crystal X-ray crystallography.

### 3.3.1.3 Electron Paramagnetic Resonance

The EPR spectrum of the soluble [III-1 -· ][Co(Cp\(\ast\))\(_2\)\(^+\)] in deoxygenated methylene chloride shows a strong EPR signal (Figure 3.10). The best-fit parameters are \(g = 2.0044\), \(a_N = 0.460\) G for two equivalent nitrogen atoms, \(a_{H1} = 1.116\) G for two equivalent hydrogen atoms, and \(a_{H2} = 0.398\) G for a second set of two equivalent hydrogen atoms. The same EPR spectrum is obtained with III-1 -· [K(cryptand)]\(^+\) salt.
The EPR spectrum of the III-1$^{-}$ Co(Cp$^*$)$_2$$^+$ in methylene chloride (top) and simulation (bottom) (parameters: $g = 2.0044$, $a_N = 0.460$ G, $a_{III} = 1.116$ G, $a_{II} = 0.398$ G)

The EPR spectrum was simulated using the Public EPR Software Tools software. The hyperfine coupling constants found are comparable to those predicted by computational studies of III-1$^{-}$ (vide infra).

Due to the lack of solubility in low dielectric constant solvents (i.e. low polarity) the cobaltocenium salts of III-1$^{-}$, III-2$^{-}$ and III-3$^{-}$, EPR spectroscopy was not performed for these compounds.

3.3.1.4 X-ray crystallography

$$[\text{TDNQ}^- \mid \text{Co(Cp$^*$)$_2$}^+]$$
From the reaction of TDNQ and Co(Cp*)₂, black microcrystalline material was obtained by slow evaporation of the solvent. This material is a 1 : 1 ionic complex, pure by elemental analysis. However, the crystals obtained were not suitable for XRD and the material was recrystallized from a mixture of DCM and cyclohexane to generate crystallography quality crystals. The crystals were found to be solvated with 3 molecules of DCM per asymmetric unit as seen in Figure 3.11.

![Figure 3.11 An ORTEP drawing of the asymmetric unit of III-1 − Co(Cp*)₂⁺ (H atoms excluded and with thermal ellipsoids at 50 %)](image)

The most important feature of the 1 : 1 salt of III-1 is the carbon-oxygen bond lengths, which should increase with respect to III-1 (vide supra). The C=O bond lengths in the neutral species range from 1.209(3) to 1.217(4) Å respectively. There is some discrepancy of these bond lengths which is due to multiple polymorphs reported in the literature.²¹,²² In this 1 : 1 SQ species, the C–O distances of C24 – O25 and C34 – O35 are 1.244(8) and 1.260(8) Å, considerably larger than those of the neutral species. Other
changes in bond distances of neutral quinones reduced to semiquinones, such as chloranil, increase from 1.211 to 1.248 Å.\textsuperscript{23} Therefore this increase of bond length observed in III-1 \( \cdot \) Co(Cp*)\(_2\)\(^+\) is consistent with similar observations in the literature and thus is a good indication that the reduction of III-1 was complete, generating a radical anion.

It is interesting to note the crystal packing observed in III-1 \( \cdot \) Co(Cp*)\(_2\)\(^+\). There is an alternating column array of TDNQ radical anion and decamethylcobaltocenium cation as shown in Figure 3.12. This leads to an array of completely parallel stacks throughout the crystal structure with three methylene chloride molecules packing between the stacks. As expected the Cp* rings are staggered rather than eclipsed.
Figure 3.12 Crystal packing of III-1 $\cdots$ Co(Cp*)$_2^-$ as viewed from the perpendicular stacking (top) and from the a axis (bottom) (H atoms removed for clarity)
[TDNQ]_3[Co(Cp)]_2

The other salt of III-1 -, crystallizes as a 3 : 2 ionic complex, [TDNQ]_3[Co(Cp)]_2 from an equimolar ratio of reagents. It is not as simple to explain as the salt described above. At first glance, (Figure 3.13) the charge balance does not appear to be correct in the asymmetric unit. The structure could be interpreted as two individual III-1 - that co-crystallized with one completely neutral III-1 species.

However, when the C—O bond distances are taken into account, it is clear that there is one III-1 - radial anion (molecule containing S71), and two crystallographically distinct bimolecular radical anion units of [III-1]_2 - (the pairs of molecules containing S51 and S71). The bond distances of the molecule containing S71 are similar to that of the of III-1 - Co(Cp^*)_2^+ salt, with C74—O75 and C82—O83 bond lengths of 1.259(3) and 1.256(3) Å, respectively. This indicates a fully reduced III-1 - species. However in the molecules containing S51 and S31, the C—O bond distance are shorter than the SQ range but longer than the neutral TDNQ. The bond lengths for the S31 molecule are C34—O35 (1.230(3) Å) and C42—O43 (1.245(3) Å). The bond lengths for the S51-molecule are C54—O55 (1.237(3) Å) and C62—O63 (1.235(3) Å). Thus the S31 and S51 molecules appear to be in an intermediate oxidation state. Recognizing there are two positively charged species in the asymmetric unit (Co(Cp)_2^+) and one radical anion, the last remaining negative charge must be divided among the other two units, therefore each account for half of the remaining negative charge per asymmetric unit.
This is easier understood when looking beyond the asymmetric unit as in Figure 3.14. In this example, there are four positively charged species and two radical anions identified (Figure 3.14 boxed). The remaining two charges must be distributed between the S31 and S51 containing molecules, which are actually bimolecular radical anion units. Therefore the unpaired electron and the negative charge are delocalized equally across both molecular pairs.
Looking at these \([\text{III-1]}_{2}^{-}\) bimolecular radical anion units closely, neither the S31 or S51 molecules are strictly planar. There is a slight bend at the C—O atoms such that the angle between the planes of the thiazyl ring and the terminal phenyl ring are 12.13° and 7.67° from planarity for the S31 and S51 molecules respectively. Each pair has close intermolecular contacts via slipped trans-cofacial π-stacking. The closest contacts of the S31 and S51 molecule are 3.03 and 3.2 Å respectively.
<p>| Table 3.1 Crystal data and selected C—O (Å) distances of TDNQ, TDNQ — · Co(Cp*)₂⁺ and [TDNQ]₃[Co(Cp)₂]₂ |
|---------------------------------|---------------------------------|-----------------|------------------|
| <strong>TDNQ²²</strong>                      |                                 |                 |                  |
| Empirical formula               | C₁₀H₄O₂N₂S                     | Density         | 1.61             |
| Formula weight                  | 216.22                         | Unit cell volume| 1748.15          |
| Crystal system                  | Monoclinic                     | Space group     | P₂₁/c            |
| a                               | 15.072(5)                      | α               | 90°              |
| b                               | 8.295(3)                       | β               | 107.38(5)°       |
| c                               | 13.740(12)                     | γ               | 90°              |
| Z                               | 8                              | Temperature     | 298 K            |
| Bond                            |                                | Bond            | Length (Å)       |
| C3—O1                           | 1.2107(3)                      | C16—O4          | 1.2171(3)        |
| C6—O2                           | 1.2096(3)                      | C13—O3          | 1.2093(3)        |
| <em><em>TDNQ — · Co(Cp</em>)₂⁺</em>*          |                                 |                 |                  |
| Empirical formula               | (C₁₀H₄O₂N₂S)(Co(C₁₀H₁₅)₂₂)     | Density         | 1.468            |
| (CH₂Cl₂)₃                        |                                 |                 |                  |
| Formula weight                  | 800.40                         | Unit cell volume| 1809.94          |
| Crystal system                  | Triclinic                      | Space group     | P -1             |
| a                               | 10.359(3)                      | α               | 90.486(5)        |
| b                               | 11.832(3)                      | β               | 102.525(4)       |
| c                               | 15.753(4)                      | γ               | 105.695(4)       |
| Z                               | 2                              | Temperature     | 100 K            |
| Bond                            |                                | Bond            | Length (Å)       |
| C24—O25                         | 1.244(6)                       | C32—O33         | 1.260(7)         |
|                                 |                                 |                 |                  |
| R₁ = 6.68 %                     |                                 |                 |                  |
| <strong>[TDNQ]₃[Co(Cp)₂]₂</strong>           |                                 |                 |                  |</p>
<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>((C_{10}H_4O_2N_2S)_3((Co(C_5H_5))_2))</th>
<th>Density</th>
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<tr>
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<td>Triclinic</td>
<td>Space group</td>
<td>P -1</td>
</tr>
<tr>
<td>a</td>
<td>10.601(2)</td>
<td>(\alpha)</td>
<td>78.53(3)</td>
</tr>
<tr>
<td>b</td>
<td>12.185(2)</td>
<td>(\beta)</td>
<td>77.04(3)</td>
</tr>
<tr>
<td>c</td>
<td>16.651(3)</td>
<td>(\gamma)</td>
<td>80.68(3)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>Temperature</td>
<td>100 K</td>
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</tbody>
</table>

R1 = 4.19 %

\([\text{TDNQ}]_3[\text{Co(Cp)}_2]\)

\(\text{TDNQ}^{--}\)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C74—O75</td>
<td>1.259(3)</td>
<td>C82—O83</td>
<td>1.256(3)</td>
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\((\text{TDNQ})_2^{--}\)

<table>
<thead>
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<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C34—O35</td>
<td>1.230(3)</td>
<td>C42—O43</td>
<td>1.245(3)</td>
</tr>
<tr>
<td>C54—O55</td>
<td>1.237(3)</td>
<td>C62—O63</td>
<td>1.235(3)</td>
</tr>
</tbody>
</table>

\([\text{SDNQ}]_2[\text{Co(Cp)}_2]\)

From the reaction of SDNQ and Co(Cp)_2, golden brown microcrystalline material was obtained by stirring the two starting materials together in dry DCM for 3h. The material recovered was a 2 : 1 ionic complex, confirmed by elemental analysis. However, once formed, the product was completely insoluble in most common organic solvents except for DMF and DMSO. X-ray quality crystals were grown by a layered diffusion reaction between the two reagents in a ratio of 2.5 mL : 1 mL DCM/DMF. The crystal
structure confirmed the 2:1 ratio determined by elemental analysis, as shown in Figure 3.16.

As with the [TDNQ]$_3$[Co(Cp)$_2$]$_2^-$ product, this is not a simple 1:1 salt and therefore close inspection of the C—O bond lengths must be used in order determine the location of the unpaired electron and negative charge. The molecule containing Se21 has C24—O25 and C32—O33 bond lengths of 1.246(8) and 1.248(8) Å respectively. The molecule containing Se41 has C44—O45 and C52—O53 bond lengths of 1.257(8) and 1.253(1) Å respectively. The neutral structure has C3—O1 and C6—O2 of 1.207(3) bond lengths of 1.227(3) Å respectively. As expected, the bimolecular [III-2]$_2^-$ unit values in the 2:1 salt are considerably higher compared to the neutral SDNQ reported crystal structure.$^{22}$ Therefore, using charge balancing rules with the carbon-oxygen bond
lengths and one positively charged ion identified, the remaining negative charge and unpaired electron must be equally distributed between the two SDNQ molecules.

The packing within the crystal structure should also be mentioned. Each bimolecular radical anion pair, [III-2]_2^−−, is not strictly planar as shown in Figure 3.17. There is a slight bend at the C—O atoms such that the angles between the planes of the selenazyl ring and terminal phenyl ring are 5.55° and 8.22° away from planarity for the Se21 and Se41 molecules respectively.

![Figure 3.17](image)

**Figure 3.17** Bimolecular radical anion unit (asymmetric unit) showing the non-planarity of the molecules

Each pair has close intermolecular contacts *via* slipped *trans*-cofacial π-stacking. The closest contacts between the Se21 and Se41 molecule is a C—C contact with a distance of 3.094(5) Å. Also, each radical anion pair has close intermolecular contacts laterally with another pair which forms close Se—N contacts of 2.648(5) Å. This yields a structural array of “columns” of radical anion pairs as seen in Figure 3.18.
Figure 3.18 Crystal packing of III·2−·Co(Cp)2 as viewed from the perpendicular stacking down the $a$ axis (top) and from the down the columns via the $b$ axis (bottom).

These vertical columns of radical anion pairs can lead to a Mott-insulator type of conductivity mentioned in chapter 1 and will also be discussed *vide infra*. 
<table>
<thead>
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<th>SDNQ$^{22}$</th>
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<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>$C_{10}H_4O_2N_2Se$</td>
<td>Density</td>
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</tr>
<tr>
<td>Formula weight</td>
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<td>Unit cell volume</td>
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<td>Monoclinic</td>
<td>Space group</td>
<td>$P_2_1$</td>
</tr>
<tr>
<td>$a$</td>
<td>3.885(1)</td>
<td>$\alpha$</td>
<td>90</td>
</tr>
<tr>
<td>$b$</td>
<td>7.319(3)</td>
<td>$\beta$</td>
<td>92.14(2)</td>
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<td>$c$</td>
<td>15.156(4)</td>
<td>$\gamma$</td>
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</tr>
<tr>
<td>C3—O1</td>
<td>1.207(3)</td>
<td>C6—O2</td>
<td>1.227(3)</td>
</tr>
</tbody>
</table>

| [SDNQ]$_2$[Co(Cp)$_2$]                         |                 |                |                |
| Empirical formula                             | $(C_{10}H_4O_2N_2Se)(Co(C_5H_5)_2)$ | Density       | 1.86           |
| Formula weight                                | 715.333         | Unit cell volume | 5109.94        |
| Crystal system                                | Monoclinic      | Space group    | $C_2/c$        |
| $a$                                           | 22.730(2)       | $\alpha$       | 90             |
| $b$                                           | 6.7871(6)       | $\beta$        | 102.046(6)     |
| $c$                                           | 33.869(3)       | $\gamma$       | 90             |
| $Z$                                           | 8               | Temperature    | 100 K          |
| Bond                                          | Length (Å)      | Bond           | Length (Å)     |
| C24—O25                                       | 1.246(8)        | C32—O33        | 1.248(8)       |
| C44—O45                                       | 1.257(8)        | C52—O53        | 1.253(1)       |

R1 = 3.83 %
Similarly to TDNQ and SDNQ, the radical anion generated with cobaltocene as the reducing again, $\text{III-3} \rightarrow \text{Co(Cp)}_2^+$ is completely insoluble in common organic solvents except for DMF and DMSO. Crystallographic quality crystals were grown by a layered diffusion reaction between the two reagents in a ratio of $2.5 \text{ mL} : 1 \text{ mL}$ in DCM : DMF respectively. Unfortunately, the blue-black material obtained from stirring the two starting materials together in dry DCM for 3h did not yield elementally pure product and recrystallization was not an option due to insolubility. Unlike the two Co(Cp)$_2^+$ salts mentioned *vide supra*, the product formed was a 1 : 1 salt as seen in Figure 3.19.

![Figure 3.19 An ORTEP drawing of the asymmetric unit of III-3 \text{--} \text{Co(Cp)}_2^+ (H atoms excluded and thermal ellipsoids at 50 %)](image)

The packing within the crystal structure should also be mentioned. Although the radical anion is a 1 : 1 stoichiometry, there is a similar packing motif as that seen for TDNQ and SDNQ radical anion pairs. Each molecule is not completely planar as seen in Figure 3.20. There is a slight bend at the C—O atoms such that the angle between the
planes of the thiazyl rings with S21 and S28 are 5.60° and 5.21° away from planarity respectively.

![Two radical anions illustrating the non-planarity of between them](image)

Each radical anion has close C—C contacts to a neighbouring radical anion (2.728 Å) and each pair of radical anions have close C—S contacts to perpendicular radical anion pairs (3.266 Å). This forms a ‘zig-zag’ pattern of pairs of radical anions throughout the structure as seen in Figure 3.20. These close contacts of the pairs of radical anions can lead to a Mott-insulator type of conductivity mentioned in chapter 1 and *vide infra*.

Although the synthesis of the neutral closed shell **III-3** is in the literature, no single crystal structure is reported. The only structure containing BTDABQ is a charge transfer salt with TTF. The C—O bond distances of the **III-3**− Co(Cp)₂⁺ in comparison to the reported [BDTABQ][TTF] are remarkably longer. Also, the distances of **III-3**− Co(Cp)₂⁺ comparable to both reduced quinone species mentioned *vide supra*. Therefore it is very likely that the reported charge transfer salt is a co-crystallization, with little or no charge transfer as with **III-1**. Thus, the C—O bond distances of [BDTABQ][TTF] are actually of the neutral **III-3** species.
Figure 3.21 Close contacts of the crystal packing of III-3 $\rightarrow^\cdot$ Co(Cp)$_2^-$ (H atoms and Co(Cp)$_2^+$ molecules removed)

Table 3.3 Crystal data and selected C—O (Å) distances of [BTDABQ][TTF] and [BTDABQ][Co(Cp)$_2$]

<table>
<thead>
<tr>
<th>[BTDABQ][TTF]$^{12}$</th>
<th>[C$_6$N$_4$S$_2$O$_2$][C$_6$H$_4$S$_4$]</th>
<th>Density</th>
<th>1.85</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>428.58</td>
<td>Unit cell volume</td>
<td>765.696</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
<td>Space group</td>
<td>P2$_1$/n</td>
</tr>
<tr>
<td>$a$</td>
<td>7.376(2)</td>
<td>$\alpha$</td>
<td>90</td>
</tr>
<tr>
<td>$b$</td>
<td>7.720(2)</td>
<td>$\beta$</td>
<td>101.14(2)</td>
</tr>
<tr>
<td>$c$</td>
<td>13.705(3)</td>
<td>$\gamma$</td>
<td>90</td>
</tr>
</tbody>
</table>
Z | 2 | Temperature | 298 K
---|---|---|---
Bond Length (Å) | Bond Length (Å)
C3—O1 | 1.205 | C6—O2 | 1.213

**BTDABQ −· Co(Cp)$_2$$^+$**

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>(C$_6$O$_2$N$_4$S$_2$)(Co(C$_5$H$_5$)$_2$)</th>
<th>Density</th>
<th>1.792</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>413.33</td>
<td>Unit cell volume</td>
<td>1532.2</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Space group</td>
<td>P2$_1$/c</td>
</tr>
<tr>
<td>$a$</td>
<td>10.476(2)</td>
<td>$\alpha$</td>
<td>90</td>
</tr>
<tr>
<td>$b$</td>
<td>10.518(2)</td>
<td>$\beta$</td>
<td>108.518(2)</td>
</tr>
<tr>
<td>$c$</td>
<td>14.682(3)</td>
<td>$\gamma$</td>
<td>90</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>Temperature</td>
<td>100 K</td>
</tr>
</tbody>
</table>
| Bond Length (Å) | Bond Length (Å)
C24—O25 | 1.232(4) | C31—O32 | 1.264(4) |

R1 = 3.98 %

### 3.4 Molecular orbital studies

The quantum-mechanical calculations on the electronic structures of the [III-1 $\rightarrow$ ][Co(Cp$^*$)$_2$$^+$], [III-1]$[\text{Co(Cp)}_2]$$_2$, [III-2]$[\text{Co(Cp)}_2]$$_2$, and [III-3 $\rightarrow$ ][Co(Cp)$_2$$^+$] were performed using the Gaussian 09 Rev.A.02 package for Mac OSX.$^{24}$ The method and basis set, B3LYP and 6311-G(d) (split basis set: SDD-6-31Gd for metal complexes) respectively, were chosen as they are known to be compatible with our systems$^{25-27}$ and provide satisfactory data that we can compare to previous literature reports. The open shell species were calculated using unrestricted methods and calculations either used the gas phase optimized or crystal structure geometries as indicated (vide infra).
TDNQ $^\cdot\cdot$

The singly occupied molecular orbital (SOMO) of **III-1 $^\cdot\cdot$** (geometry optimized, gas phase structure) is a $\pi^*$ orbital that is nodal through the sulfur atom (Figure 3.22). Since it is antibonding with respect to carbon–oxygen, the occupation of this orbital is expected to increase the C–O bond distance. Both FT-IR experiments and the crystal data *vide supra* confirm this phenomenon. Closer inspection of the SOMO also shows little contribution from the nitrogen atoms, but the oxygen atoms having a dominant role. Thus the system should not be interpreted as a thiazy radical with a dione moiety, but rather as a semiquinone with a fused thiadiazole ring.

![Figure 3.22 Pictorial representation of the SOMO of the geometry optimized gas phase structure of III-1 $^\cdot\cdot$](image)
**TDNQ −· Co(Cp*)₂⁺**

The π stacked 1D arrays of alternating geometry of [III-1 −· and Co(Cp*)₂⁺] as shown in Figure 3.11 can be explained via inspection of the molecular orbitals of the system.

![Figure 3.23 LUMO of the CoCp*₂ cation using the crystal geometry (B3LYP/SDD-6-31 g(d) split basis)](image)

The radical anion SOMO has symmetry very similar to the lowest unoccupied molecular orbital (LUMO) of the decamethylcobaltocenium cation as seen in Figure 3.23. This accounts nicely for the alternating anion-cation 1D array as seen in the crystal structure (Figure 3.11).

**[TDNQ]₃[Co(Cp)₂]₂**

The SOMOs of the two bimolecular radical anion pairs, as shown in Figure 3.14, are slightly different which is likely due to the subtle differences in structural geometry. The individual SOMOs are reminiscent of Figure 3.21, however since they are bimolecular radical anion units both molecules must be taken into consideration. Each pair of radical anion units (S31 and S51 containing molecules) can be described as having
σ-bonding interactions between π molecular orbitals of the individual molecules. This is illustrated in Figure 3.24.

The LUMO of the cobaltocenium cation has similar symmetry compared to the decamethylcobaltocenium cation illustrated in Figure 3.22. Therefore, by viewing the SOMOs of the bimolecular radical anion units down the stacking direction (Figure 3.25), the same reasoning can be used for the creation of the Co(Cp)₂⁺ —(TDNQ)₂⁻ — Co(Cp)₂⁺ “sandwiches” in the solid-state structure as seen Figure 3.13.
The singly occupied molecular orbital (SOMO) of \textbf{III-2} (geometry optimized, gas phase structure) is similar to that of \textbf{III-1}. It is a $\pi^*$ orbital that is nodal through the selenium atom.

\textbf{[SDNQ]_2[Co(Cp)_2]}

As with the \textbf{[TDNQ]_2} bimolecular units, the SOMO of the \textbf{[SDNQ]_2} bimolecular radical anion unit are slightly different, likely due to the subtle differences in geometry. However, unlike \textbf{[TDNQ]_2}, the bimolecular radical anion unit has little of what can be described as $\sigma$-bonding interactions between $\pi$ molecular orbitals of the individual molecules as seen in Figure 3.25. This accounts for the longer C—O bonds in the Se41 containing molecule compared to that of the Se21 containing molecule. This lack of $\sigma$-bonding interactions likely prevents complete and equal delocalization between the each independent molecule in the bimolecular radical anion pair; thus one (Se41) has more than the other (Se21), however both are in intermediate oxidation states between Q and SQ.
The singly occupied molecular orbital (SOMO) of III-3$^{--}$ (geometry optimized, gas phase structure) is a π orbital (Figure 3.26 left) and delocalized throughout the system. It is interesting to note that there is a non-zero coefficient on the sulfur atoms. As with III-1$^{--}$ and III-2$^{--}$, it is antibonding with respect to the carbon – oxygen interaction and the occupation of this orbital is expected to increase the C—O bond distance. Both FT-IR experiments and the crystal data *vide supra* confirm this phenomenon. This system differs from the interpretation of III-1$^{--}$ and III-2$^{--}$ as a semiquinone with a fused thiadiazole ring but can be described more as a thiazyl radical with a dione moiety due to the relative contribution to the SOMO from all the atoms in the molecule.

Since the radical anion is not completely planar, the SOMO using the crystal structure geometry was also calculated (Figure 3.26 right). The differences are subtle, with contribution from all atoms still occurring.
Unlike that of TDNQ and SDNQ, the reduction of III-3 with cobaltocene resulted in a 1 : 1 ratio. Close inspection of the crystal structure shows two radical anions in close contact with one another and this interaction alters the planarity of each molecule (Figure 3.19). Since both are fully reduced radical anions, the interaction between them could either lead to a singlet ($S = 0$ either closed shell or open shell) or a triplet ($S = 1$) state. Using the crystal structure geometry, all possibilities of interactions were calculated (a broken symmetry function was utilized for the open shell singlet). Not surprisingly, the closed shell singlet has a much lower energy than that of the triplet and the open shell singlet. However, in both instances, there is a large amount of what can be described as $\sigma$-bonding interactions between the two molecules as seen in Figure 3.27.
3.5 Magnetometry

General

All data were collected by Prof. R. Clérac at Centre de Recherche Paul Pascal CRPP-CNRS UPR 8641, where the magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 K and 400 K for DC applied fields ranging from -7 to 7 T.
**TDNQ − ∙ Co(Cp^*)_2^+**

Since the structure of the solvent-free TDNQ − ∙ Co(Cp^*)_2^+ could not be obtained, and rapid desolvation was observed for the solvated species (3 CH₂Cl₂) to generate an amorphous species (0.5 CH₂Cl₂ confirmed by elemental analysis), it was not possible to measure the solid-state magnetic properties of this complex and gain any meaningful information based on the known structure.

**[TDNQ]_3[Co(Cp)_2]_2**

To avoid any possible interference from ferromagnetic impurities, the measurement of magnetization as a function of the applied field was performed at 100 K, as described in chapter 1. For paramagnetic or diamagnetic systems, a perfectly linear line that extrapolates to \( M = 0 \) at 100 K is expected (Figure 3.28). The slope of the line gives the susceptibility at 100 K as 0.0068 cm³/mol, which is in good agreement with the susceptibility measurements done at 1000 Oe.

![Figure 3.29 The plot of magnetization vs. applied field at 100 K for [TDNQ]_3[Co(Cp)_2]_2](image)
The magnetic susceptibility of $[\text{TDNQ}]_3[\text{Co(Cp)}_2]_2$ was measured as a function of temperature at an applied dc field of 1000 and 10000 Oe. At room temperature, the $\chi T$ product is 0.74 cm$^3$K/mol which is two $S = \frac{1}{2}$ spin carriers (or three TDNQ molecules; one TDNQ $-\cdot$ and one $[\text{TDNQ}]_2-\cdot$). The expected value for two non-interacting $S = \frac{1}{2}$ spins is 0.75 cm$^3$K/mol for $g = 2$; thus the result is in good agreement with the expected value. When the temperature is lowered, the $\chi T$ product decreases and reaches a minimum value of 0.39 cm$^3$K/mol at 5 K. This decrease in value demonstrates dominant antiferromagnetic (AF) coupling. This coupling likely arises between the TDNQ (S71) radicals with the TDNQ (S51) bimolecular radical pair and/or the TDNQ (S71) with the TDNQ (S31) bimolecular radical pair. It is unlikely that the TDNQ (S71) radicals would couple with each other given the crystal structure geometry. Below 5 K, the $\chi T$ product plateaus and begins to increase with decreasing temperature. This increase in value demonstrates the onset of ferromagnetic (FM) interactions below 5 K.

![Figure 3.30 Measured $\chi T$ vs. $T$ data of $[\text{TDNQ}]_3[\text{Co(Cp)}_2]_2$ (inset: a semi-logarithmic scale is used to emphasize the low temperature region) at 1000 Oe](image)
Unfortunately, modeling the magnetic data was extremely complicated and even collaboration with Dr. Rodolphe Clérac (CRPP, France) and Dr. Alessandro Vindigni (Laboratorium für Festkörperfysik, Zurich) a formal model could not be achieved. Therefore further interpretation of the data is speculative at best.

Within the crystal structure there are two one-dimensional packing arrays with a repeat unit of “– [TDNQ(S31)]_2 – [TDNQ(S71)] – [TDNQ(S51)]_2 –” which forms a complex three-dimensional network of magnetic interactions. From this, there are at least four different coupling constants, $J$, which should be considered to model the magnetic data. It was not possible to generate an acceptable model that relates the magnetic data to the given crystal structure since it is unclear which of these close contacts are magnetically important. Attempts at modeling the data using simplified molecular and other one-dimensional models (spin chains, spin dimers, spin trimers, ring systems, etc.) although the results were close, failed to reproduce the experimental data. Two of the closest attempts are seen below (Figure 3.31).

Attempts at determining the contacts that control the magnetic pathways via density functional calculations did not yield satisfactory results. This likely failed because all the possible values of $J$ are quite small and similar in magnitude.
As mentioned above, prior to each experiment, the field-dependent magnetization is measured at 100 K in order to detect the presence of any bulk ferromagnetic impurities. For paramagnetic or diamagnetic systems, a perfectly linear relationship is expected. It can be seen from the $M$ vs $H$ plot at 100 K (Figure 3.31) that there is, unfortunately, a very tiny amount of ferromagnetic impurity present in the sample, likely in the ppm amount, as the elemental analysis was satisfactory.

$[\text{SDNQ}_2\text{Co(Cp)}_2]$

Figure 3.31 Measured $\chi T$ vs. $T$ data with various attempts of modeling
Above ~ 1 T, the linear decrease in $M$ is characteristic of the bulk sample being diamagnetic. It should be noted that it is difficult to correct for a ferromagnetic impurity when the bulk sample of interest is diamagnetic but after a rough correction factor of the $\chi T$ vs. $T$ plot, the $\chi T$ product was essentially zero. This confirms the diamagnetic behaviour of this compound. As seen in Figure 3.17 the radical anion bimolecular units are all $\pi$-stacked with each other, therefore the [SDNQ]$_2$ bimolecular radical anion units are likely dimerized leading to the diamagnetic behaviour described above.

**BTDABQ $\cdot \text{Co(Cp)}_2^+$**

Bulk material of this species was never obtained in large quantities which yielded satisfactory elemental analysis and thus magnetometry was not performed. However, the radical anions, as seen in Figure 3.19, are paired with one another (dimerized). Referring to the SDNQ magnetometry, it is very likely that this system is diamagnetic. The singlet state ($S = 0$) was also calculated to be lower in energy than the triplet state ($S = 1$) as
mentioned in the computational section of this chapter. This evidence leads to the conclusion that the system is most likely to be diamagnetic.

### 3.6 Conductivity & Electronic Band Structures

Prior to any synthesis, the gas-phase ionization potentials ($IP$), and electron affinities ($EA$) for the three radicals were calculated to determine the gas-phase disproportionation enthalpies, $\Delta H_{\text{disp}}$. As mentioned in chapter 1, this is an approximation of the on-site Coulombic repulsion energy ($U$). Larger bandwidth, $W$, and smaller $U$, yields higher potential conductivity.

<table>
<thead>
<tr>
<th>Compound</th>
<th>III-1 (eV)</th>
<th>III-2 (eV)</th>
<th>III-3 (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$EA_1$</td>
<td>2.60</td>
<td>3.43</td>
<td>2.87</td>
</tr>
<tr>
<td>$EA_2$</td>
<td>-1.47</td>
<td>-1.76</td>
<td>-1.85</td>
</tr>
<tr>
<td>$\Delta H_{\text{disp}}$</td>
<td>4.07</td>
<td>5.19</td>
<td>4.72</td>
</tr>
</tbody>
</table>

*All values were generated using B3LYP/6-31G(d) Gaussian 09 reported as reference 24*

All conductivity measurements were performed under inert atmosphere using a crude pressed pellet device as explained in chapter 1. For more accurate conductivity results, single crystal measurements can be performed. A large single crystal is needed and four contacts are glued to the surface. Unfortunately, communication with groups that utilize such techniques, were not able to do so under inert conditions as the compounds are air and moisture sensitive.
All EHT electronic band structures were calculated in collaboration with Professor Richard Oakley at the University of Waterloo and were performed with the Caesar suite of programs\textsuperscript{28} using the Coulomb parameters of Basch, Viste and Gray\textsuperscript{29} and a quasi-split valence basis set adapted from Clementi and Roetti.\textsuperscript{30} The band structure calculations used the respective crystallographic coordinates for each molecule. The results are illustrated as dispersion curves of the crystal orbitals (COs), which arise from interactions between SOMOs mentioned above. As seen with related thiazyl compounds\textsuperscript{31,32} this method provides a decent insight into the interactions within and between radical $\pi$-stacks.

\textbf{TDNQ $\cdot$ Co(Cp*)$_2$}$^+$

Pressed pellet electrical conductivity measurements were taken and did not show any activated conductivity within the measureable range (\textasciitilde$10^{-6}$ S cm\textsuperscript{-1}). This was expected, as there are no close contacts between radical anions or any type or $\pi$-stacking in the solid-state structure. No further measurements or calculations were performed.

\textbf{[TDNQ]$_3$[Co(Cp)$_2$]$_2$}

Although there is little evidence of $\pi$-stacking within the crystal structure there are many close lateral contacts and thus crude conductivity measurements were performed. The conductivity was measured to be $1.0 \times 10^{-5}$ S cm\textsuperscript{-1} and reproducible. The conductivity is not only reproducible, but appears to be highly pressure dependent and could be increased as much as two orders of magnitude, up to $\sim1.0 \times 10^{-3}$ S cm\textsuperscript{-1}. Band calculations were performed as mentioned above but revealed no dispersion throughout the system as shown in Figure 3.32. The nature of the crystal structure makes it difficult
to interpret the materials properties and as with the magnetic data, is speculative at best. The experimental activated conductivity could be due to partial charge transfer in the system. This is a possibility since the reducing agent, cobaltocene, has a reduction potential very close the reductive wave of TDNQ. This would also explain the low activated conductivity, as it would not be a very good conductor.

![3D dispersion curves](image)

**Figure 3.33 The 3D dispersion curves of [TDNQ]$_2$[Co(Cp)$_2$]$_2$**

**[SDNQ]$_2$[Co(Cp)$_2$]**

Within the crystal structure of this species, there are columns of bimolecular radical anion units (shielded on one side with cobaltocene cations) and close contacts to other bimolecular radical anion units (which are also shielded with cobaltocene cations) as shown in Figure 3.17. These slipped π-stacks were presumed to have some interactions and thus conductivity measurements were taken. The activated conductivity was measured to be $\sim 1.0 \times 10^{-4}$ S cm$^{-1}$ and reproducible. The results of the calculations on this material are illustrated in Figure 3.34.
Figure 3.34 The 1D dispersion curves of two stacks with lateral Se contacts (right) and a single stack (left) for [SDNQ]_2[Co(Cp)_2]

As mentioned in chapter 1, the bandwidth of a system, \( W \), is expressed in terms of the dispersion, \( W = |\Delta E_k| = [E (k = \pi /a) – E (k = 0)] \) of the crystal orbitals. It can be difficult to predict how the SOMOs overlap, especially in this system since it is a bimolecular radical anion unit, but the band diagram above provides some insight into the interactions along and between the \( \pi \)-stacked columns. It can be seen from the EHT calculations that the energy goes down with increasing \( k \)-vector for both systems, \( i.e. \frac{dE}{dk} \) is negative and therefore \( \Delta E_k < 0 \). This change in energy is very small, > 0.05 eV for both systems (\( i.e. \) the dispersion is minimal) and thus any conductivity will be minimal. The calculations also illustrate that the lateral contacts (Se—N and Se—Se) between stacks do not increase the dispersion. This can be explained by the SOMO shown in Figure 3.21; there is no electron density located on the Se atoms in the SOMO and thus charge transfer is incapable of occurring through these contacts. This very low
dispersion is typical for a Mott insulator as explain in chapter 1, and corresponds with the experimental values of \( \sim 1.0 \times 10^{-4} \text{ S cm}^{-1} \).

**BTDABQ \cdot \text{Co(Cp)}_2^+**

This species in the solid state illustrates the classic ‘herringbone’ structure as shown in Figure 3.20. Two radical anions that appear to be dimerized have perpendicular close contacts to another set of dimerized radical anions, which also have perpendicular close contacts to another set, etc. The cobaltocenium cations are separating the columns of herringbones. The pressed pellet conductivity measurement was observed to be \( 1.0 \times 10^{-2} \text{ S cm}^{-1} \). Again, the electronic band calculations showed no dispersion throughout the system. In fact, the calculations show a large energy gap (Figure 3.34) between the HOMO and LUMO, suggesting the system should be diamagnetic (as suggested in the magnetometry section). This system is more difficult to explain, as unlike \( \text{III-1, III-3} \) should be readily reduced, as the reduction potential of cobaltocene is much greater than required. The difficult synthesis of this molecule along with it being an overall poor ligand due to solubility, led to the discontinuation of this project. At time of writing, the reproduction of the conductivity measurements had yet to be confirmed.
3.7 Summary

The intention of this chapter was to generate radical anion ligands to be coordinated to paramagnetic transition metal ions. The ultimate goal was to produce – [radical anion – metal – radical anion]– polymers, which could lead to conductivity and ferromagnetism simultaneously (ideally in the same temperature regime). This concept was first demonstrated with a mercaptopurinate (closed shell) ligand and a diamagnetic metal center in 1988\(^1\) which was mentioned in chapter 1. The molecules that were chosen had all the required features of the proposed ligand design; bidentate coordination, stability in a variety of oxidation states and the quinoidal backbone which would draw electron density away from the thiaadiazole heterocycle to assist in preventing dimerization. Although many coordination reactions to paramagnetic transition metal...
ions were attempted, the insolubility of the reduced ligands prevented coordination. \( \text{III-1} \ - \cdot \text{Co(Cp*)}_2^+ \), the one ligand that was soluble enough for metal coordination, likely reduces any metal ion when coordination reactions were attempted. Nonetheless, the properties of the synthesized reduced ligands had interesting material properties themselves.

After synthesizing \([\text{TDNQ}]_3[\text{Co(Cp)}_2]_2\) and obtaining the interesting crystal structure, the obvious plan of action was to characterize the properties it may have. Magnetometry measurements were taken multiple times, always resulting with the same data. The increase below 5 K was thought to be a ferromagnetic impurity, only seen at low temperatures. After thorough investigation of the solid-state structure, we determined it was indeed a function of the material itself. Unfortunately, the data could not be modeled with any conventional system and collaboration to generate a decent model was attempted. After much effort, the data was still was unable to be modeled. Conductivity measurements were taken and it was found to have low activated conductivity \((\sim 10^{-6} \, \text{S cm}^{-1})\). Extended Hückel Theory calculations illustrated no dispersion in the system, however the experimental measurements were repeatable. Again, explanation of the data is speculative at best as there are many close contacts throughout the structure and with the likelihood of having a partial charge transfer system, would result in the low conductivity data obtained. Attempts in synthesizing a soluble ligand resulted in \( \text{III-1} \ - \cdot \text{Co(Cp*)}_2^+ \) and this was fully characterized. Magnetometry could not be obtained as the crystals desolvate to a known amount and crystallographic quality crystals of the non-solvated material could not be obtained. Conductivity
measurements were taken, however no activated conductivity was observed. All data for \textbf{III-1} has been published.$^{33}$

The selenium analogue was synthesized because of the interesting data that resulted from the reduction of \textbf{III-1} with cobaltocene. Unlike the above 3 : 2 ratio, when \textbf{III-2} was reduced with cobaltocene, a 2 : 1 ratio, resulting in [SDNQ]\(_2\)[Co(Cp)\(_2\)]. Within the obtained crystal structure, there are columns of bimolecular radical anion units with close contacts to another column of bimolecular radical anion units. Conductivity measurements were taken and it was found to have low activated conductivity ($\sim 10^{-4}$ S cm\(^{-1}\)) and theoretical investigation using EHT calculations illustrated some minimal dispersion. Magnetometry measurements were performed, however a small ferromagnetic impurity (likely in the ppm) was present. The resulting data was corrected, although it is difficult to correct for a ferromagnetic impurity when the material is likely diamagnetic. After the correction, the magnetic data illustrated that the system was indeed diamagnetic.

The final ligand synthesized was \textbf{III-3} = Co(Cp*)\(_2\)^+, and unlike the two mentioned above using cobaltocene as the reducing agent, this species crystallizes as a 1 : 1 product. The crystal structure illustrates a herringbone structure of radical anions, which appear to be dimerized. Columns of cobaltocenium counter cations surround the radical anion herringbone columns. The conductivity measurements were performed and found to have higher values than previously measured, $\sim 10^{-2}$ S cm\(^{-1}\). Unfortunately, synthesis of pure crystalline material is extremely difficult and the data has not been reproduced. The EHT calculations illustrate no dispersion in the system, so the measurement was very well a false positive. It is possible however, to have a partial
charge transfer between the radical anions and the cations, which could explain the phenomenon seen, although these systems typically have lower conductivity. Magnetometry was never performed, as the material never passed elemental analysis.

3.8 Future work

Although the ligands mentioned in this chapter have interesting charge-transfer and magnetic properties, the main intention of this project was the coordination of radical anions to paramagnetic transition metal ions. The intelligent design of the ligands discussed earlier in this chapter provides an optimal bis-bidentate coordination site that has been incorporated successfully into other ligands to coordinate a variety of metal precursors.\textsuperscript{34-36} This can lead to many different complexes such as monomers, oligomers, one-dimensional chains, and even two- or three-dimensional complexes. However, many of these ligands, which coordinate in this fashion, are neutral closed shell whereas the ligands discussed here are radical anions. This is the single biggest problem in the synthetic methodology for coordination of these ligands because the reduction potential required is so large. Unfortunately, the large reduction potential needed to synthesize the isolated radical anions also makes the radical anions a strong reducing agent themselves. When attempting coordination, these ligands can reduce the metal it is coordinating to, leaving a closed shell ligand (coordinated or not) and a reduced metal center ion. A literature investigation as to why these systems require such strong reducing agents resulted in the quinone moiety as the main cause. Therefore slight modifications to the design of the ligands could yield lower reduction potentials and thus better ligands for coordination.
Keeping in mind that the primary focus of this thesis is to design, develop and synthesize materials which would offer both interesting magnetic and conductive properties, the future work section modifies the quinone portion with a known charge transfer agent, TCNQ, specifically the malonitrile portion. The below molecules are all synthetically known and found in the literature for charge transfer agents and have been co-crystallized with TTF and other donors yielding interesting conductivity properties.\(^{37-42}\)

\[
E = \text{S, Se, O}
\]

![Molecules](III-4.png)

**Figure 3.36 Potential future work molecules utilizing the malonitrile backbone**

Isolation of the radical anions and subsequent coordinations nor reduction while coordination attempts has not been attempted. The reduction potentials are much smaller than those with the quinone backbone (\(\text{III-1 } E_1 = -0.96 \text{ V vs. III-4 } E_1 = -0.21 \text{ V}\)), thus cheaper and more soluble reducing agents could be utilized. Metal carbonyls (such as \(\text{Co}_2(\text{CO})_8\)) reactions could also be employed to reduce and coordinate the ligand simultaneously as seen with previous ligands.\(^{43-46}\) The coordination geometry between the nitrogen atoms on the cyano- and thiadiazole is not as optimal in comparison to the quinones mentioned in this chapter. Coordination can still occur in a mono-dentate
fashion. It should be noted that III-6 has very recently been coordinated to a non-paramagnetic transition metal ion (Ru). III-6 remains as a closed shell, neutral ligand. The method of coordination is in a mono-dentate fashion via the cyanogen nitrogen atoms.\(^{47,48}\)

![III-7](image1.png) ![III-8](image2.png)

**Figure 3.37 Two potential future work molecules with bidentate coordination pockets**

For a better coordination environment, III-7 and III-8 were synthesized by Rees et. al. in 2001\(^ {49}\) however further studies were not pursued because the compounds did not yield satisfactory conductivity properties when co-crystallized with TTF and other donors. These bis-thiadiazole molecules have an optimal coordination moiety similar to that of the thiadiazole-naphthoquinones however they have a lower reduction potential to the radical anion. Also, recent research of open shell ligands with a cyano- functional group has yielded interesting magnetic results.\(^ {50,51}\) Further research into these malonitrile substituted 1,2,5-thiadiazole molecules may be more successful in forming metal complexes with interesting magnetic and conductive properties.
3.9 Experimental

3.9.1 General

All operations were carried out using Schlenk techniques under argon atmosphere. TDNQ III-1, SDNQ III-2 and BTDABQ III-3 were prepared according to literature procedures.\textsuperscript{2,5,6,52} Cobaltocene and decamethylcobaltocene were purchased from Sigma-Aldrich and used as received. Dichloromethane and cyclohexane (CyHex) were distilled from calcium hydride and acetonitrile was distilled from phosphorous pentoxide. The EPR spectrum was measured with a Brüker EMX Spectrometer in dichloromethane. Elemental analyses were performed by MHW Laboratories (Phoenix, AZ).

3.9.2 Synthesis of [TDNQ][CoCp*\textsubscript{2}], III-1 -- Co(Cp*)\textsubscript{2}\textsuperscript{+}

A solution of III-1 (0.0970 g, 4.49 mmol) in CH\textsubscript{3}CN (15 mL) was placed in a 50 mL round bottom flask and a solution of decamethylcobaltocene (0.148 g, 4.49 mmol) in CH\textsubscript{3}CN (15 mL) was placed in an identical round bottom flask. The decamethylcobaltocene solution was added via cannula into the solution of III-1 and the reaction was stirred for 1 hour at room temperature. An amorphous black precipitate was removed by filtration from the resulting dark red solution. The remaining filtrate was slowly concentrated in vacuo at 0 °C. Black microcrystals of III-1 -- Co(Cp*)\textsubscript{2}\textsuperscript{+} were formed during the removal of the solvent and collected. Yield: 0.111 g (45%) C\textsubscript{30}H\textsubscript{34}CoN\textsubscript{2}O\textsubscript{2}S (545.17 g/mol): calcd. C 66.03, H 6.29, N 5.14; found C 65.66, H 6.25, N 5.15%. Crystallography quality crystals of the solvated [TDNQ][CoCp*\textsubscript{2}]-3CH\textsubscript{2}Cl\textsubscript{2} complex were grown from a 3 : 1 solution of CH\textsubscript{2}Cl\textsubscript{2}: CyHex at 4 °C for 16 h. When removed from the mother liquor, these crystals partially desolvated to an amorphous
material. After drying under vacuum, the composition was determined by elemental analysis to be [TDNQ][CoCp*2]·0.5CH₂Cl₂, C₃₀H₃₄CoN₂O₂S(CH₂Cl₂)₀.₅: calcd. C 62.29, H 6.00, N 4.76; found C 62.20, H 6.08, N 4.76%. IR (KBr): 2962.2(m), 2917.2(m), 1685.6(w), 1510.1(w), 1491.3(s), 1448.0(w), 1425.4(w), 1375.7(m), 1325.2(s), 1263.1(s), 1091.5(m), 1025.5(m), 967.0(w), 919.6(w), 824.6(m), 777.3(m), 719.4(w), 695.5(m), 515.4(m), 443.6(w) cm⁻¹.

3.9.3 Synthesis of [TDNQ]₃[CoCp₂]₂

The reaction was carried out in an U-shaped Schlenk vessel with vertical tubes of the dimensions 2.5 x 17 cm and a horizontal tube of the dimensions 1.5 x 5 cm, with a medium porosity glass frit at the mid-point. A solution of III-I (0.104 g, 0.479 mmol) in CH₂Cl₂ (10 mL) was placed in a 20 mL round bottom flask, which was attached to one tube, and a solution of cobaltocene (0.0908 g, 0.479 mmol) in CH₂Cl₂ (10 mL) was placed in an identical round bottom flask, attached to the other tube of the upside-down U-vessel. The whole vessel was then gently inverted and slanted slightly to allow slow diffusion of the cobaltocene solution through the frit into the solution of III-I. The tilt angle of the vessel was slowly adjusted over a period of 3 hours until all the cobaltocene solution had been added to the solution of III-I. The initial formation of crystalline product was observed after 5 h at RT. The vessel was kept at ambient temperature overnight. The solvent was removed via syringe and the large, black needle-shaped crystals of [TDNQ]₃[CoCp₂]₂ were washed twice with CH₂Cl₂ and dried under vacuum. Yield: 0.0855 g (17%) C₅₀H₃₂Co₂N₆O₆S₃ (1026.02 g/mol): calcd. C 58.48, H 3.14, N 8.19; found C 58.45, H 3.42, N 7.92%. IR (KBr): 3083.6(m), 1685.9(w), 1617.9(m),
The reaction was carried out in a four-dram vial under inert atmosphere. A solution of \textbf{III-2} (0.0111 g, 0.422 mmol) in DMF (1 mL) was carefully syringed onto a solution of cobaltocene (0.00790 g, 0.422 mmol) in CH$_2$Cl$_2$ (2.5 mL) in a four-dram vial. The two solutions were left layered undisturbed for one week to allow for slow diffusion. The vessel was kept at ambient temperature throughout. The solvent was removed via syringe and the large, golden needle-shaped crystals of \[\text{[SDNQ]}_2[\text{CoCp}_2]\] were washed twice with CH$_2$Cl$_2$ and dried under vacuum. Bulk reaction was carried forward by adding \textbf{III-2} (0.0966 g, 3.67 mmol) to a 50 mL side arm round bottom flask under argon and syringing in DCM (10 mL). A solution of cobaltocene (0.0350 g, 1.84 mmol) in 10 mL DCM was slowly added. The solution was stirred for 2 hours and a golden brown precipitate formed. The precipitate was filtered, washed with 10 mL DCM and dried \textit{in vacuo}. Yield: 0.0921 g (69 \%) Calc for (C$_{10}$H$_4$N$_2$O$_2$Se)$_2$(CoC$_{10}$H$_{10}$): C 50.23, H 2.81, N 7.81; found C 50.12, H 2.59, N 7.73\%. IR (KBr): 1685.6(m), 1617.7(w), 1570.4(m), 1483.4(m), 1439.6(m), 1412.9(m), 1379.8(w), 1287.5(s), 1231.2(w), 1172.5(m), 1101.3(s), 1009.3(s), 964.3(m), 936.6(m), 869.7(w), 817.3(w), 749.3(w), 462.6(w), 445.9(s).
3.9.5 Synthesis of BTDABQ Co(Cp)$_2^+$, III-3 $\cdots$

The reaction was carried out in the same manner as above. A solution of III-3 (0.0116 g, 0.517 mmol) in DMF (1 mL) was carefully syringed onto a solution of cobaltocene (0.00980 g, 0.517 mmol) in CH$_2$Cl$_2$ (2.5 mL) in a four-dram vial. The two solutions were left layered undisturbed for one week to allow for slow diffusion. The vessel was kept at ambient temperature throughout. The solvent was removed via syringe and the large, blue-black needle-shaped crystals of [BTDABQ][CoCp$_2$] were washed twice with CH$_2$Cl$_2$ and dried under vacuum. IR (KBr): 1566.3(s), 1452.6(s), 1397.6(s), 1326.9(w), 1263.3(s), 1104.5(w), 1080.7(w), 1049.8(w), 1019.6(w), 1003.7(w), 878.2(m), 828.1(m), 786.7(w), 755.3(w), 532.0(w), 502.1(m), 463.2(m).
3.10 References


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Chapter 4

Synthesis, characterization and clinical cancer studies of poly-fluorinated naphthoquinones
Chapter 4  Synthesis, characterization and clinical cancer studies of poly-fluorinated naphthoquinones

4.1  General

The target molecule for this chapter is 5,6,7,8-tetrafluoronaphtho[2,3-c][1,2,5]thiadiazole-4,9-dione (F₄TDNQ) IV-1. It has been designed as a closed shell, neutral molecule, which should have a lower reduction potential to the semi-quinone oxidation state compared to III-1. Both the neutral species (IV-1) and the radical anion (IV-1⁻) were unknown prior to our research.

![IV-1 and IV-1⁻](image)

Figure 4.1 The project compound, IV-1 and IV-1⁻

Although the initial purpose behind the synthesis of IV-1 was to allow for a lower reduction potential to synthesize IV-1⁻ for coordination to paramagnetic transition metals, the research took a significant tangent with the realization that poly-fluorinated naphthoquinones have been known to have anti-tumor properties.¹⁻³ More importantly, it has been recently discovered that aminated-polyfluorinated para-naphthoquinones have higher activity towards inhibition of tumor cell growth.⁴ Cyclin-dependent kinase complexes (CdK) are regulatory enzymes, which control cell cycle regulation, cell growth and other important cellular functions. The CdKs are activated and controlled by the Cdc25 (cell division cycle) family of phosphatase enzymes. Thus, overexpression of
certain Cdc25s can lead to a number of tumoral cells, of various origins, and the cells can be quite aggressive.\textsuperscript{2} Many Cdc25 inhibitors are known, and some of them are quinones or quinone-type compounds,\textsuperscript{5} 2,3-bis[(2hydroxyethyl)thio]-1,4-naphthoquinone, being the most potent in the National Cancer Institute (NCI) library.\textsuperscript{6} However, many of the reported Cdc25 quinone inhibitors not only perform the intended function, but also degrade over time to generate toxic reactive oxygen species (ROSs) that tends to damage normal tissue and thus reduce their therapeutic value.\textsuperscript{7} One strategic solution is to modify the same quinone-based inhibitors but including fluoro groups on the naphthalene backbone. Polyfluorinated quinone based Cdc25 inhibitors allow for a more stable reduced species, which prevents radical formation and are less prone to formation of ROS’s, thus unlikely to indiscriminately attack neighboring normal tissue cells.\textsuperscript{3}

4.2 Synthetic approach to the polyfluorinated thiadiazole naphthoquinone

4.2.1.1 Hexafluoro-1,4-naphthoquinone (F\textsubscript{6}NQ)

The main difficulty encountered at the beginning of this project was the synthesis of IV-2, hexafluoro-1,4-naphthoquinone, which although commercially available, is very expensive and only supplied in “milligram quantities”. The procedure that we followed initially for the preparation of IV-2 was based on a known literature method,\textsuperscript{8} however modification of the procedure was needed in order to improve the yields to make the project economically feasible. The optimized procedure is as follows: the direct anodic oxidation of octafluoronaphthalene to generate IV-2 is performed in trifluoroacetic acid (TFA), methylene chloride (DCM) and triethylamine (TEA) (3.0 mol equivalents) to prevent formation of hydrofluoric acid (HF). The experiment is performed in a 3-necked
round bottom flask with a large surface area Pt wafer anode and a Pt wire cathode at room temperature with a constant current density of 10 mA/cm² for 16 hours.

![Diagram of the two potential routes to anodic oxidation of octafluoronaphthalene]

The reaction mixture is then slowly poured into a beaker containing a mixture of diethyl ether with small amount of water (<1% v/v) for the reaction to come to completion at higher yields (60+ %) than reported (< 50%)⁸. The solution was dried over anhydrous magnesium sulphate. The solids were vacuum filtered and the magnesium sulphate was washed copiously with ether until the filtrate ran colourless to optimize yields. The filtrate was evaporated slowly in air to afford IV-2 as a yellow crystalline product. No further purification was necessary.

### 4.2.1.2 National Cancer Institute (NCI) Cancer Clinic Studies of F₆NQ

The cell lines within the NCI-60 panel of human tumor cell lines are perhaps some of the most extensively characterized cell lines in broad laboratory use. Structures are generally selected for screening based on their ability to add diversity to the NCI small molecule compound collection and NCI particularly encourages submission of novel heterocyclic ring systems, thus the target molecule (IV-1) was of interest. Initial
tests use a single high dose ($10^{-5}$ M), which tested the full NCI-60 cell panel. Only compounds which satisfied pre-determined threshold inhibition criteria by NCI progress to the five-dose screen. The criteria for progression to the five-dose screen are designed to efficiently capture compounds with anti-proliferative activity and are based on careful analysis of historical DTP screening data. If the molecule is deemed to have sufficient anti-proliferative activity after a second five-dose screening, no further in vitro testing will occur and in vivo testing begins. NCI will request additional samples at any point in time to continue experimental assays. The data are reported as a mean graph of the percent growth of treated cells and will be similar in appearance to mean graphs from the five-dose assay. The product, IV-2, was sent to NCI for clinical cancer studies using a large variety of known cancer cells. All samples were deemed pure by elemental analysis to minimize false-positive results. Table 4.1 illustrates that there was indeed some inhibition of cellular growth in certain tumoral cells. However, the “mean-growth vs. growth percent” requirements set for the NCI-60 one dose screening of IV-2 were not met and further experiments were discontinued.
Table 4.1 Results of NCI-60 one dose application of F4NQ

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4.2.2.1 2,3-Diazido-5,6,7,8-tetrafluoronaphthalene-1,4-dione

(F$_4$(N$_3$)$_2$NQ)
2,3-Diazido-naphthoquinone, IV-3a, was not the intended product of the reaction as seen in Figure 4.4. However, this led to an excellent route to provide the fluorinated-thiadiazole naphthoquinone, IV-1. The equimolar reaction of IV-2 with sodium azide (NaN$_3$) was expected to yield IV-3b, however the products isolated and were found to be a mixture of starting material (IV-2) and IV-3a. The aminated product, IV-3c could also have been generated in situ due to the acidic environment provided by the acetic acid, as seen in other reported reactions under similar conditions$^{10,11}$ but this was not observed either. The starting material, IV-2 was placed in a beaker with acetic acid and water (~50 % v/v) and a solution of equimolar sodium azide in water was added slowly. After warming the solution for 1 hour, the product was filtered and washed with copious amounts of water.

**Figure 4.3 The reaction and potential products of sodium azide and IV-2**

Although the product was isolated, any diazido- product should not be isolated in purity and dried, due to other similar products being potentially explosive.$^{12}$ Although this product did not provide evidence to be potentially explosive, all glass frits, metal spatulas and light should be avoided. After multiple attempts at purification (three recrystallizations and two column chromatography) the product was not deemed pure enough by elemental analysis. The azido functional groups are highly reactive and although the analysis was almost within experimental error, the product was not sent for to NCI for clinical cancer studies. Fittingly, NCI discourages sending products with
“problematic” functional groups (nitro, nitrosyl, azido, etc.) as they tend to be an issue with drug development.⁹

4.2.3.1 2,3-Diamino-5,6,7,8-tetrafluoronaphthalene-1,4-dione (F₄(NH₂)₂NQ)

Reduction of the diazidonaphthoquinone (IV-3a) can be performed by a variety of techniques, all of which include a reducing agent. The first attempt was following a reported literature method,¹³ which utilizes sodium iodide and iron trichloride as the reducing agent in acetonitrile. Although this method did yield the desired diaminated product, IV-4, the reaction was incomplete and contaminated with starting material and mono-aminated products. Another literature method¹² which utilizes only iron powder and an acidic media gave excellent yields and purity. The diazidonaphthoquinone IV-3a was dissolved in a solution of ethanol, water and acetic acid (50 : 50 : 1 respectively) in an Erlenmeyer and iron powder was added. After refluxing for 10 minutes the solution was decanted with a magnet to prevent any iron from contaminating the product. The product precipitated out using an ice bath and was purified by a plug of silica using ethyl acetate as the eluent. No further purification was necessary.

![Synthetic route to the diamino-product, IV-4](image)

**Figure 4.4 Synthetic route to the diamino-product, IV-4**
4.2.3.2 NCI Cancer Clinic Studies of $F_4(\text{NH}_2)_2\text{NQ}$

The product, IV-4, was sent to NCI for clinical cancer studies and the results are illustrated in Table 4.2.

<table>
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<th>Panel/Cell Line</th>
<th>Growth Percent</th>
<th>Mean Growth Percent - Growth Percent</th>
</tr>
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Mean: -60.11
Delta: 38.64
Range: 168.47
Table 4.2 illustrates that there was indeed some inhibition of cellular growth in certain tumoral cells and in comparison to IV-2, IV-4 performed much better and additional sample was requested for the five dose test as shown in Table 4.3.

**Table 4.3 Results of NCI-60 five dose application of \((F_4(NH_2)_2NQ)\)**

The five-dose experiment uses the exact same preparation as the one dose screening however it is over a period of five times as long and utilizes more sample. Table 4.3 illustrates that IV-4 was more effective at inhibiting certain cellular structures such as colon cancer (HT-29), lung cancer (NCI-H522) and breast cancer (MDA-MDB-468) but otherwise were relatively ineffective throughout the experiment for the other strains of cancer cells. Unfortunately, this does not meet the requirements for a second five-dose screening, which is a set requirement for further testing.
4.2.4.1 5,6,7,8-Tetrafluoronaphtho[2,3-c][1,2,5]thiadiazole-4,9-dione - F₄(TDNQ)

Ring closure from a diamino-product to form a thiadiazole ring is broadly reported throughout the literature\textsuperscript{14} as discussed in chapter 1 and the synthetic strategies are fairly straightforward with high yields. The most direct method uses thionyl chloride as both the solvent and reagent in a \textit{neat} reaction. Although this procedure provides relatively impure material, the product can be purified \textit{via} numerous routes including recrystallization, column chromatography or simply, sublimation. The synthesis of IV-1 follows the direct method of \textit{neat} thionyl chloride at reflux for one hour. Afterwards, the solution was flash distilled to leave behind an impure golden brown powder, which can be both recrystallized in denatured ethanol and sublimed on a gradient furnace (~10\textsuperscript{-2} torr) at 110 °C to provide an off-white amorphous powder. Elemental analysis provided confirmation that the desired product was formed in very high purity.

![Reaction Scheme](image)

**Figure 4.4 – The synthetic route to F₄TDNQ (IV-1)**

4.2.4.2 - NCI Cancer Clinic Studies of F₄TDNQ

The product, IV-1, was sent to NCI for clinical cancer studies the results are illustrated in Table 4.4.
Table 4.4 Results of NCI-60 one dose application of F6NQ

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</table>

As with IV-4, IV-1 passed the initial one-dose assay and additional sample was requested for the five-dose experiment. However, unlike IV-4, IV-1 passed the initial five-dose assay and a second five-dose performance test was required prior to the next levels of in vivo screening; hollow fibre assay, human xenograft and rodent tumor models.
Unfortunately, after the second five-dose assay, the molecule was deemed inappropriate for further testing. The results of the five-dose screening are illustrated in Table 4.5.

<table>
<thead>
<tr>
<th>Table 4.5 Results of NCI-60 five dose repeat application of (F4TDNQ)</th>
</tr>
</thead>
</table>

As with IV-4, F4TDNQ (IV-1) appeared to only inhibit certain strains of particular cancer cells at low enough concentrations ($<10^{-6}$ M) to continue the screening experiments. The cellular structures most inhibited were Leukemia (SR), non-small lung cell cancer (NCI-522) and renal cancer (RXR-393). The average concentration needed for inhibition of activity was $>10^{-5}$ M which is too high for human applications. This average concentration was not related to solubility, but to the activity of the compound.
Modification could potentially allow for higher activity, as explained in the future work section below.

4.2.5.1 5,6,7,8-Tetrafluoronaphtho[2,3-c][1,2,5]selenadiazole-4,9-dione - F₄(SeDNQ)

As with thiadiazoles, ring closures from a diamino-product to form a selenadiazole ring are well reported throughout the literature. The most direct method is using selenium oxychloride in a chlorinated solvent, typically methylene chloride. This procedure provides impure material, however the product can be purified via sublimation. After completion of the reaction, the solution was flash distilled to leave behind an impure shiny purple powder, which can be sublimed on a gradient furnace (~10⁻² torr) at 120 °C to provide an off-white amorphous powder. Unfortunately, elemental analysis was beyond the acceptable amount of 0.4 % and thus was not sent for cancer screening to prevent any false-positive results. It should be noted that further sublimations would allow for higher purity of the product however, the synthesized amount of material was not large enough to do so. Recently, much interest has illustrated that 1,2,5-selenadiazoles have anti-cancer properties themselves. Including this heterocycle in the 1,4-fluorinated naphthoquinone backbone may increase the inhibition in comparison to F₄TDNQ.
4.3.1 Physical Properties of F$_4$TDNQ (IV-1)

4.3.1.1 FT-IR

The FT-IR spectra of the fluorinated diazido- IV-3a, the diamino- IV-4 and the thiadiazolo-naphthoquinone IV-1 are shown in Figure 4.5. The samples for FT-IR were prepared as KBr pellets. Upon closer inspection of the spectra, we find that there are many similarities which include peaks around 1620 cm$^{-1}$ and 520 cm$^{-1}$ which are C=C and out-of-plane C-F stretches$^{19}$ which are labeled in Figure 4.6. The $\nu$(C=O) of the quinone is a distinct peak and can be used for diagnostic purposes. The (C=O) orbital is a $\pi$ antibonding orbital, thus any increase of electron density will lengthen the bond and vice versa and either shift the frequency lower or higher respectively. Both the diazido- (IV-3a) and thiadiazole (IV-1) are electron withdrawing and the reduced diamino- (IV-4) is electron donating. Figure 4.7 illustrates the corresponding shifting of the $\nu$(C=O) stretch.
4.3.1.2 NMR

The $^{19}$F isotope is 100% abundant ($I = \frac{1}{2}$) and therefore easily measured by NMR and thus is a convenient monitoring tool. All $^{19}$F NMR spectra were recorded on a Bruker Avance-400 spectrometer at ambient temperature. Spectra were used to monitor the progress of reactions and to determine organic purity of samples. Table 4.6 provides a comparison of these data. The same trend appears in the $^{19}$F NMR data as in the FT-IR data. As the electron donation/withdrawal ability of the substituted 2,3-carbons changes, so does both the location of the diagnostic doublets and the coupling constant of said peaks.
4.3.1.3 Cyclic Voltammetry

Cyclic voltammetry measurements of IV-1 (Figure 4.7) were performed in dry DCM under argon atmosphere at ambient temperature with 0.05 M nBu$_4$NPF$_6$ as supporting electrolyte and with substrate concentrations ca. 2.0 mM and a sweep rate of 100 mV/s. The ferrocene/ferrocenium (fc/fc$^+$) redox couple was used as the internal reference for $E^o$(fc/fc$^+$) = +0.48 V in CH$_2$Cl$_2$. All potentials are thus reported vs. SCE. The ferrocene was sublimed before use.

The main objective of synthesizing the fluorinated thiadiazole naphthoquinone was twofold. First, it would allow for a smaller reduction potential to the radical anion

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<td>IV-4</td>
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<td>IV-1</td>
<td>-137.049, ($J = 7.2$ Hz)</td>
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</tbody>
</table>
due to the electronegative substituents. Second, the reduced species would potentially be more soluble. This would also bypass the requirement of using the expensive decamethylcobaltocene as a reducing agent in order to produce a soluble radical anion ligand as seen in chapter 3. This would also potentially allow for simultaneous reduction and coordination of the ligand by using metal precursors (e.g. Fe(CO)$_5$, Mn$_2$(CO)$_{10}$, Ni(CO)$_4$, etc.) as seen with other quinone compounds.$^{21-23}$

\[ E_{1/2} = -1.23 \text{ V} \]

\[ E_{1/2} = -0.59 \text{ V} \]

**Figure 4.7** The cyclic voltammogram for IV-1 in CH$_2$Cl$_2$ solution vs. SCE (0.05M $^+$Bu$_4$PF$_6$)

**Figure 4.8** The oxidation states of IV-1
In the cyclic voltammogram, two reversible reductive processes are found; one at $E_{1/2} = -0.54$ V ($\Delta E_{pp} = 120$ mV) and another at $-1.24$ V ($\Delta E_{pp} = 210$ mV). The first is the reduction of the neutral species to the radical anion, and the latter is the reduction to the dianionic species as illustrated in Figure 4.8. The reversibility of both peaks suggests it is possible to synthesize and isolate each individual species. The reduction potential to the radical anion of $-0.54$ V, when compared to the literature value of TDNQ (III-1) - 0.66 V$^{24}$ suggests that the fluorine substituents are withdrawing electron density thus making it easier to reduce, as expected. However, the reduction potential is still larger than expected and unfortunately strong reducing agents (cobaltocene, decamethylcobaltocene, sodium, etc.) must still be employed.

4.3.1.4 X-ray crystallography

Growth of single crystals of the $\text{F}_4(\text{NH}_2)_2\text{NQ (IV-4)}$ and $\text{F}_4\text{TDNQ (IV-1)}$ for X-ray crystallography was attempted by sublimation and slow evaporation of CH$_3$CN, CH$_2$Cl$_2$ and ethyl acetate. Only crystals of $\text{F}_4(\text{NH}_2)_2\text{NQ}$ suitable for diffraction were obtained. Although the diffraction pattern was strong, unfortunately, the crystals were in the shape of “tear drops” and were in actuality, multiple crystals. Both attempting to solve the tear drop diffraction pattern, and cutting the multicrystals to try an isolate a single crystal failed. No single crystal X-ray structures were obtained for any material in this sequence of experiments. This is most likely due to the “greasy” fluorine substituents on the naphthalene backbone of the quinone. Multiple platelets, not suitable for diffraction, can be easily grown and are of high purity.
4.3.1.5 Electron Paramagnetic Resonance

The F$_4$TDNQ radical anion, generated by *in situ* reduction of IV-1 with (CoCp*)$_2$ in deoxygenated methylene chloride, shows a strong X-band EPR signal (Figure 4.9). The spectral simulation for the best-fit parameters yield coupling to two nitrogen atoms and two sets of two fluorine atoms. The $a_N$ values (two nitrogen atoms) are 0.378 G and the $a_F$ values (two fluorine atoms each) are 3.67 G and 0.642 G which results in a best fit value of $R = 0.94$.

![Experimental and simulated EPR spectra of the F4TDNQ radical anion in methylene chloride.](image)

The $g$-factor is 2.0045. The EPR signal appearance is remarkably different to that of the corresponding TDNQ radical III-1$^{25}$ due to the EPR active $^{19}$F substituents. Also, as expected, the coupling to the nitrogen atom is significantly smaller due to the electron
withdrawing substituents throughout the naphthalene backbone. It should be noted that this radical anion species is extremely sensitive to moisture.

### 4.4 Molecular Orbital Studies

Investigation of the molecular structure and the electrochemical properties of the F₄TDNQ radical anion and TDNQ radical anion system by computational methods may explain the necessary use of non-equivalent parameters for fitting the EPR spectrum and confirm the experimental results of the cyclic voltammogram. For comparison, the closest species synthesized is its sister analogue, TDNQ, \( \text{III-1} \), as seen in chapter three. The quantum-mechanical calculations on the electronic structures of the F₄TDNQ and TDNQ radical anion system were performed using the Gaussian 03W packages. The method and basis set, B3LYP and 6311-Gd respectively, were chosen as they are known to be compatible with our systems and provide accurate and satisfactory data. The open shell species were calculated using unrestricted methods.

Comparing the SOMO of \([\text{F₄TDNQ}^-]\) and \([\text{TDNQ}^-]\) it can be seen in Figure 4.11 that there is a wider delocalization of electron density throughout the naphthalene backbone as expected with the electronegative fluorine substituents. However, in both species, the SOMO is \( \pi^* \) and bisects the molecule through the sulfur atom. As mentioned in chapter 3, both of these systems should not be thought of as a thiazyl radical fused on a quinone, but better considered as a semiquinone radical anion with a thiadiazole fused ring.
Comparing the calculated data in Table 4.8 illustrates how large of a factor the electron withdrawing fluoro-substituents actually make. The spin densities are more spread out throughout the system and the atomic charges are also slightly smaller. The reduction of spin density on the expected coordination sites (N, O) suggests that if coordinated to a paramagnetic transition metal ion, the coupling between the radical and ligand would be less in F₄TDNQ. The smaller atomic charges on the coordinating atoms actually may inhibit coordination, however, the overall radical system is still negatively charged and thus should not affect the coordination. Overall the TDNQ radical anion is actually a better ligand, however, as seen in chapter 3 it is very insoluble and thus the fluorinated derivative, F₄TDNQ, was synthesized to alter the solubility properties.

<table>
<thead>
<tr>
<th>Mulliken Spin Densities</th>
<th>TDNQ (%)</th>
<th>F₄TDNQ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>2.7698</td>
<td>2.1681</td>
</tr>
<tr>
<td>O</td>
<td>24.3028</td>
<td>28.0068</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>S</td>
<td>-3.0605</td>
<td>-2.7681</td>
</tr>
<tr>
<td>C5</td>
<td>3.0402</td>
<td>3.0432</td>
</tr>
<tr>
<td>C8</td>
<td>-1.1033</td>
<td>-2.2165</td>
</tr>
<tr>
<td>C9</td>
<td>4.9739</td>
<td>5.9732</td>
</tr>
</tbody>
</table>

Mulliken Atomic Charges

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>-0.552442</td>
<td>-0.553486</td>
</tr>
<tr>
<td>O</td>
<td>-0.576470</td>
<td>-0.450721</td>
</tr>
<tr>
<td>S</td>
<td>0.457941</td>
<td>0.504784</td>
</tr>
</tbody>
</table>

4.5 Summary

The initial goal of this chapter was to generate a more soluble, neutral radical as seen in chapter 2, \textit{(e.g. a fluorinated DTANQ (II-1))}, in which IV-3c would be used to generate the corresponding 1,2,3-DTA ring. It was found that primary amines \((NR_2, R = H)\), do not exist in the 1 position when the naphthalene backbone was fluorinated as the free-base is extremely sensitive to atmospheric air and moisture. Only primary amines where \(R = \text{Me, } \text{tBu and other protecting groups were found to be stable}^{30}\). These reported protected amines were synthesized but found not to undergo the Herz reaction to generate the desired DTA ring. However, the discovery of the diazido, IV-3a, led to an interesting, although outside the projection of this thesis research.

After synthesizing and characterizing the diazido product, the obvious reaction was to pursue development of a 1,2,5-TDA ring system, a fluorinated TDNQ, as seen in chapter 3. As with the DTA ring, the final product, IV-1 would be more soluble for coordination attempts. The fluoro-groups would also allow for less harsh reductions to
the radical anion. As predicted, the fluorinated TDNQ was indeed more soluble and easier to reduce. However, the reduction potential was still large enough that Co(Cp\(^*\))\(_2\) was needed in order to generate a soluble radical anion for coordination attempts. The problems associated with the radical anion were that it was extremely sensitive to any moisture/air and thus decomposed rapidly, even in the glove box if the ppm of O\(_2\) and H\(_2\)O increased suddenly and the product, as per its precursors, would not crystallize. It should be noted that although crystallization of all the steps in the synthesis failed, the products were pure by elemental analysis.

Throughout the literature of the fluorinated 1,4-naphthoquinone, many of the published reports are found in medicinal journals for clinical testing of cancer cells. After corresponding with NCI, it was found that two of the three synthetic products which have anti-cancer properties. IV-1, the new synthetic goal, had the highest inhibition properties, proceeding to the third and final stage of \textit{in vitro} screening, however, ultimately, it did not meet the expectations set by NCI to proceed to the \textit{in vivo} studies.

The work described here for the fluorinated thiadiazole naphthoquinone radical anion, IV-1\(-\cdot\), suggests that although the fluorine substituents did allow for a lower reduction potential, it was not enough and a soluble radical anion via this route may not be ideal at all, due to the crystallization issues. However, the clinical work of IV-2, IV-4 and IV-1 suggested that these fluorinated heterocyclic naphthoquinones might have interesting anti-cancer properties, which could be further pursued.
4.6 Future Work

The potential future work of this chapter is twofold: a) the continuation of the development of radical anions and attempt coordination to paramagnetic transition metals and b) the synthetic challenge and clinical studies by developing different fluorinated backbones to optimize the conditions needed for cancer inhibition. Regardless of which is to be followed the largest issue in the synthetic scheme of generating IV-1 was synthesizing the starting material, octafluoronaphthalene. As seen in chapter 2, recent developments in this thesis allows substitution throughout the naphthalene backbone, in relatively high yields by utilizing a Diels-Alder type reaction with substituted 1,1’-thiophene dioxides. This allows for a diverse selection of substitution throughout the naphthalene backbone.

![Chemical structure](image1)

**Figure 4.11 General scheme for developing substituted 1,4-naphthoquinones**

For further pursuing the radical anion project, synthesis of electron withdrawing functionalities on the backbone appeared to yield the desired results, except that crystallization was extremely challenging. Removing the electron withdrawing halogen, which is also electron donating by resonance, and inserting solely electron withdrawing groups in either the 5,8- or the 6,7-positions, such as trifluoromethyl, should allow for both the lower reduction potential and still allow for crystallization (IV-6). Another pursuit of the preferred properties may be by having an anthracene backbone (IV-7) with
highly withdrawing groups on one side, such as fluoro- or trifluoromethyl, and the thiadiazole on the other side.

In these derivatives, more electron density would be delocalized throughout the system, the reduction potential to the radical anion would be lowered but the ‘bare anthracene backbone’ may lead to contacts in the solid state and thus crystallize. By using a modified procedure as in Figure 4.10, these systems could be easily produced: two different substituted 1,1’-thiophene dioxides would be used with parabenzoquinone and the anthracene analogues could be synthesized.

For further pursuing novel compounds for anti-cancer screening, all the compounds mentioned above would be suitable as they are all unreported however, there is a lot of literature work on fluorinated para-naphthoquinone compounds but there is considerably less for fluorinated ortho-naphthoquinones. Hexafluoro-1,2-naphthoquinone is a known material,\textsuperscript{31} however no clinical screening has been performed.
Figure 4.13 Possible future work for the generation of compounds with interesting anti-cancer properties

Synthesis of the corresponding thiadiazole, including products from all the synthetic stages, diazido and diamino, would be unreported materials with unknown anti-cancer properties. One other synthetic material that could be made would be similar to IV-1 as shown in Figure 4.14 and potentially have increased cancer inhibiting properties. This compound could be made via the same route as previously shown for the synthesis of [TDNQ]$_2$.\textsuperscript{32} It should be noted that all products mentioned in this section could also be sent for anti-bacterial screening as well.\textsuperscript{33-35}

Figure 4.14 Possible future work for the generation of compound with interesting anti-cancer properties
4.7 Experimental

4.7.1 General

All operations were carried out using Schlenk techniques under argon atmosphere unless otherwise stated. Cobaltocene and decamethylcobaltocene were purchased from Sigma-Aldrich and used as received. Dichloromethane and acetonitrile were obtained from a solvent purification system (SPS from LC Tech) through dried molecular sieves. IR spectra were measured on a Nicolet 4700FT-IR. The EPR spectra were measured with a Brüker EMX Spectrometer in dichloromethane. Elemental analyses were performed by MHW Laboratories (Phoenix, AZ).

4.7.2 Synthesis of 2,3-diazido-5,6,7,8-tetrafluoronaphthalene-1,4-dione (F₄(N₃)₂NQ), IV-3a

Hexafluoro-1,4-naphthoquinone⁸ (0.8163 g, 31 mmol) was added to a 25 mL round bottom flask and acetic acid (8 mL) as added. Sodium azide (0.4987 g, 77 mmol) in 5 mL of water was slowly added to the solution and warmed to ~ 40 °C. After two hours, the transparent yellow solution turned orange. The solution was cooled to room temperature and filtered, and the precipitated was washed with copious amounts of water to be used directly in the next step. Isolation of dried material is potentially dangerous and was only performed for spectroscopic reasons. IR(KBr) ν/cm⁻¹: 2326.4(w), 2248.6(w), 2139.2(s), 2111.2(s), 1660.1(s), 1615.4(m), 1581.3(m), 1514.6(m), 1480.4(m), 1407.1(m), 1347.6(s), 1316.4(s), 1201.7(m), 1124.4(m), 969.1(s), 844.3(w), 788.0(m), 762.1(w), 745.1(m), 622.0(w), 521.9(w), 474.7(w). ¹⁹F NMR (400 MHz, CDCl₃, 25 °C, ppm) δ: -138.349 (d, 1F), -145.400 (d, 1F).
4.7.3 Synthesis of 2,3-diamino-5,6,7,8-tetrafluoronaphthalene-1,4-dione

F$_4$(NH$_2$)$_2$NQ), IV-4

Wet 2,3-diazido-5,6,7,8-tetrafluoronaphthalene-1,4-dione was added to a 50 mL Erlenmeyer flask with a 2 : 2 : 1, water: ethanol, acetic acid solution. Iron powder (1.5 g) was added and the solution was refluxed for 30 minutes. The orange solution quickly turned purple and was decanted hot into a beaker and cooled to 0 °C. Purple crystals were generated and recovered by filtration and air dried. 76 % yield. IR(KBr) ν/cm$^{-1}$: 3449.0(s), 3356.1(s), 2116.1(s), 1835.3(m), 1788.0(w), 1635.3(s), 1604.8(s), 1570.7(s), 1503.4(m), 1476.8(m), 1410.6(s), 1314.9(m), 1289.4(w), 1259.1(w), 1180.5(m), 1063.4(w), 1012.0(m), 973.2(m), 777.3(m), 746.5(m). Elemental Anal. Calc for C$_{10}$H$_4$F$_4$N$_2$O$_2$; C 46.17, H 1.55, N 10.77; found C 46.33, H 1.75, N 10.63 %.

19F NMR (400 MHz, CDCl$_3$, 25 °C, ppm) δ: -141.410 (m, 1F), -149.241 (m, 1F).

4.7.4 Synthesis of 4 (F$_4$TDNQ), IV-1

Excess thionyl chloride (15 mL) was added to 0.6126 g (24 mmol) of 2,3-diamino-5,6,7,8-tetrafluoronaphthalene-1,4-dione and refluxed for one hour. The golden brown solution was evaporated in vacuo and the brown solid sublimed on a gradient furnace (40 °C, 10$^{-2}$ torr) to obtain an off-white amorphous powder. 0.3807 g 55 % yield. Elemental Anal. Calc for C$_{10}$F$_4$N$_2$O$_2$S; C 41.68, H 0, N 9.72 %; found C 41.58, H 0, N 9.71 %. IR(KBr) ν/cm$^{-1}$: 1697.4(s), 1617.7(s), 1507.3(m), 1479.4(m), 1424.4(w), 1377.0(m), 1312.5(w), 1290.0(w), 1205.3(m), 1164.0(m), 1093.0(m), 969.9(s), 803.4(m), 755.8(m), 687.0(w), 523.1(m). 19F NMR (400 MHz, CDCl$_3$, 25 °C, ppm) δ: -137.049 (m, 1F), -149.241 (m, 1F).
4.7.5 Synthesis of 5,6,7,8-tetrafluoronaphtho[2,3-c][1,2,5]selenadiazole-4,9-dione (F<sub>4</sub>SeDNQ)

Selenium oxychloride (2.43 mL, 35 mmol) was added to 0.4528 g (17 mmol) of 2,3-diamino-5,6,7,8-tetrafluoronaphthalene-1,4-dione and refluxed for one hour. The golden brown solution was evaporated in vacuo and the purple shiny solid sublimed on a three stage gradient furnace (80 °C, 10<sup>-2</sup> torr) to obtain an off-white amorphous powder. 57 % yield. **Elemental Anal.** Calc for C<sub>10</sub>F<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Se; C 35.85, H 0, N 8.36 %; found C 34.64, 0.18, 8.15 %. **IR(KBr) v/cm<sup>-1</sup>:** 1697.4(s), 1617.7(s), 1507.3(m), 1479.4(m), 1424.4(w), 1377.0(m), 1312.5(w), 1290.0(w), 1205.3(m), 1164.0(m), 1093.0(m), 969.9(s), 803.4(m), 755.8(m), 687.0(w), 523.1(m). **<sup>19</sup>F NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C, ppm) δ: -140.012 (d, 1F), -145.086 (d, 1F)
4.8 References for Chapter 4


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Jaramillo; R. Gomperts; R. E. Stratmann; O. Yazyev; A. J. Austin; R. Cammi; C. Pomelli; J. W. Ochterski; R. L. Martin; K. Morokuma; V. G. Zakrzewski; G. A. Voth; P. Salvador; J. J. Dannenberg; S. Dapprich; A. D. Daniels; O. Farkas; J. B. Foresman; J. V. Ortiz; J. Cioslowski; Fox, D. J.; Gaussian Inc.: Wallingford, CT, 2009.

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5.1 Summary

This thesis describes a pioneer study leading to the successful syntheses and full characterization of three new 1,2,5-thiadiazolyl radical anion ligands (TDNQ, SDNQ and bis-BTDABQ), two new 1,2,3-dithiazolyl radical ligands (DTANQ and 5,8-Me₂DTANQ), and a series of new poly-fluorinated naphthoquinones. While the 1,2,5-TDA radical ligands were not suitable for coordination chemistry, they had interesting magnetic and conductive properties. Collaboration with Dr. Rodolphe Clérac and Dr. Alessandro Vindgini led to a publication in the high impact, Journal of Crystal Growth and Design (ACS).

This thesis also describes the first metal complexes that contain a coordinated 1,2,3-DTA radical (DTANQ). Coordination complexes of two transition metal ions (Mn²⁺ and Ni²⁺) and one lanthanide ion (Gd³⁺) were synthesized and characterized by X-ray crystallography. These coordination complexes demonstrated that a variety of metal complexes can be achieved using DTANQ. Thus far, momomeric, trimeric and polymeric complexes of DTANQ have been obtained. Although the complexes of DTANQ could not be produced in significant quantities for magnetometry experiments, they demonstrated proof of concept. The modified derivatives of DTANQ have produced metal complexes in quantities appropriate for magnetic measurements, as demonstrated by our group. Also, the ligand, DTANQ, is interesting on its own right. DTANQ generates two different crystal phases, one of which (α-phase, green block habit) demonstrates interesting singlet-triplet solid-state properties. Collaboration with Dr. Stephen Hill at Florida State University is currently ongoing to investigate this phenomenon.
Modification of DTANQ to the 5,8-Me₂DTANQ analogue was performed. The syntheses and full characterization is described. As with DTANQ, 5,8-Me₂DTANQ has two crystal distinct crystal phases. It was found that the extra methyl groups allowed for improved solubility and σ-donation properties that DTANQ lacked and led to two new coordination complexes with transition metal ions (Mn²⁺ and Co²⁺). Both the Mn and Co complexes of 5,8-Me₂DTANQ have been fully characterized and both species are currently being investigated by magnetometry to unveil their magnetic properties.

Lastly, a series of novel poly-fluorinated naphthoquinone materials is described. The intention was to lower the reduction potential of TDNQ by modification with electron withdrawing substituents. This, in theory, would generate a more soluble, less reducing species which would potentially allow for successful metal coordinations. The radical anion appeared to be unstable. The project took an interesting turn and after an in-depth investigation of the current literature of fluorinated naphthoquinones, clinical cancer testing was performed on the final product, F₄TDNQ, and all the precursors through collaboration with the National Cancer Institute (USA). The screening proved successful, as many of the compounds demonstrated cancer inhibition of a variety of cancer strains.
Appendix A

Compound Data Sheets
**Compound Name:**

(3:2 TDNQ \( \cdot \) Co(Cp)_2\(^+\))

**MW:** 1026.02 g/mol

**Appearance:**

Black Crystals

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

IM03-13

**First made on date:**

05Dec12

**Made by:**

Ian Morgan

**Experimental Data:**

**IR(KBr) \( \nu / \text{cm}^{-1} \):** 3083.6(m), 1685.9(w), 1617.9(m), 1548.6(m), 1490.9(s), 1411.3(s), 1366.5(m), 1350.5(w), 1287.6(s), 1169.8(m), 1097.1(m), 1028.7(w), 1005.7(w), 973.5(m), 923.8(w), 884.8(w), 837.0(s), 827.8(s), 793.5(w), 723.0(m), 697.7(m), 639.9(w), 519.1(m), 467.1(s), 431.6(m) cm\(^{-1}\).

**Elemental Anal.** Calc for C\(_{50}\)H\(_{32}\)Co\(_2\)N\(_6\)O\(_6\)S\(_3\): C 58.48, H 3.14, N 8.19; found C 58.45, H 3.42, N 7.92%.

**Crystal data** collected on Bruker APEX-II CCD radiation source MoK\(\alpha\), wavelength = 0.71073 Å at McMaster University, T = 150(2) K, orthorhombic space group \(Pbca\), \(a = 17.0537(17), b = 6.4960(6), c = 25.224(3)\) Å, \(V = 2794.3(5)\) Å\(^3\), \(Z = 8\), \(D_{\text{calc}} = 1.822\) g cm\(^{-1}\), 208 parameters were refined using 1854 unique reflections to give \(R = 0.0341\) and \(R_w = 0.0694\).
IR: KBr pressed pellet
Compound Name:

(2:1 SDNQ\[\text{−}] \text{Co(Cp)}_2\[\text{+}])

MW: 845.53 g/mol

Appearance:

Gold Crystals

Lit. and/or notebook # and page:

IM03-48

First made on date:

28Feb09

Made by:

Ian Morgan

Experimental Data:

IR(KBr) ν/cm\(^{-1}\): 1685.6(m), 1617.7(w), 1570.4(m), 1483.4(m), 1439.6(m), 1412.9(m), 1379.8(w), 1287.5(s), 1231.2(w), 1172.5(m), 1101.3(s), 1009.3(s), 964.3(m), 936.6(m), 869.7(w), 817.3(w), 749.3(w), 462.6(w), 445.9(s)

Elemental Anal. Calc for (C10H4N2O2Se)\(_2\) (CoC10H10): C 50.23, H 2.81, N 7.81; found C 50.12, H 2.59, N 7.73%.

Crystal data collected on Bruker APEX-II CCD radiation source MoK\(\alpha\), wavelength = 0.71073 Å at McMaster University, T = 150(2) K, orthorhombic space group \(\text{Pbc}a\), \(a = 17.0537(17)\), \(b = 6.4960(6)\), \(c = 25.2243(3)\) Å, \(V = 2794.3(5)\) Å\(^3\), \(Z = 8\), \(D_\text{calc} = 1.822\) g cm\(^{-1}\), 208 parameters were refined using 1854 unique reflections to give R = 0.0341 and \(R_w = 0.0694\).
IR: KBr pressed pellet
Compound Name:
(TDNQ⁻ · Co(Cp*)₂⁺)

MW: 545.17 g/mol

Appearance:
Black Crystals

Lit. and/or notebook # and page:
IM04-12

First made on date:
07Nov08

Made by:
Ian Morgan

Experimental Data:

IR(KBr) ν/cm⁻¹: 2962.2 (m), 2917.2 (m), 1685.6 (w), 1510.1 (w), 1491.3 (s), 1448.0 (w), 1425.4 (w), 1375.7 (m), 1325.2 (s), 1263.1 (s), 1091.5 (m), 1025.5 (m), 967.0 (w), 919.6 (w), 824.6 (m), 777.3 (m), 719.4 (w), 695.5 (m), 515.4 (m), 443.6 (w)

Elemental Anal. Calc for C₃₀H₃₄CoN₂O₂S: C 66.03, H 6.29, N 5.14; found C 65.66, H 6.25, N 5.15%.

Calc for C₃₀H₃₄CoN₂O₂S(CH₂Cl₂)₀.5: C 62.29, H 6.00, N 4.76; found C 62.20, H 6.08, N 4.76%.

Crystal data collected on Bruker APEX-II CCD radiation source MoKα, wavelength = 0.71073 Å at McMaster University, T = 150(2) K, orthorhombic space group Pbcα, a = 17.0537(17), b = 6.4960(6), c = 25.224(3) Å, V = 2794.3(5) Å³, Z = 8, D calc = 1.822 g cm⁻³, 208 parameters were refined using 1854 unique reflections to give R = 0.0341 and R_w = 0.0694.
IR: KBr pressed pellet
Compound Name:

(BisTDABQ$^-$ Co(Cp)$_2$)$^+$

**MW:** 413.34 g/mol

**Appearance:** Black Blue Crystals

**Lit. and/or notebook # and page:** IM03-40

**First made on date:** 19Feb12

**Made by:** Ian Morgan

**Experimental Data:**

**IR(KBr)** v/cm$^{-1}$: 1566.3(s), 1452.6(s), 1397.6(s), 1326.9(w), 1263.3(s), 1104.5(w), 1080.7(w), 1049.8(w), 1019.6(w), 1003.7(w), 878.2(m), 828.1(m), 786.7(w), 755.3(w), 532.0(w), 502.1(m), 463.2(m)

**Crystal data** collected on Bruker APEX-II CCD radiation source MoK$\alpha$, wavelength = 0.71073 Å at McMaster University, T = 150(2) K, orthorhombic space group $Pbca$, $a = 17.0537(17)$, $b = 6.4960(6)$, $c = 25.224(3)$ Å, $V = 2794.3(5)$ Å$^3$, $Z = 8$, $D_{calc} = 1.822$ g cm$^{-1}$, 208 parameters were refined using 1854 unique reflections to give $R = 0.0341$ and $R_w = 0.0694$. 
IR: KBr pressed pellet
Compound Name:

(F4TDNQ\(^-\) Co(Cp\(^*\))\(_2\)\(^+\))

MW: 617.56 g/mol

Appearance:
Black Powder

Lit. and/or notebook # and page:
IM06-45

First made on date:
22Jul11

Made by:
Ian Morgan

Experimental Data:

\[ \text{IR(KBr)} \text{ v/cm}^{-1}: 2976.6(\text{m}), 2921.9(\text{m}), 2851.6(\text{w}) 1685.5(\text{m}), 1577.4(\text{s}), 1477.4(\text{m}), 1369.0(\text{s}), 1312.2(\text{w}), 1280.3(\text{m}), 1219.9(\text{w}), 1146.8(\text{w}), 1101.6(\text{w}), 1027.1(\text{w}), 968.4(\text{w}), 803.2(\text{m}), 749.1(\text{w}), 680.7(\text{w}), 521.9(\text{m}) \]
IR: KBr pressed pellet
**Compound Name:** 2,3-Diazido-5,6,7,8-tetrafluoronaphthalene -1,4-dione  
(F4(N3)2NQ)

**MW:** 240.04 g/mol

**Appearance:** Orange Powder

**Lit. and/or notebook # and page:** IM05-68

**First made on date:** 07Mar11

**Made by:** Ian Morgan

**Experimental Data:**

**IR(KBr) v/cm⁻¹:** 2326.4(w), 2248.6(w), 2139.2(s), 2111.2(s), 1660.1(s), 1615.4(m), 1581.3(m), 1514.6(m), 1480.4(m), 1407.1(m), 1347.6(s), 1316.4(s), 1201.7(m), 1124.4(m), 969.1(s), 844.3(w), 788.0(m), 762.1(w), 745.1(m), 622.0(w), 521.9(w), 474.7(w)

**¹⁹F ÅR (400 MHz, CDCl₃, 25 °C, ppm) δ:** -138.349 (m, 1F), -145.400 (m, 1F)

**WARNING – DO NOT ISOLATE DRY – POTENTIALLY EXPLOSIVE**

IR: KBr pressed pellet
**Compound Name:** 2,3-Diamino-5,6,7,8-tetrafluoronaphthalene-1,4-dione

(F4(NH2)2NQ)

**MW:** 240.04 g/mol

**Appearance:**
Purple Crystals

**Lit. and/or notebook # and page:**
IM05-74

**First made on date:**
14Mar11

**Made by:**
Ian Morgan

**Experimental Data:**

**IR(KBr) \( \nu / \text{cm}^{-1} \):** 3449.0(s), 3356.1(s), 2116.1(s), 1835.3(m), 1788.0(w), 1788.0(w), 1635.3(s), 1604.8(s), 1570.7(s), 1503.4(m), 1476.8(m), 1410.6(s), 1314.9(m), 1289.4(w), 1259.1(w), 1180.5(m), 1063.4(w), 1012.0(m), 973.2(m), 777.3(m), 746.5(m)

**Elemental Anal.** Calc for C_{10}H_{4}F_{4}N_{2}O_{2}; C 46.17, H 1.55, N 10.77; found C 46.33, H 1.75, N 10.63%.

**\(^{19}F \text{ ÅR} (400 \text{ MHz, CDCl}_3, 25 \degree \text{C, ppm}) \delta: \)** -141.410 (m, 1F), -149.241 (m, 1F)
IR: KBr pressed pellet
ÅR: $^{19}$F, CDCl$_3$, 400MHz, 32 Scans

IM07- Diamine-F4NQ std w/ Hexafluorobenzene
**Compound Name:** 5,6,7,8-Tetrafluoronaphtho[2,3-c][1,2,5]thiadiazole-4,9-dione (F4TDNQ)

**MW:** 288.18 g/mol

**Appearance:**
Off White Powder

**Lit. and/or notebook # and page:**
IM05-77

**First made on date:**
22Mar11

**Made by:**
Ian Morgan

**Experimental Data:**

**IR(KBr) v/cm⁻¹:** 1697.4(s), 1617.7(s), 1507.3(m), 1479.4(m), 1424.4(w), 1377.0(m), 1312.5(w), 1290.0(w), 1205.3(m), 1164.0(m), 1093.0(m), 969.9(s), 803.4(m), 755.8(m), 687.0(w), 523.1(m)

**Elemental Anal.** Calc for C₁₀F₄N₂O₂S ; C 41.68, H 0, N 9.72%; found C 41.58, H 0, N 9.71%.

**¹⁹F ÁR** (400 MHz, CDCl₃, 25 °C, ppm) δ: -137.049 (m, 1F), -143.589 (m, 1F)
**IR:** KBr pressed pellet
ÅR: $^{19}\text{F}$, CDCl$_3$, 400MHz, 32 Scans
Compound Name: 5,6,7,8-Tetrafluoronaphtho[2,3-c][1,2,5]selenadiazole-4,9-dione (F4SDNQ)

MW: 335.07 g/mol

Appearance:
Off White Powder

Lit. and/or notebook # and page:
IM06-80

First made on date:
08Nov11

Made by:
Ian Morgan

Experimental Data:

IR(KBr) ν/cm⁻¹: 1697.4(s), 1617.7(s), 1507.3(m), 1479.4(m), 1424.4(w), 1377.0(m), 1312.5(w), 1290.0(w), 1205.3(m), 1164.0(m), 1093.0(m), 969.9(s), 803.4(m), 755.8(m), 687.0(w), 523.1(m)

¹⁹F ÅR (400 MHz, CDCl₃, 25 °C, ppm) δ: -140.012 (m, 1F), -145.086 (m, 1F)
IR: KBr pressed pellet
ÅR: $^{19}$F, CDCl$_3$, 400MHz, 32 Scans
**Compound Name:** 4,9-Dioxo-naphtho[2,3-\(d\)][1,2,3]dithiazol-2-ium chloride (pDTANQ\(^+\)Cl\(^-\))

**MW:** 269.73 g/mol

**Appearance:** Orange Powder

**Lit. and/or notebook # and page:** SV01-11

**First made on date:** 09Jul12

**Made by:** Ian Morgan & Scott van Doormal

**Experimental Data:**

**IR(KBr) v/cm\(^{-1}\):** 1699 (s), 1668 (s), 1580 (m), 1418 (w), 1318 (w), 1292 (s), 1260 (s), 1144 (w), 1052 (w), 1024 (w), 977 (w), 907 (s), 874 (m), 824 (m), 789 (m), 701 (s), 686 (m), 660 (w), 621 (w), 561 (w), 538 (w), 517 (w), 470 (w), 443 (w), 419 (w).
**IR**: KBr pressed pellet
**Compound Name:** Naphtho[2,3-\(d\)][1,2,3]dithiazolyl-4,9-dione (pDTANQ)

**MW:** 234.27 g/mol

**Appearance:**
Green and Red Crystals

**Lit. and/or notebook # and page:**
SV01-12

**First made on date:**
25Jul08

**Made by:**
Ian Morgan & Scott van Doormal

**Experimental Data:**

**IR(KBr) \(\text{v/cm}^{-1}\):** 1671 (s), 1590 (m), 1575 (m), 1543 (s), 1475 (w), 1416 (m), 1361 (m), 1322 (m), 1305 (m), 1252 (s), 1215 (s), 1161 (m), 1043 (w), 1017 (w), 995 (w), 895 (w), 861 (w), 801 (m), 774 (s), 728 (w), 708 (m), 683 (w), 669 (w), 658 (w), 557 (w), 523 (w), 484 (w).

**Elemental Anal.** Calc for C_{10}H_{4}NO_{2}S_{2}: C, 51.27; H, 1.72; N, 5.98. Found C, 51.21; H, 1.96; N, 6.01%.

**Crystal data** of the green block was collected on a Nonius CCD radiation source MoK\(\alpha\), wavelength = 0.71073 Å at University of Western Ontario, T = 150(2) K, monoclinic space group \(P2_1/c\), \(a = 11.569(2)\), \(b = 8.8345(18)\), \(c = 8.7975(18)\)Å, \(\beta = 103.61(3)^\circ\), \(V = 873.912 \text{ Å}^3\), \(Z = 4\), \(D_{\text{calc}} = 1.07 \text{ g cm}^{-1}\), \(R = 0.0386\). **Crystal data** of the red needles were collected on a Bruker APEX-II CCD radiation source MoK\(\alpha\), wavelength = 0.71073 Å at McMaster University, 100(2) K, orthorhombic space group \(Pna2_1\), \(a = 30.37(2)\), \(b = 7.997(6)\), \(c = 3.531(3)\) Å, \(V = 857.6(11) \text{ Å}^3\), \(Z = 4\), \(D_{\text{calc}} = 1.814 \text{ g cm}^{-1}\), 137 parameters were refined using 997 unique reflections to give \(R = 0.0699\), \(wR2 = 0.1254\).
IR: KBr pressed pellet
Phases (green & red) PXRD

Calculated powder pattern (green phase)

Calculated powder pattern (red phase)

Actual powder pattern of mixed phases
**Compound Name:** [Mn(hfac)$_2$]$_3$(DTANQ)$_2$

**MW:** 1144.64 g/mol

**Appearance:**
Blue amorphous powder
Sublimed:
brown blocks

**Lit. and/or notebook # and page:**
CH01-24

**First made on date:**
10Jun10

**Made by:**
Ian Morgan & Colin Hesp

**Experimental Data:**

**IR(KBr) v/cm$^{-1}$:** 1647.5(s), 1602.0(w), 1560.2(m), 1541.2(w), 1482.9(w), 1465.8, 1449.7(w), 1382.5(m), 1368.2(m) 1341.4(w), 1259.7(s), 1203.8 (s), 1184.2(s) 1095.6(m), 803.5(w), 781.0(w), 665.4(w), 585.5(w).

**Crystal data** of the brown block was collected on a Nonius CCD radiation source MoK$\alpha$, wavelength = 0.71073 Å at University of Western Ontario, T = 150(2) K, triclinic space group P-1, $a = 11.1494(15)$, $b = 12.9941(16)$, $c = 13.6531(18)$Å, $a = 116.267(2)$, $\beta = 109.368(2)$, $g = 90.408(2)$ $^{\circ}$ $V = 1645.47$ Å$^3$, $Z = 1$, $D_{\text{calc}} = 1.15$ g cm$^{-3}$, R = 0.0462.
IR: KBr pressed pellet
**Compound Name:** Ni(hfac)$_2$(DTANQ)

**MW:** 707.07 g/mol

**Appearance:**
Blue/Green amorphous powder
Sublimed golden crystals

**Lit. and/or notebook # and page:**
IM02-50

**First made on date:**
05Aug08

**Made by:**
Ian Morgan

**Experimental Data:**

**IR(KBr) v/cm$^{-1}$:** 1644.9(s), 1558.2(w), 1532.3(w), 1484.0(m), 1257.9(s), 1206.2(s), 1184.9(s), 799.4(w), 715.4(w), 675.0(m), 588.9(w)

**Crystal data** of the golden needle was collected on a Nonius CCD radiation source MoKα, wavelength = 0.71073 Å at University of Western Ontario, T = 150(2) K, triclinic space group $P-1$, $a = 7.2162(14)$, $b = 12.947(3)$, $c = 13.162(3)$Å, $α = 88.96(3)$, $β = 81.96(3)$, $γ = 84.30(3)$° $V = 1211.58$ Å$^3$, $Z = 2$, $D_{calc} = 1.94$ g cm$^{-1}$, $R = 0.0547$. 
IR: KBr pressed pellet
**Compound Name:** [Gd(hfac)₃(DTANQ)]ₓ

**MW:** 1012.68 g/mol

**Appearance:** Orange crystals

**Lit. and/or notebook # and page:** IM05-17

**First made on date:** 13Oct10

**Made by:** Ian Morgan

**Experimental Data:**

**IR(KBr)** ν/cm⁻¹: 1649.7(s), 1611.1(w), 1560.7(m), 1535.0(m), 1498.8(m), 1257.8(s), 1209.7(s), 1145.6(s), 1100.8(m), 1046.3(m), 1021.4(w), 867.2(w), 804.6(s), 741.5(w), 708.0(w), 660.4(m), 586.3(m), 528.1(w), 468.9(w)

**Crystal data** of the red needles were collected on a Bruker APEX-II CCD radiation source MoKα, wavelength = 0.71073 Å at McMaster University, 100(2) K, monoclinic space group P₂₁/c a = 20.0514(17), b = 16.2128(14), c = 21.0854(18) Å, β = 108.981(2)° V = 6481.93 Å³, Z = 8, D calc = 2.07 g cm⁻³, R = 0.0650
IR: KBr pressed pellet
Compound Name: 5,8-Dimethylnaphthalene-1,4-dione
(pDiMeNQ)
MW: 186.21 g/mol

Appearance:
Yellow/orange crystalline powder

Lit. and/or notebook # and page:
IM07-41

First made on date:
24Jul12

Made by:
Ian Morgan

Experimental Data:

IR(KBr) $\nu$/cm$^{-1}$: 3075.0 (w), 3017.8 (w), 2963.3 (w), 2924.2 (w), 1961.3 (w), 1657.9 (s), 1618.4 (m), 1555.2 (m), 1458.0 (w), 1438.2 (w), 1382.5 (w), 1370.9 (w), 1328.7 (m), 1260.6 (m), 1104.1 (s), 1020.1 (m), 853.4 (w), 821.0 (m), 800.7 (m), 718.0 (w), 594.5 (w), 502.7 (w), 466.2 (w), 438.2 (w).

$^1$H ÅR (300 MHz, CDCl$_3$, 25 °C, ppm) $\delta$: 7.378 (s, 1H), 6.820 (s, 1H), 2.686 (s, 3H).
IR: KBr pressed pellet
$^1$H ÅR: 300 MHz, CDCl$_3$, 25 °C:
**Compound Name:** 2-Amino-3-bromo-5,8-dimethylnaphthalene-1,4-dione

**MW:** 278.99 g/mol

**Appearance:**
Orange amorphous powder

First made on date:
17Jun12

Made by:
Ian Morgan

**Experimental Data:**

IR(KBr) v/cm\(^{-1}\): 3495.6 (m), 3382.1 (m), 2965.7 (w), 2923.9 (w), 1659.4 (m), 1639.4 (s), 1618.1 (s), 1589.0 (s), 1547.9 (m), 1455.4 (w), 1430.9 (w), 1384.6 (m), 1366.2 (m), 1328.1 (w), 1235.8 (s), 1123.0 (w), 1070.4 (m), 996.2 (w), 826.3 (w), 784.7 (w), 755.0 (w), 743.3 (w), 693.0 (w), 582.0 (w), 512.9 (w).

\(^1\text{H} \ AR\) (300 MHz, CDCl\(_3\), 25 °C, ppm) δ: 7.315 (d, 1H), 7.245 (d, 1H), 5.419 (br s, 2H), 2.676 (s, 3H), 2.631 (s, 3H).
IR: KBr pressed pellet
$^{1}H \text{ ÅR}$: 300 MHz, CDCl$_3$, 25 °C:

IM07-35 - 2-aminoo-3-bromo
 aliquot from rxn
 CDCl$_3$ 300MHz
 17Jan12
Compound Name: 2-Amino-3-thioacetate-5,8-dimethyl-1,4-naphthoquinone

MW: 275.32 g/mol

Appearance:
Brown/orange powder

Lit. and/or notebook # and page:
IM07-67

First made on date:
14Apr12

Made by:
Ian Morgan

Experimental Data:

IR(KBr) ν/cm⁻¹: 3490.0 (w), 3368.2 (s), 2967.0 (w), 2925.5 (w), 1701.7 (w), 1671.6 (w), 1607.1 (s), 1577.8 (m), 1540.3 (m), 1378.4 (m), 1328.4 (m), 1238.4 (m), 1198.4 (w), 1119.1(w), 1068.4 (w), 1036.4 (w), 992.9 (w), 949.0 (w), 824.9 (w), 797.9 (w), 763.1 (w), 699.9 (w), 616.5 (w), 593.8 (w).
IR: KBr pressed pellet
**Compound Name:** 5,8-Dimethyl-4,9-dio xo-naphtho[2,3-d][1,2,3]dithiazol-2-ium chloride

(5,8-Me₂DTANQ)

**MW:** 297.78 g/mol

**Appearance:**
Orange amorphous powder

**Lit. and/or notebook # and page:**
IM07-72

**First made on date:**
20Apr12

**Made by:**
Ian Morgan

**Experimental Data:**

IR(KBr) ν/cm⁻¹: 2963.0 (w), 2917.3 (w), 2848.9 (w), 1685.2 (m), 1654.6 (m), 1647.9 (w), 1637.6 (w), 1617.9 (w), 1609.1 (w), 1544.7 (w), 1375.7 (w), 1318.4 (m), 1263.1 (w), 1222.3 (s), 1171.1 (w), 1101.3 (m), 1031.6 (w), 950.7 (w), 921.5 (w), 859.7 (w), 811.8 (m), 800.1 (m), 744.9 (w).
IR: KBr pressed pellet
**Compound Name:** 5,8-Dimethyl-naphtho[2,3-d][1,2,3]dithiazolyl-4,9-dione

(5,8-Me₂DTANQ)

**MW:** 297.78 g/mol

**Appearance:**
Blue/Black amorphous powder

**Lit. and/or notebook # and page:**
IM07-74

**First made on date:**
21Apr12

**Made by:**
Ian Morgan

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**Experimental Data:**

**IR(KBr) v/cm⁻¹:**
- 2969.1 (m), 2925.7 (s), 2851.8 (m), 1675.1 (s), 1655.1 (sh, w), 1603.3 (s), 1577.4 (w), 1571.3 (w), 1560.3 (w), 1550.3 (m), 1419.6 (m), 1375.7 (sh, m), 1368.5 (m), 1328.1 (m), 1292.4 (w), 1262.5 (w), 1222.5 (s), 1187.4 (sh, w), 1177.6 (w), 1106.1 (m), 1033.3 (w), 1004.3 (w), 939.1 (w), 909.7 (w), 827.2 (w), 813.9 (w), 771.0 (w), 744.8 (w), 629.4 (w), 526.4 (w), 497.4 (w).  **Elemental Anal.**
- Calc: C: 54.94  H: 3.07  N: 5.34
- Found: C: 54.78  H: 3.23  N: 5.21

**Crystal data**

- The red needles were collected on site on a SuperNova Dual diffractometer with Atlas CCD system and the source MoKα, wavelength = 0.71073 Å at, T = 298(2) K, monoclinic space group P2₁/c, a = 8.0663(16), b = 7.8899(16), c = 34.794(7) Å, β = 101.20(3)° V = 2179.37 Å³, Z = 2, D_cal = 1.60 g cm⁻³, R = 0.496. **Crystal data**
- The red blocks were collected on site on a SuperNova Dual diffractometer with Atlas CCD system and the source MoKα, wavelength = 0.71073 Å at, T = 298(2) K, triclinic space group P-1, a = 16.9485(3), b = 17.0034(4), c = 23.4658(5) Å, α = 86.653(2), β = 81.895(2), γ = 78.748(2)° V = 6562.87 Å³, Z = 12, D_cal = 1.59 g cm⁻³, R = 0.0546.
IR: KBr pressed pellet
Compound Name: [Mn(hfac)$_2$]$_3$(5,8-Me$_2$DTANQ)$_2$

MW: 1466.76 g/mol

Appearance:
Blue amorphous powder
Sublimed: brown blocks

Lit. and/or notebook # and page:
RM01-11

First made on date:
16Jul12

Made by:
Ian Morgan & Alex Mayo

Experimental Data:

IR(KBr) $\nu$/cm$^{-1}$: 3142.1 (w), 2963.3 (w), 2917.3 (w), 2849.1 (w), 1647.5 (s), 1602.0 (m), 1560.2 (m), 1541.5 (m), 1482.9 (s), 1465.8 (m), 1449.7 (w), 1396.3 (w), 1382.5 (w), 1368.2 (w), 1341.4 (w), 1259.7 (s), 1203.8 (s), 1148.6 (s), 1095.6 (w), 1032.9 (w), 948.6 (w), 922.3 (w), 847.0 (w), 803.5 (s), 781.9 (sh, m), 742.3 (w), 665.4 (s), 585.5 (m), 528.4 (w).

Elemental Anal. Calc: C: 33.57 H: 1.15 N: 1.45 Found: C: 33.41 H: 1.20 N: 1.43%.

Crystal data of the brown block was collected on site on a SuperNova Dual diffractometer with Atlas CCD system and the source MoK$\alpha$, wavelength = 0.71073 Å at, $T = 298(2)$ K, triclinic space group $P-1$, $a = 11.5566(9)$, $b = 12.9756(9)$, $c = 13.5080(10)$Å, $a = 115.306(7)$, $\beta = 92.468(6)$, $g = 93.764(6)$ ° $V = 1821.5$ Å$^3$, $Z = 1$, $D_{\text{calc}} = 1.76$ g cm$^{-3}$, $R = 0.0589$. 
IR: KBr pressed pellet
Compound Name: [Co(hfac)$_2$]$_3$(5,8-Me$_2$DTANQ)$_2$

MW: 1474.75 g/mol

Appearance:
Blue amorphous powder
Sublimed: brown blocks

Lit. and/or notebook # and page:
RM01-24

First made on date:
10 Aug 12

Made by:
Ian Morgan & Alex Mayo

Experimental Data:

IR(KBr) $\nu$/cm$^{-1}$: 3142.1 (w), 2963.3 (w), 2917.3 (w), 2849.1 (w), 1647.5 (s), 1602.0 (m), 1560.2 (m), 1541.5 (m), 1482.9 (s), 1465.8 (m), 1449.7 (w), 1396.3 (w), 1382.5 (w), 1368.2 (w), 1341.4 (w), 1259.7 (s), 1203.8 (s), 1148.6 (s), 1095.6 (w), 1032.9 (w), 948.6 (w), 922.3 (w), 847.0 (w), 803.5 (s), 781.9 (sh, m), 742.3 (w), 665.4 (s), 585.5 (m), 528.4 (w).  


Crystal data of the brown block was collected on site on a SuperNova Dual diffractometer with Atlas CCD system and the source MoK$\alpha$, wavelength = 0.71073 Å at, T = 298(2) K, triclinic space group $P-1$, $a = 11.672(2)$, $b = 12.934(3)$, $c = 13.517(3)$Å, $a = 115.26(3)$, $\beta = 101.25(3)$, $g = 93.88(3)$ $^\circ$ $V = 1783.63$ Å$^3$, $Z = 1$, D$_{calc}$ = 1.81 g cm$^{-3}$, $R = 0.0388$. 
IR: KBr pressed pellet
Appendix B

General Information
B.1 Procedures

B.1.1 – General

Many of the reactions that were performed in this thesis were done so under an inert atmosphere of dry argon. These reactions were mostly performed with standard Schlenk (or slightly modified) glassware using a double-manifold glass vacuum line (argon/vacuum) with an Edwards E25 direct drive vacuum pump. All sensitive reagents and products were handled and stored in an argon-filled Braun lab master 150 glovebox.

B.1.2 – Crystallization Techniques

Sublimation Techniques

Approximately half of the crystals grown in this thesis were done so by sublimation. There are two distinct types that were utilized – dynamic and static which will be described below.

B.1.2.1 – Dynamic Sublimation

Material is placed in a variable temperature furnace under reduced pressure (ca. $10^{-2}$ to $10^{-5}$ torr) as shown in figure A-1. Multiple temperature zones (either three or four depending) can be set which allows for separation and sublimation of the product, by-products and any starting materials which did not react. Typically, the first zone would be the hottest, second zone would collected the desired product and the third/fourth zone(s) would collect the by-products and/or starting materials. The furnace would be back filled with argon, the glass tube then scored/cut and the material brought into the glove box for further collection.
Figure B-1 The setup of dynamic sublimation and scheme of different temperature zones

B.1.2.2

Often dynamic sublimation would not yield crystals suitable for single crystal X-ray crystallography and static sublimation would be utilized. The extremely pure material would be placed in a thick walled thin glass tube (diameter ~0.8 mm) and placed under vacuum \((ca. \ 10^{-2} \text{ to } 10^{-5} \text{ torr})\) for 24 hours. The tube would be flame sealed while under vacuum. The material would now be under static vacuum and placed in a single state furnace set at the desired temperature. The tube must be placed both inside (to sublime) and outside (to land) for crystals to be grown. Figure A-2 illustrates this technique.

Solution Crystallization Techniques

If materials could not be grown via the methods above, solution recrystallizations were undertaken. There are a variety of techniques that were utilized described below to generate high-quality crystals.

B.2.1.3 – H-cell reactions
The typical reaction of solution crystallization is by use of a H-cell which is illustrated in figure A-3. This procedure involves making two separate solutions of the reactants in either the solvent (or of miscible solvents), in the round bottom flasks which have long necks as seen below. The apparatus would be combined and three freeze-pump-thaw cycles would ensure the solutions were fully degassed. The whole vessel is then gently inverted and slanted slightly to allow for slow diffusion of the solutions through a glass frit. The tilt angle of the vessel should be adjusted over a period of 8 hours to ensure full diffusion of the reactants. Crystals of the product are grown at the interface of the two solutions. Once the reaction is completed, the resulting filtrate is carefully syringed off, the crystals washed with solvent, dried in vacuo and brought into the glovebox.

![Diagram of H-cell reaction](image)

**Figure B-3** The setup of H-cell reaction: a) initial setup with both solvent bulbs with reagents b) slight angling to allow slow diffusion through the glass frit to generate crystals

**B.1.2.4 – Diffusion Cell**
When the diffusion of the two reactants is too fast, the crystals that are grown can be of poor quality, or not grown at all resulting in amorphous material. The diffusion cell was used to allow for extremely slow reactions to occur. Concentrated solutions of the reactants were carefully syringed into each vertical tube under argon as seen in figure A-4. On top of each solution, the same solvent was carefully added slowly, not to disturb the concentrated reagents. Solvent was added until it met at the interface of the two tubes. The diffusion.cell was left undisturbed for 2-4 weeks and crystals grown at the interface. The resulting filtrate is carefully syringed off, the crystals washed with solvent, dried in vacuo and brought into the glovebox.

![Diagram of diffusion cell](image)

**Figure B-4** The setup of a D-cell reaction: a) initial high concentration of reagents b) layered dilutions on both sides to allow for slow diffusion between the two solvents

**B.1.2.5 – In-Vial Layered Reactions**

In this procedure a 4 Dram vial is utilized as seen in figure A-5. Two solutions of the reactants are made, but it is necessary that the two solvents be relatively different in
density. The solution with the higher density solvent is carefully place in the bottom of the vial. The other solution is very carefully syringed in down the side of the vial, resulting in two layers. The solutions grown crystals at the interface of the layers, and after 1-2 weeks, crystals form. The filtrate is carefully syringed off, the crystals washed with solvent, dried \textit{in vacuo} and brought into the glovebox.

\section*{B.1.2.6 – Vial-In-Vial Slow Evaporation}

The typical procedure of this recrystallization technique is as follows (Figure A-5): a dilute solution of the product was made and placed in a 1-Dram vial. In a 4-Dram vial, dry DMF or DMSO was added. The 1-Dram was carefully placed into the 4-Dram and put the lid on tightly. The DMF/DMSO will absorb the more volatile solvent. After 1-2 weeks, crystals can be seen in the 1-Dram vial and dried \textit{in vacuo}. Note: the lid on the 1-Dram vial can be modified for slower diffusion by adding small holes.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{vial_in_vial.png}
\caption{Figure B-5 Depiction of vial-in-vial slow evaporation crystallization}
\end{figure}
B.2 Techniques

B.2.1 Density Function Theory Calculations

All DFT calculations used the uB3LYP method with a basis set of 6-31G(d). All calculations were either run on Gaussian 03W or Gaussian 09 Mac OSX suite of programs.

B.2.2 Ionization Potentials, Electron Affinities and $\Delta H_{\text{disp}}$

All calculations for ionization potentials and electron affinities were obtained from total adiabatic electronic energy calculations using the uB3LYP method with a triple zeta calculation of 6-31Gd via Gaussian 09 for OSX.

B.2.3 Band Structure Calculations

All EHT electronic band structures were calculated in collaboration with Professor Richard Oakley at the University of Waterloo with the Caesar suit of programs using the Coulomb parameters of Basch, Viste and Gray and a quasi-split valence basis set adapted from Clementi and Roetti. The band structure calculations used the respective crystallographic coordinates for each molecule.

B.2.4 NMR Spectra

All $^1\text{H}$, $^{13}\text{C}$ and $^{19}\text{F}$ NMR spectra were collected either on a Bruker Avance 300 MHz or 400 MHz spectrometer.

B.2.5 Infrared Spectra
All infrared spectra were recorded (at 4 cm\(^{-1}\)) resolution as pressed KBr pellets or as neat liquids on KBr plates on a Nicolet 4700 FT-IR infrared spectrometer.

**B.2.6 Mass Spectrometry**

All mass spectrometry experiments were performed at low resolution (EI, CI and ESI) at the WATSPEC Mass Spectrometry Facility or the McMaster Regional Centre for Mass Spectrometry (MRCMS).

**B.2.7 Cyclic Voltammetry**

Electrochemical measurements were performed at ambient temperature, using an Autolab PGSTAT 30 instrument. Analyte solutions (ca. 2 mM) were prepared in anhydrous, degassed DCM, with 0.05 M \(^n\)Bu₄NPF₆ as supporting electrolyte. A three electrode glass cell, sealed under argon atmosphere, was employed; Pt wire electrodes (working, reference, and counter). Electrodes were decontaminated using a hydrogen flame prior to use. Addition of freshly sublimed ferrocene was used as an internal standard where the Fc/Fc\(^+\) couple is taken to be 0.46 V vs. SCE. All cyclic voltammetry results were measured at a sweep rate of 100 mV/s and are reported vs. SCE.

**B.2.8 EPR Spectra**

All solution EPR spectra were measured with a Brüker EMX Spectrometer in dichloromethane or toluene. Hyperfine coupling constants were obtained by spectral simulation Public EPR Software Tools software (WinSim). All solid-state EPR spectra were measured on the same spectrometer and attempts at simulation were done with Pip4Win.
B.2.9 Elemental Analysis

Elemental analyses were performed by MHW Laboratories (Phoenix, AZ).

B.2.10 Magnetic Susceptibility Measurements

The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL housed at the Centre de Recherche Paul Pascal. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. Measurements were performed on polycrystalline samples introduced in polyethylene bags (3x 0.5x 0.02 cm) sealed under argon. The magnetic data were corrected for the sample holder (plastic bag) and the diamagnetic contribution.

B.2.11 Crude Pressed Pellet Conductivity Measurements

All conductivity measurements were performed under inert atmosphere using a crude pressed pellet device seen in figure A-7. The device consists of two conductive plates separated by an insulated spacer. The sample is placed in an insulated holder while two screws, which are connected to the conductive plates, touch the sample. This allows for the only path of conductivity to be through the sample of question. A multimeter is attached to both plates and measures the resistance of the material.
B.2.12 X-ray Crystallography

Single crystal X-ray data was collected at room temperature (unless otherwise stated) using phi and omega scans with a) Brüker APEX-II CCD (McMaster University) b) Nonius CCD system (Western University) c) Nonius Kappa CCD system (University of Toronto) d) SuperNova Dual diffractometer with Atlas CCD system (University of Guelph). The SHELXTL/PC V6.14 for Windows NT suite of programs was used to solve the structures by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located. Independent molecules were formed.

B.3 Source of Starting Materials

B.3.1 Purchased Chemicals That Were Used As Received
<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>A21 base resin</td>
<td>(Sigma-Aldrich)</td>
</tr>
<tr>
<td>Acetic acid, glacial</td>
<td>(Fisher)</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>(Fisher)</td>
</tr>
<tr>
<td>2-Amino-3-chloro-1,4-naphthoquinone</td>
<td>(Acros)</td>
</tr>
<tr>
<td>Ammonia gas</td>
<td>(Linde)</td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>(Fisher)</td>
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<tr>
<td>Argon gas</td>
<td>(Linde)</td>
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<tr>
<td>1,4-Benzoquinone</td>
<td>(Acros)</td>
</tr>
<tr>
<td>Bromine</td>
<td>(Fisher)</td>
</tr>
<tr>
<td>Calcium hydride</td>
<td>(Linde)</td>
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<tr>
<td>Chloranil</td>
<td>(Fluka)</td>
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<tr>
<td>Chlorobenzene</td>
<td>(Sigma-Aldrich)</td>
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<tr>
<td>Chloroform-d</td>
<td>(Sigma-Aldrich)</td>
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<tr>
<td>Cobaltocene</td>
<td>(Strem)</td>
</tr>
<tr>
<td>Decamethylcobaltocene</td>
<td>(Strem)</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>(Caldeon)</td>
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<tr>
<td>Dimethylsulfoxide-d</td>
<td>(Cambridge Isotopes &amp; Sigma-Aldrich)</td>
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<tr>
<td>2,5-Dimethyl-thiophene</td>
<td>(Acros)</td>
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<tr>
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<td>Ethyl acetate</td>
<td>(Fisher)</td>
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<tr>
<td>Ferrocene</td>
<td>(Sigma-Aldrich (sublimed))</td>
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<tr>
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<tr>
<td>Hexane</td>
<td>Caldeon</td>
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<td>Chemical Name</td>
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<tr>
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<tr>
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<tr>
<td>Potassium hydroxide, pellets</td>
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<tr>
<td>Pyridine</td>
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<td>Triphenylantimony</td>
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### A.3.2 Solvents Purified/Distilled Prior To Use

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<thead>
<tr>
<th>Solvent</th>
<th>Purification Method</th>
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<tbody>
<tr>
<td>Acetonitrile</td>
<td>Distilled from P₂O₅</td>
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<tr>
<td>Chlorobenzene</td>
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<tr>
<td>Cyclohexane</td>
<td>Distilled from CaH₂</td>
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<tr>
<td>Dichloromethane</td>
<td>Distilled from CaH₂</td>
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<tr>
<td>Dichloroethane</td>
<td>Distilled from CaH₂</td>
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<tr>
<td>Dimethylformamide</td>
<td>Distilled from BaO</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>Distilled from Na(s)</td>
</tr>
<tr>
<td>Toluene</td>
<td>Distilled from Na(s)</td>
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</tbody>
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