Inclusion Chemistry and Crystal Engineering of Dithiadiazolyl and Diselenadiazolyl Radicals

Nadia Theresa Stephaniuk

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Inclusion Chemistry and Crystal Engineering of Dithiadiazolyl and Diselenadiazolyl Radicals

By

Nadia Theresa Stephaniuk

A Thesis
Submitted to the Faculty of Graduate Studies through the Department of Chemistry and Biochemistry in Partial Fulfillment of the Requirements for the Degree of Master of Science at the University of Windsor

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2019

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Inclusion Chemistry and Crystal Engineering of Dithiadiazoly1 and Diselenadiazoly1 Radicals

by

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September 11, 2019
DECLARATION OF CO-AUTHORSHIP/PREVIOUS PUBLICATION

I hereby declare that this thesis consists of material which has been completed either individually, or as the result of joint research as described here. All the work presented in Chapter 2 was completed by the author, except for: (i) the crystal structure determination from PXRD data which was undertaken by Dr. J. Rawson and (ii) magnetic measurements which were completed by Dr. A. Arauzo (U. Zaragoza, Spain). Some aspects of the work presented in Chapter 3 were collaborative. Specifically, all compounds were prepared by the author who also prepared samples for EA, undertook PXRD studies and EPR measurements. The growth of single crystals involving DTDA and TEMPO radicals was undertaken by Mr. M. A. Nascimento and those results have been published in the original research article “On the Design of Radical-Radical Cocrystals” (M. A. Nascimento, E. Heyer, J. J. Clarke, H. J. Cowley, A. Alberola, N. Stephaniuk, and J. M. Rawson, *Angew. Chem. Int. Ed.*, 2019, 58, 1371 – 1375). The assistance of L. Watanabe for structure determination of cocrystal structures presented in Chapter 3 as well as elemental analysis is acknowledged. The author is grateful to Dr. J. Auld for high-resolution mass spectra presented in Chapter 2.

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I declare that this is a true copy of my thesis, including any final revisions, as approved by my thesis committee and the Graduate Studies office, and that this thesis has not been submitted for a higher degree to any other University or Institution.
Chapter 2 describes the inclusion chemistry of dithiadiazolyl (DTDA) radicals (and diselenadiazolyl (DSDA) radicals into the porous metal-organic framework MIL-53(Al) [Al(BDC)(OH)], where BDC = 1,4-benzenedicarboxylate]). The structures and physical properties of these host-guest complexes are characterized through powder X-ray diffraction, EPR spectroscopy and SQUID magnetometry, thermal analysis (DSC and TGA) as well as mass spectrometry, IR spectroscopy and elemental analysis. Preliminary reactivity studies show that halogens can percolate into the channel structure leading to complete (Cl₂ and Br₂) or partial oxidation (I₂) of the incorporated guest molecules.

Chapter 3 identifies a new robust supramolecular synthon for radical-radical cocrystal formation. Cocrystallization of perfluoroaryl DTDA and DSDA radicals with the nitroxide radicals TEMPO and TEMPONE formed a series of nine 2:1 cocrystals of general formula \( [\text{Ar}_7\text{CNEEN}]_2[\text{TEMPO}(\text{NE})] \) which were characterized by X-ray diffraction and EPR spectroscopy, with all derivatives exhibited a common tetrafurcated \( E_4 \cdots O-N \) interaction.
DEDICATION

To my parents and sisters for their unwavering support and always believing in me.

“Working hard is important, but there’s something that matters even more: believing in yourself.”

– J. K. Rowling
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Firstly, this thesis would not have been possible without the support of my advisor Dr. Jeremy Rawson. I am extremely grateful to have been a part of Dr. Rawson’s research group for the past four years, where I have been fortunate enough to have had such a wonderful research advisor, teacher, and mentor. His dedication and passion to his research and his students are just two of the many qualities I admire about him. He does everything in his power to help us succeed, and I owe my entire research experience to him. Thank you for everything Jeremy.

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LIST OF ABBREVIATIONS

°C        degrees Celsius
Å         Angstrom
λ         spin-orbit coupling constant
χ         magnetic susceptibility
A         Acceptor molecule
a_F       fluorine hyperfine coupling constant
a_N       nitrogen hyperfine coupling constant
a_se      selenium hyperfine coupling constant
Ar        aryl substituent
ASAP+     positive ion Atmospheric Solids Analysis Probe
Bcc       body-centred cubic
BDC       1,4 – benzenedicarboxylate
BDTA      benzo-1,3,2-dithiazolyl
BET       Brunauer-Emmett-Teller
'tBu      tert-butyl
C         Curie constant
ccp       cubic close-packed
Cl₂dhbq   2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone ligand
COF       covalent organic framework
D         donor molecule
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>DSDA</td>
<td>diselenadiazolyl radical</td>
</tr>
<tr>
<td>DTA</td>
<td>dithiazolyl radical</td>
</tr>
<tr>
<td>DTDA</td>
<td>dithiadiazolyl radical</td>
</tr>
<tr>
<td>EA</td>
<td>Elemental Analysis or electron affinity</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron Paramagnetic Resonance</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>Et₂O</td>
<td>diethyl ether</td>
</tr>
<tr>
<td>g</td>
<td>g-factor (EPR spectroscopy)</td>
</tr>
<tr>
<td>G</td>
<td>Gauss</td>
</tr>
<tr>
<td>hfac⁻</td>
<td>hexafluoroacetylacetonate anion</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>HOF</td>
<td>hydrogen-bonded organic framework</td>
</tr>
<tr>
<td>HRMS</td>
<td>High Resolution Mass Spectrometry</td>
</tr>
<tr>
<td>IE</td>
<td>ionization energy</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared Spectroscopy</td>
</tr>
<tr>
<td>K</td>
<td>degrees Kelvin</td>
</tr>
<tr>
<td>kV</td>
<td>kilovolts</td>
</tr>
<tr>
<td>lp</td>
<td>Large pore (form of MIL-53(Al)).</td>
</tr>
<tr>
<td>Acronym</td>
<td>Full Form</td>
</tr>
<tr>
<td>---------</td>
<td>-----------</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>mA</td>
<td>milli-amps.</td>
</tr>
<tr>
<td>MBDTA</td>
<td>4-methylbenzo-1,3,2-dithiazolyl radical</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>MIL</td>
<td>Materials Institut Lavoisier</td>
</tr>
<tr>
<td>MOF</td>
<td>Metal-Organic Framework</td>
</tr>
<tr>
<td>np</td>
<td>narrow pore (form of MIL-53(Al))</td>
</tr>
<tr>
<td>NRC</td>
<td>neutral radical conductor</td>
</tr>
<tr>
<td>OAc⁻</td>
<td>acetate anion</td>
</tr>
<tr>
<td>P</td>
<td>pairing energy</td>
</tr>
<tr>
<td>PCP</td>
<td>Porous coordination polymer</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>PHTP</td>
<td>Perhydrotriphenylene</td>
</tr>
<tr>
<td>PLY</td>
<td>phenalenyl radical</td>
</tr>
<tr>
<td>p-NPNN</td>
<td>para-nitrophenyl-nitronyl nitroxide.</td>
</tr>
<tr>
<td>PSM</td>
<td>post-synthetic modification</td>
</tr>
<tr>
<td>PVC</td>
<td>poly-vinyl chloride</td>
</tr>
<tr>
<td>py</td>
<td>pyridyl</td>
</tr>
<tr>
<td>PXRD</td>
<td>Powder X-Ray Diffraction</td>
</tr>
<tr>
<td>r</td>
<td>atomic radius</td>
</tr>
<tr>
<td>R</td>
<td>alkyl group</td>
</tr>
<tr>
<td>ROS</td>
<td>reactive oxygen species</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>SBU</td>
<td>secondary building unit</td>
</tr>
<tr>
<td>S·cm⁻¹</td>
<td>Siemens per cm (unit of conductivity)</td>
</tr>
<tr>
<td>[SN]ₓ</td>
<td>poly(sulfur nitride)</td>
</tr>
<tr>
<td>s.o.f.</td>
<td>site occupancy factor</td>
</tr>
<tr>
<td>SOMO</td>
<td>Singly Occupied Molecular Orbital</td>
</tr>
<tr>
<td>SQUID</td>
<td>Superconducting Quantum Interference Device</td>
</tr>
<tr>
<td>T</td>
<td>Tesla</td>
</tr>
<tr>
<td>T&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Curie temperature</td>
</tr>
<tr>
<td>TCNQ</td>
<td>tetracyanoquinodimethane</td>
</tr>
<tr>
<td>TEMPO</td>
<td>(2,2,6,6-tetramethylpiperidin-1-yl)oxyl radical</td>
</tr>
<tr>
<td>TEMPONE</td>
<td>(4-oxo-2,2,6,6-tetramethyl-piperidin-1-yl)oxyl radical</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TTTA</td>
<td>trithiaziapentalenyl radical</td>
</tr>
<tr>
<td>U</td>
<td>Hubbard energy</td>
</tr>
<tr>
<td>UV/vis</td>
<td>ultraviolet-visible</td>
</tr>
<tr>
<td>W</td>
<td>band width</td>
</tr>
<tr>
<td>Z</td>
<td>atomic number</td>
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Chapter 1  Introduction

1.1 Free-Radical Chemistry

Over the last century, scientists have been striving to gain a better understanding of the structure and reactivity of organic compounds. One sub-group of organic compounds are those containing an odd number of electrons, known as free radicals. As a result of the unpaired electron, free radicals readily react with other molecules and often exist only for a very brief period of time. Radicals play an important role in biology, where a number of important biological processes depend on free radicals, including hydroxyl (HO•) and superoxide (O2•−) radicals as well as the oxygen diradical (O2). The stabilization and removal of these reactive oxygen species (ROS) as well as other radicals is in itself a large field of research. In contrast to naturally-occurring and often short-lived free radicals, the field of stable synthetic free radicals was born in 1900 when Moses Gomberg inadvertently discovered the triphenylmethyl radical, while attempting to synthesize hexaphenylethane, C2Ph6. Gomberg’s remarkable discovery that carbon does not always have to maintain a tetravalent occupancy was a milestone and ultimately set the stage for the evolution of free radical chemistry.1 Gomberg’s first attempts at synthesizing hexaphenylethane resulted in a white crystalline powder which readily oxidized upon exposure to air. To avoid this unintentional oxidation, he reduced triphenylmethyl chloride with zinc in benzene under a carbon dioxide atmosphere, which resulted in a dark yellow oil. Removal of the benzene solvent resulted in the formation of a highly reactive white powder, which had the tendency to rapidly oxidize, as well as readily react with
halogens. From these reactivity patterns (unexpected for C₂Ph₆), Gomberg proposed the formation of a novel trivalent carbon species, the triphenylmethyl radical, Ph₃C• (1). In a series of further studies, Gomberg discovered that radical 1 (commonly referred to as Gomberg’s radical) could readily form the peroxo-bridged species 2 upon exposure to atmospheric conditions, as well as had a strong tendency to dimerize in the solid state. Later spectroscopic data confirmed the dimer formed was not the sterically strained dimer 3 but the less symmetric dimer, 4.

Figure 1.1: Formation of Gomberg's radical, adapted from [2]
Gomberg’s discovery did not come without scrutiny from the scientific community, where most were unconvinced\(^3\) that this white powder, which was yellow in benzene solution, was in fact a radical species. Indeed, molecular weight studies\(^4\) showed that Gomberg’s radical bore a similar molecular weight to hexaphenylethane. In an effort to explain this observation, Gomberg proposed that the two species were in fact in equilibrium with each other (Figure 1.2):

![Monomer-Dimer Equilibria of Gomberg's radical](image)

**Figure 1.2: Monomer-Dimer Equilibria of Gomberg's radical**

Gomberg’s early work established many aspects of future radical chemistry research, including the subtle interplay which exists between monomeric and dimeric states, central to many areas of radical chemistry. In 1958 Reid successfully isolated the phenalenyl radical, which exhibited unique characteristics of long-lived stability in solution, and existed in equilibrium with its \(\sigma\)-bonded dimer (Figure 1.3a).\(^5\) In an effort to inhibit formation of a \(\sigma\)-bonded dimer, bulky tert-butyl group substituents were incorporated into the parent structure.\(^6\) Instead of forming a \(\pi\)-bonded dimer with loss of aromaticity,\(^7\) this derivative formed a \(\pi\)-dimer in the solid state, in which full delocalization was retained and a weak multi-centre bond was formed through close \(\pi\cdots\pi\) contacts, subsequently described as ‘pancake bonds’.\(^8\) These pancake bonds differ significantly from conventional
\(\pi-\pi\) contacts since the ‘pancake bonds’ favor eclipsed arrangements of rings at distances less than the sum of the van der Waals’ radii, whereas conventional aromatic-aromatic \(\pi-\pi\) interactions adopt staggered conformations with C atoms located over the centroid of another ring at distances comparable to the sum of the van der Waals radii (ca. 3.4 Å for graphite).⁹

![Figure 1.3: (top) Monomer-Dimer Equilibria of Phenalenyl (PLY) radical with its \(\sigma\)-bonded dimer⁵; (bottom) 2,5,8-(tBu)₃-PLY radical and its \(\pi\)-dimer⁷](image)

Additional classes of small organic radicals which have been extensively studied include the nitroxide and verdazyl radicals. Nitroxide radicals, \(\text{R}_2\text{NO}\), consist of some of the most well-known stable organic radicals in which the unpaired electron is delocalized over N and O atoms and includes the common commercially available (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl, more commonly known as TEMPO (Figure 1.4), which
will be discussed in more detail in Chapter 3. Unlike the PLY radical shown above, nitroxide and the closely related nitronyl nitroxide radicals (Figure 1.4) are typically able to withstand dimerization as they tend to bear sterically bulky groups which act as good dimerization inhibitors.²

![Figure 1.4: Examples of a nitroxide (left) and nitronyl nitroxide radical (right)](image)

Additionally, nitroxide radicals are typically highly air stable, and as a result they are often employed as EPR spin traps¹⁰ and fluorescent probes.¹¹ There are a few examples of nitroxide radicals which do dimerize, and in all cases these radicals lack the steric bulk which those that do not dimerize possess. These include the biphenyl-3,5-diyl bis(t-butyl nitroxide) radical (Figure 1.5), which saw the addition of a second phenyl ring added with the hopes of improving stability and intermolecular interactions, which in turn became one of the first reported nitroxide radicals known to dimerize.¹²
Figure 1.5: Molecular structure (left) and crystal structure (right) of biphenyl-3,5-diylbis(t-butyl nitroxide) radical, one of the few nitroxide radicals known to dimerize

As a result of their unique properties, nitroxide and nitronyl nitroxide radicals have been readily employed in the design and fabrication of molecular magnetic materials. Work in this field has found nitroxide derivatives excellent molecular building blocks for this type of work, as they are able to bind to a metal through a metal-oxygen bond. This has been exploited in the formation of an array of transition metal-radical complexes. One notable example saw the formation of a copper complex upon treatment of Cu(hfac)$_2$ with a thienyl-substituted nitroxide radical to form a trinuclear copper(II) complex (Figure 1.6) which displays both antiferromagnetic and ferromagnetic interactions within the complex, illustrating the capacity these organic molecules possess for the design of magnetic materials.$^{13}$ Free radical carboxylic acid derivatives derived from a parent nitroxide radical have been shown to bind to copper acetate, resulting in the formation of novel coordination polymers (Figure 1.7) with interesting properties.$^{14}$
Figure 1.6: Crystal structure of a trinuclear Cu(II) coordination polymer with a thienyl-substituted nitrooxide radical

Figure 1.7: Chain compounds designed with nitrooxide radical carboxylic acids (left), linked via a bidentate ligand, L
Similar chemistry has been observed with verdazyl radicals, which are also air and water stable, similarly to most nitroxides. The first verdazyl radical was reported in 1963 by Kuhn and Trischmann (Figure 1.8), which consisted of a saturated carbon atom within the radical heterocyclic ring. Subsequently verdazyl radicals have also been widely studied for use in molecule-based magnets. Work by Hicks et al. expanded the field through implementing oxo-verdazyl radicals with pyridine or pyrimidine functional groups which favor metal-binding as N,N’-chelate radicals. Work by Hicks implemented EPR and theoretical calculations to reveal significant spin density on the verdazyl nitrogen atoms, which is important for magnetic communication between these radicals and the coordinated metals.

![Verdazyl Radicals](image)

**Figure 1.8**: Examples of verdazyl radicals, illustrating the Kuhn’s verdazyl (left) a pyridine-substituted (middle) and pyrimidine-substituted (right) oxo-verdazyl derivative

While the various organic radicals mentioned above have all played a key role in the development of free-radical chemistry, one notable class of organic radicals which has been extensively studied is that of the thiazyl radical, and it is this class of radicals which are integral to this thesis and will be described in the following sections.
1.1.2 Sulfur-Nitrogen Chemistry

The field of materials science has been revolutionized with the introduction of molecules which have the ability, either individually or in particular arrangements, to conduct electricity and even preserve magnetic information, ultimately leading to the construction of molecular devices. The advantage of these materials in such next-generation technology is the ability to tune the physical properties of these materials at the molecular level, in an effort to better understand and optimize the subtle interplay between structure and function. The emergence of sulfur-nitrogen chemistry has allowed for this new found potential to be applied in the design of molecular materials within the field of materials chemistry. Poly(sulfur nitride), $[\text{SN}]_x$, is comprised of a chain of alternating sulfur and nitrogen atoms, and was the first discovered synthetic polymeric metal.$^{17}$ This material is unique as it was the first example of a synthetic polymer which did not contain any metallic elements, yet displayed the ability to conduct from 1.5 to 300 K, and even becomes superconducting below 0.26 K, making it the first reported example of a true synthetic metal.$^{18}$ The conductivity of single crystals of $[\text{SN}]_x$ is highly anisotropic which stems from the highly anisotropic one-dimensional structure of the polymer chain. For a crystal structure to be anisotropic, the crystallographic axes of the structure are required to be inequivalent, and this phenomenon gives rise to many intriguing qualities, where effects such as piezoelectricity, pyroelectricity, and pleochromism can occur.$^{17}$
The conductivity of poly(sulfur nitride) [SN]$_x$ can be illustrated by band theory. Metals exhibit a band structure with no energy gap between the valence and conduction bands (Figure 1.10). In poly(sulfur nitride), the $\pi$-orbitals of sulfur and nitrogen overlap to create a conduction band with $\pi$-delocalization of electrons throughout the polymer chain, affording the experimentally observed conductivity. Each S atom provides 2 $\pi e$ and one $p$ orbital for bonding while each N atom provides 1 $\pi e$ and one orbital for the $\pi$-system leading to a $\frac{3}{4}$ filled band. In addition to its conducting capabilities, characteristic properties of [SN]$_x$ such as its high electronegativity, lack of reactivity exhibited towards water or acidic solutions, and its strong interaction with metal ions allows for the potential of this material to enhance catalytic properties as well as device effectiveness.\textsuperscript{17}
Significant interest in the physical properties of [SN]$_x$ brought about attempts to modify the electronic properties of this chain to further explore the capabilities of this new material. This work initially began through chemical doping with Br$_2$ and I$_2$ to modify the position of the Fermi level in order to enhance conductivity. Subsequently, Hoffman proposed that modifying the polymer's electronic properties could be possible through the addition of functionalized carbon atoms to the backbone of the polymer, wherein the electrons of the polymer chain would be modified as a direct result of the addition of electron-donating or electron-withdrawing groups. This proposal drove a search for the formation of C/N/S-based polymers, in an effort to discover a functionalized material with these unique properties. However, experimental studies initiated by Oakley and others revealed a propensity to form a range of C/N/S-based heterocycles rather than polymers.

Figure 1.10 Simple band theory diagram for conductors, semiconductors and insulators, adapted from [17]
and this led to the emergence of a variety of C/N/S-based redox active heterocyclic rings, many of which form stable radicals, generically referred to as thiazyl radicals.\textsuperscript{21}

![Diagram of isolobal relationship with CN$_2$S$_2$ heterocyclic ring](image)

**Figure 1.11: Isolobal relationship with CN$_2$S$_2$ heterocyclic ring, adapted from [22]**

Within this class of radicals, there is a well-established isolobal relationship between these 7\(\pi\) systems, and their derivatives. Figure 1.11 illustrates a few examples of this relationship, where conceptual replacement of S\(^+\) by N or R-C can lead to variations on the initial heterocyclic ring system, with distinct physical and chemical properties.\textsuperscript{22}
1.1.3 Synthesis of 1,2,3,5-Dithiadiazolyl radicals

Synthetic pathways to obtain DTDA radicals have been extensively studied, since Banister’s first report in 1977. A key contribution to DTDA chemistry was the contribution by Oakley who reported the versatile synthesis of a variety of benzamidines or benzamidinates which are readily converted to dithiadiazolylum chloride salts through condensation with SCl$_2$ (Figure 1.12). This method is particularly attractive due to the great diversity of commercially available nitriles. However, the basic character of Li[N(SiMe$_3$)$_2$] generates certain limitations to this approach and protic nitrile precursors such as nitriles with an $\alpha$-CH$_2$ group (e.g. PhCH$_2$CN) tend to undergo deprotonation rather than nucleophilic attack at the nitrile. In addition, the bulky nature of the base makes sterically protected nitriles poor substrates for DTDA preparation. One electron reduction of the dithiadiazolium chloride salt typically employs a reducing agent such as triphenyl antimony or silver powder. Organic reductants such as Ph$_3$Sb are often favored for DTDA radicals which have limited solubility since Ph$_3$Sb and Ph$_3$SbCl$_2$ are both soluble in a variety of organic solvents, leading to facile separation. Alternatively, for radicals which exhibit a good solubility then metal-based reductants (Ag, Zn/Cu couple) are often implemented since both the metal and its chloride salt have limited solubility in organic solvents. After initial separation, the dithiadiazolylium radical can be purified via vacuum sublimation. It should be noted that for high temperature sublimations, Ph$_3$SbCl$_2$ is volatile and was found to cocrystallize with the radical on one occasion.
The selenium analogues can be prepared in a similar fashion, replacing SCl\(_2\) with SeCl\(_2\).

Due to the long-term instability of SeCl\(_2\), it is typically generated in situ. It has been reported that SeCl\(_2\) can be obtained from a stoichiometric mixture of Ph\(_3\)Sb and SeCl\(_4\), however this combination has proven to be strongly exothermic (occasionally uncontrolled) and a 1:1 mixture of SeCl\(_4\) and Se is preferred in the studies described here.\(^{26}\) The diselenadiazolyl radicals can also be purified in a similar manner with slightly elevated sublimation temperatures.

\[^{26}\] The diselenadiazolyl radicals can also be purified in a similar manner with slightly elevated sublimation temperatures.
1.1.4 Electronic Properties of 1,2,3,5-Dithiadiazolyl (DTDA) Radicals

The family of 1,2,3,5-dithiadiazolyl radicals comprise a group of molecules (Figure 1.13) of general formula, RCNSSN which have just one R substituent which can be modified. The heterocyclic ring is fully $\pi$-conjugated with a total of 7$\pi$ electrons. The singly occupied molecular orbital (SOMO) is of $a_2$ symmetry (Figure 1.13) and is nodal at the C atom which means that the spin density is largely unaffected by the nature of R. This is reflected in DTDA radicals exhibiting similar redox behaviour,\textsuperscript{27} comprising a reversible 1$e^-$ oxidation to form the 6$\pi$ DTDA$^+$ cation and a quasi-reversible 1$e^-$ reduction, forming the DTDA$^-$ anion. Similarly, DTDA radicals tend to exhibit similar EPR spectra with a $g$-value around 2.01 and hyperfine coupling to two equivalent $^{14}$N nuclei (I = 1) generating a 1:2:3:2:1 pentet with $a_N \sim 5.0$ G.\textsuperscript{28} High resolution EPR spectra sometimes reveal additional hyperfine coupling to $^1$H or $^{19}$F nuclei on the substituent R group.\textsuperscript{29} Various synthetic pathways have been explored which permit a range of alkyl and aryl groups to be attached to the DTDA framework.\textsuperscript{28} Such changes affect the solid-state structure and magnetic properties without changing significantly the electronics of the radical.

![Figure 1.13: The SOMO of the PhCNSSN radical](image)
1.1.5 Dimerization in 1,2,3,5-dithiadiazolyl radicals

As with the PLY system described previously, DTDA radicals tend to exhibit ‘pancake bonds’, i.e. multicentre $2e^-$ bonds rather than conventional $2c,2e^-$ bonds. The observed symmetry of the SOMO allows for multiple modes of association through intermolecular interactions incorporating short S···S or S···N contacts. Both DFT calculations and EPR measurements have revealed that the majority of the spin density lies on the sulfur atoms, which favor dimerization motifs which form S···S contacts, whereas the inherent bond polarity ($\delta^+\text{S}–\text{N}\delta^-$) can offset loss of S···S interactions with electrostatically favored $\delta^+\text{S}...\text{N}\delta^-$ interactions. Of the five reported modes of association, the cis-cofacial mode (Figure 1.14a) is by far the most common with S···S distances around 2.9 – 3.2 Å, notably shorter than the sum of van der Waals radii and yet longer than the length of a typical single S-S bond.

![Figure 1.14: Modes of association in the solid state of DTDA radicals, illustrating (a) cis-cofacial, (b) twisted, (c) trans-cofacial, (d) trans-antarafacial, and (e) edge-to-face dimerization motifs, adapted from [27]](image_url)
The ultimate consequence of these pancake bonds is to render the system diamagnetic, effectively quenching their paramagnetism. The dissociation of these dimers into two monomers in solution effectively establishes a monomer-dimer equilibrium, where the paramagnetic monomer is detectable on the EPR timescale in solution, and yet in the solid state no or very minimal EPR signal is detected for the diamagnetic dimer. Both variable temperature EPR and UV/vis spectroscopy have been used to assess the enthalpy of dimerization which has been found to be around 35 kJ·mol⁻¹ for a series of derivatives (R = Ph, py, ‘Bu).³⁰

1.1.6 Conductivity in DTDA Radicals

Previous work on the design of organic molecular conductors primarily focused on π-stacked charge-transfer salts. These charge-transfer salts derive from the combination of electron-rich organic donor molecules (D) with electron-poor acceptor (A) molecules. Both donor and acceptor molecules have closed shell configurations, i.e. both donor and acceptor molecules have no unpaired electrons. However partial charge transfer from the electron-rich donor to the electron-poor acceptor yield partially oxidized donor and partially reduced acceptor stacks (Figure 1.15). This charge transfer produces partially filled donor and acceptor bands that render the system conductive. The ability to tune the donor and acceptor capability at the molecular level governs the extent of charge transfer, while the overlap of molecular orbitals along the stacking direction affords a delocalized band structure of width W. Efficient orbital overlap leads to a greater band width, so that the degree of charge transfer and the band width dictate the overall conductivity.
Figure 1.15: Energy matching in donor-acceptor materials to yield conductivity (top) a mismatch in energy between ‘donor’ and acceptor’ leads to no charge transfer and an insulating or poorly semiconducting state; (bottom) good energy matching between donor and acceptor bands leads to charge transfer. Figure adapted from [27]
Theoretical studies by Haddon\textsuperscript{31} marked the emergence of a new single-component design strategy based on neutral radical conductors (NRCs), with the concept that a regularly spaced stack of \(\pi\)-radicals would yield a half-filled conduction band. Poor orbital overlap would lead to a narrow band, whereas efficient orbital overlap would lead to a greater band width \((W)\). A second term which dictates whether such systems will conduct is the Hubbard energy, \(U\). The Hubbard energy is associated with electron transport and can be viewed as the energy to remove the electron from one molecule (which can be approximated to its ionization energy, IE) which is partially offset by the electron affinity (EA) of the next molecule to accept this electron,\textsuperscript{32} i.e. \(U \sim IE - EA\).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Band theory diagrams for (left) regular \(\pi\)-stack of radicals with Mott insulating behaviour \((U > W)\), (center) regular \(\pi\)-stack of radicals with good orbital overlap, and (right) distorted \(\pi\)-stack yielding formation of a band gap, adapted from [28]}\end{figure}
The value of $U$ reflects the extent of inter-electron repulsion between electrons. If $U < W$ the system should conduct whereas if $U > W$, then the system is described as a Mott insulator (Figure 1.16), i.e. the system should conduct but the energetic cost for electron transport is prohibitive.

Subsequent experimental work by Oakley$^{19}$ explored families of thiazyl (C/N/S) and selenazyl (C/N/Se) radicals as building blocks to construct NRCs. Initial studies employed DTDA radicals as the molecular building block in which the localized nature of the singly occupied molecular orbital (SOMO) meant the value of $U$ was essentially constant and modification of the R group changed the packing and orbital overlap, allowing fine-tuning of the band width, $W$. In addition, replacement of S by Se often led to isomorphous materials in which the slightly more radially expanded orbitals of Se led to increase in $W$ and yielded somewhat improved conductivities.$^{19}$

Unfortunately, the regular $\pi$-stacking of radicals required to yield the gapless conduction band (Figure 1.16a and b) is thermodynamically unstable with respect to a Peierls distortion of the lattice which is manifested in a set of alternating long-short-long-short contacts along the stacking direction. As a result of this uneven $\pi$-stacking of molecules, radical pairs with short intermolecular contacts are afforded in which stronger orbital overlap occurs to form a diamagnetic dimer with weak bonding occurring between the dimers within the stack.$^{27}$
As a result, a band gap emerges at the Fermi level between the unoccupied and occupied bands, therefore allowing the system to now be considered a semiconductor or an insulator, depending on the magnitude of the band gap, $\Delta E$ (Figure 1.16c). This distortion can potentially be suppressed if significant two or three-dimensional inter-stack interactions are incorporated which have the potential to affect the magnitude of the band gap.\textsuperscript{27} However studies on pristine DTDA radicals were all shown to be insulators or large band gap semiconductors.

In an effort to enhance conductivity, p-type doping of these materials has been explored. P-type doping (e.g. with iodine or bromine) partially oxidizes the DTDA stack, so that it combines a mixture of DTDA radicals and DTDA cations. Removal of electrons lowers the Fermi level such that it may fall in a region where there is a higher density of states and result in a system with increased and enhanced conductivity. In this way, doping of many DTDA derivatives with halogens such as Br$_2$ or I$_2$ has yielded superior conductivities comparable with other charge-transfer salts. For example, doping of $[p$-$C_6H_4(CNSSN)_2]^3$ with iodine yields a material with a conductivity of 100 S·cm$^{-1}$, while [NSSNC-CNSSN][I]$_2$ exhibits conductivity of 460 S·cm$^{-1}$ at 300 K, comparable to those values seen for a true metallic conductor.\textsuperscript{19}
1.1.7 Paramagnetic DTDA radicals

For the common DTDA dimer, the multi-centre $\pi^*-\pi^*$ bonding interaction leads to surprisingly complex magnetic behaviour. Orbital overlap between singly occupied molecular orbitals generates a bonding and antibonding set of orbitals, separated by an energy $\Delta E$. Provided the orbital overlap is good then $\Delta E > P$ and the electrons pair forming a diamagnetic (‘low spin’) ground state (Figure 1.17). If the overlap is poor then $\Delta E < P$ and a ‘high spin’ state is preferred. This high spin state (1 bonding electron and 1 antibonding electron) is effectively non-bonding and the dimer is destabilized. Two possibilities exist for this configuration; an open shell excited state singlet and an open shell excited state triplet. For the DTDA dimers the intra-dimer separation (2.9 -3.2 Å) is somewhat less than the sum of the van der Waals radii (3.6 Å for S) leading to a singlet ground state. Since both the closed shell singlet and open shell singlet have the same spin multiplicity, they are allowed to mix such that “the closed shell singlet” ground state is sometimes described as having some diradical character. The triplet configuration is an excited state. A number of variable temperature solid state EPR studies have revealed the diagnostic signal associated with the spin triplet at elevated temperatures, consistent with a singlet ground state and a thermally accessible triplet state.
Work by Constantinides and coworkers has shown that for a range of dichlorophenyl-DTDA dimers paramagnetism is observed upon warming. Structural studies from 140 K to room temperature on the 2′-chloro-5′-iodophenyl DTDA, which adopts a π-stacked structure, revealed an increase in the intra-dimer S···S interaction from 3.2 to 3.5 Å (Figure 1.18) and the onset of paramagnetism above ca. 120 K which is attributed to thermal population of the excited state triplet, identified by EPR spectroscopy. Similar behaviour was observed for the family of 2′-chloro-5′-halo-phenyl dithiadiazolyls (Figure 1.18). This increase in intra-dimer S···S distance reflects a gradual breakdown of the pancake dimer motif. Recent work by Preuss has shown a more abrupt transition from dimer to monomer on heating, leading to thermal hysteresis driven by competition between pancake bonding and hydrogen bonding supramolecular interactions.
Such abrupt spin-switching behavior has been observed in other families of thiazy radical such as the 1,3,2-dithiazolyl (DTA) radicals in which solid state transformations between diamagnetic and paramagnetic phases are well established.\textsuperscript{36}
Careful design of DTDA derivatives which suppress dimerization has been shown to lead to paramagnetic species whose magnetic properties reflect those of an $S = \frac{1}{2}$ ion. The large on-site coulomb potential for electron transfer ($U$, described in section 1.1.6) tends to favor localized spins which are well-suited for the construction of ‘organic magnets’ (materials which are magnetic but possess no paramagnetic metal ions). The magnetic moment for each radical is given by $gS$ where $g$ is the $g$-factor derived from EPR and $S = \frac{1}{2}$ for a radial with one unpaired electron. Heisenberg proposed that bulk ferromagnetic order would only be obtained in systems bearing heavy (metallic) atoms.$^{37}$ It wasn’t until almost 70 years later that the beta polymorph of the $para$-nitrophenyl nitronyl nitrooxide radial, $p$-NPNN (Figure 1.19), was discovered as the first example of an organic ferromagnet below 0.6 K.$^{38}$
Organic radicals have now been implemented as building blocks for various types of magnetic behaviour.

Ferromagnetic exchange, where the unpaired electrons on neighbouring molecules exhibit a co-parallel alignment of magnetic moments, can lead to bulk ferromagnetism, where the magnitude of the spontaneous moment is given by $gS$ per mole (Figure 1.20). Conversely, antiferromagnetism (antiparallel spin alignment) occurs if the magnetic moments are equal but opposite, leading to an overall net moment of zero. In low symmetry space groups where there is no inversion centre between spins, a third form of magnetic order can be observed, known as weak ferromagnetism or canted antiferromagnetism. The spins now align in a non-collinear fashion as a result of an antisymmetric exchange (Dzyaloshinski-Moriya) process. This gives rise to a small spontaneous magnetic moment given by $gS \cdot \sin(\theta)$ where $\theta$ is the angle between spins.

![Figure 1.19: $p$-NPNN, the first organic magnet](image)
A final form of magnetic ordering is known as ferrimagnetism. This occurs when there are antiferromagnetic interactions between spins on two different molecules whose magnetic moments are not equal. The spontaneous moment is now $|g_A S_A - g_B S_B|$. To date there are no well-characterized examples of organic ferrimagnets. In large part this is due to the ability to make stable multi-radicals with well-isolated high-spin ground states with $S > \frac{1}{2}$. This will be discussed later in this thesis. Two examples of DTDA radicals which not only retain their paramagnetism in the solid state but also exhibit long range magnetic order have been reported. The radical $\rho$-$O_2NC_6F_4CNSSN$ orders as a ferromagnet below 1.3 K,\(^{39}\) whereas the $\beta$-phase of $\rho$-$NCC_6F_4CNSSN$ orders as a canted antiferromagnet below 36 K, rising to 70 K under pressure, the highest ordering temperature reported for an organic radical.\(^{40}\) The attraction to employ DTDA (and other thiazyl radicals) as building blocks for the construction of organic magnets arises from the strength of their magnetic

![Magnetic Communication Diagram](image)

**Figure 1.20: Examples of possible magnetic communication, illustrating (a) ferromagnetic, (b) antiferromagnetic, (c) canted antiferromagnetic, and (d) ferrimagnetic exchange**

A final form of magnetic ordering is known as ferrimagnetism. This occurs when there are antiferromagnetic interactions between spins on two different molecules whose magnetic moments are not equal. The spontaneous moment is now $|g_A S_A - g_B S_B|$. To date there are no well-characterized examples of organic ferrimagnets. In large part this is due to the ability to make stable multi-radicals with well-isolated high-spin ground states with $S > \frac{1}{2}$. This will be discussed later in this thesis. Two examples of DTDA radicals which not only retain their paramagnetism in the solid state but also exhibit long range magnetic order have been reported. The radical $\rho$-$O_2NC_6F_4CNSSN$ orders as a ferromagnet below 1.3 K,\(^{39}\) whereas the $\beta$-phase of $\rho$-$NCC_6F_4CNSSN$ orders as a canted antiferromagnet below 36 K, rising to 70 K under pressure, the highest ordering temperature reported for an organic radical.\(^{40}\) The attraction to employ DTDA (and other thiazyl radicals) as building blocks for the construction of organic magnets arises from the strength of their magnetic
communication. Bulk magnetic order requires magnetic communication throughout the lattice in all three dimensions, with ordering dependent on the weakest of these interactions. Two common mechanisms for magnetic communication between radicals are (a) direct exchange which requires spatial overlap of the spin density on neighbouring interactions and (b) magnetic dipole-dipole interactions which drop off rapidly with distance as $1/d^n$. The use of sterically demanding groups to stabilize many organic radicals often suppresses direct exchange and magnetic ordering often occurs at low temperatures. Conversely direct exchange can be efficient at short distances provided (multi-centre) bond forming can be inhibited. Many thiazyl and selenazyl radicals are not sterically protected and actually favor close-intermolecular contacts due to the electrostatically favorable nature of $\delta^+\text{S} \cdots \text{N}\delta^-$ interactions. In addition, for compounds with spontaneous moments (ferromagnets, canted antiferromagnets and ferrimagnets), the coercive field required to switch the magnetic moment is dependent on the magnetic anisotropy. The incorporation of heavy p-block elements results in increased spin-orbit coupling, since the spin-orbit coupling constant $\lambda$ scales as $Z^4$ (Se $>$ S $>$ O) and greater anisotropy.\textsuperscript{38}

Extensive studies by Oakley have described families of resonance-stabilized bis-dithiazolyl radicals and their selenium derivatives. These systems not only exhibit some conductivity,\textsuperscript{43} but several are magnetically ordered. In total the work by Oakley, Rawson, Awaga and others have revealed a substantial family of radicals with some of the highest reported magnetic ordering temperatures (Figure 1.21).
1.1.8 Crystal structures of 1,2,3,5-Dithiadiazolyl Radicals

The solid-state packing of DTDA radicals is clearly intimately related to their materials properties with π-stacked radicals favoring conduction and monomeric radicals required as prerequisites for the construction of molecular magnets. The understanding and control of their intermolecular interactions is therefore critical for their use in device fabrication. The strongest intermolecular interaction in DTDA radicals is the propensity to form π*-π* dimers. In solution this dimerization enthalpy is around 35 kJ·mol\(^{-1}\) and comparable to the strength of many hydrogen bonds.\(^{30}\) Indeed the strength of this interaction has been employed by Preuss as a supramolecular synthon.\(^{45}\) Of the assorted modes of dimerization, by far the most common is the cis-oid dimer conformation,\(^8\)

![Diagram of organic ferromagnets](image)

**Figure 1.21: Examples of thiazyl and selenazyl-based organic ferromagnets**

1. **p-O\(_2\)NC\(_6\)F\(_4\)CNSSN\(^{[39]}\)**
   
   \(T_c = 1.6\) K

2. **p-NCC\(_6\)F\(_4\)CNSSN\(^{[40]}\)**
   
   \(T_c = 36\) K

3. **[BDTDA][GaCl\(_4\)]\(^{[44]}\)**
   
   \(T_c = 6.7\) K

4. **[DiSeCNSeCl\(_2\)]\(^{[42]}\)**
   
   \(T_c = 12.3\) K
though computational studies reveal only small differences between conformations.\textsuperscript{22} The strong bond polarity of each S–N bond in the DTDA ring leads to a very strong partial positive charge associated with the S–S bond and smaller partial negative charges associated with the N atoms. In the absence of strongly structure-directing groups (see later), a range of intermolecular contacts driven by S···N interactions between DTDA radicals are observed. These were first described by Rawson\textsuperscript{40} and subsequently reviewed by Haynes.\textsuperscript{46} The electron-poor nature of the S–S bond favors interactions with electronegative groups and lone pairs including nitriles, pyridyl groups, DTDA N atoms (described above) and even soft $\pi$-clouds of electron-rich aromatics (Figure 1.22).

![Figure 1.22: Crystal structures of $p$-NCC$_6$F$_4$CNSSN (top); NC$_5$F$_4$CNSSN (middle); HCNSSN (bottom left) and $m$-BrC$_6$H$_4$CNSSN (bottom right)](image-url)
The presence of electron-rich $\pi$-systems favors $S\cdots\pi$ interactions generating herringbone motifs but substitution with electronegative groups (F, CN, Cl) or incorporation of heteroatoms reduces the electron-density in the $\pi$-cloud and favors lamellar $\pi$-stacked structures. Within this set of compounds studies on perfluoroaryl groups have been particularly studied since the presence of ortho-fluorine substituents tends to result in significant twist angles between the aryl and heterocyclic ring planes in an attempt to diminish intramolecular N$\cdots$F electrostatic or lone-pair$\cdots$ lone-pair repulsions as well as reduce the $\pi$-electron density favoring lamellar structures (Figure 1.23). Other self-recognition motifs which have been studied are chlorinated phenyl derivatives, $C_6Cl_xH_{5-x}CNSSN$. A single para-Cl substituent yields a herringbone structure which strongly resembles that of PhCNSSN. Conversely highly chlorinated aromatics are known to adopt a supramolecular $\pi$-sheet structure which resembles a slipped $\pi$-stack with inter-plane distances of approximately 4.0 Å. Assorted $Cl_2C_6H_3CNSSN$ derivatives have been prepared and all exhibit distorted $\pi$-stacks with alternating long-short DTDA$\cdots$DTDA contacts but near regularly spaced aryl$\cdots$aryl intra-stack distances.
1.2 Multi-Component Systems Containing DTDA radicals

In the previous sections, the self-assembly and structure-property relationships in DTDA chemistry have been discussed with a focus on their magnetic and conducting properties. The work in this thesis focuses on the development of multicomponent systems in which DTDA radicals are a key building block in the structure. The specific interests are to establish a greater understanding of:

a) the types of intermolecular interactions which will support formation of multi-component materials;

b) the electronic properties of these materials, focusing on similarities or differences between the individual components and the multi-component system;

c) reactivity patterns of DTDA radicals within multi-component systems.

In this section previously reported studies on DTDA inclusion chemistry and cocrysal chemistry are described.
1.2.1 DTDA Cocrystal Chemistry

Cocrystals can be described as compounds consisting of two or more molecules that form a crystalline structure having physical properties which are distinct from the individual components. Cocrystals are typically considered to be distinct from solvates and charge-transfer salts (where the component molecules present in the ‘salt’ are in different oxidation states to the individual components). Cocrystals have attracted attention in a range of fields such as drugs and agrochemicals inter alia where the solubility can be modulated, leading to slower (or enhanced) release of active reagents. 

Attempts to suppress the ubiquitous pancake bonding dimerization process in DTDA radicals has focused on combinations of steric effects as well as perfluorophenyl substituents combined with structure-directing groups. The emergence of such supramolecular synthons led to the idea of implementing functional groups on two different DTDA radicals in order to drive cocrystal formation over self-recognition. In the short term the identification of groups capable of driving cocrystal formation between DTDA radicals needs to be realized which, in the longer term, could be implemented for designing more complex conducting or magnetic structures. In this context it has been established that many derivatives of general formula \( p-\text{RC}_6\text{F}_4\text{CNSSN} \) (\( \text{R} = \text{NC, NO}_2, \text{Br, I, NCC}_6\text{F}_4 \)) are monomeric, although some derivatives (\( \text{R} = \text{F, Cl, OMe} \)) are dimeric, illustrating a fine balance between other crystal packing forces and dimerization enthalpy in these systems. In this context approaches to incorporate these fluoroaryl DTDA building blocks into more complex architectures may suppress dimerization.
The first reported thiazyl-based radical-radical cocrystal was synthesized by Rawson and coworkers in 2009 which employed the established fluoroaryl/aryl $\pi$-electron-poor/$\pi$-electron-rich structure-directing interaction in which the C$_6$F$_6$·C$_6$H$_6$ cocrystal is a textbook example.$^{54}$ Their work reported the successful cocrystallization of PhCNSSN with the perfluorophenyl radical C$_6$F$_5$CNSSN radical, generating a mixed (C$_6$F$_5$CNSSN)(PhCNSSN) dimer cocrystal which exhibited aryl-perfluoroaryl $\pi$-$\pi$ interactions (Figure 1.24).$^{54}$ Charge density studies by Haynes on these radicals reveal the relative depletion of charge in the fluoroaryl ring as well as identifying the build-up of electron density in the intradimer region between S atoms.$^{55}$

![Figure 1.24: Crystal structure of (PhCNSSN)(C$_6$F$_5$CNSSN) (left) and packing of the (PhCNSSN)(NC$_5$F$_4$CNSSN) cocrystal (right)](image)

This was followed by a second study by Haynes in 2013, where a mixed 1:1 cocrystal was formed between PhCNSSN and the perfluoro-pyridyl derivative 4′-NC$_5$F$_4$CNSSN.$^{48}$ This system now exploits the structure-directing $\delta^+\text{S} \cdots \text{N}^\delta^-$ contacts between the DTDA ring and the pyridyl-N atom, as well as the electron-rich/electron-poor $\pi \cdots \pi_F$ interactions (Figure 1.25).
Figure 1.25: Alignment of PhCNSSN and NC₅F₄CNSSN cocrystal through pyridyl-N...S contacts

The ability of the disulfide bridge to form structure-directing S···X contacts to electronegative groups has recently been used to form cocrystals between DTDA radicals and two other types of radical. Cocrystallization studies described by Nascimento and coworkers showed that cocrystallization of PhCNSSN with MBDTA (MeC₆H₃S₂N) afforded the cocrystal [PhCNSSN]₂[MBDTA]₂ containing both the pancake bonded [PhCNSSN]₂ dimer as well as the pancake bonded [MBDTA]₂ with intermolecular S···N contacts between radicals (Figure 1.26).⁵⁷ Notably while (PhCNSSN)₂ adopts a cis-oid pancake dimer motif in pristine (PhCNSSN)₂ and in the cocrystal [PhCNSSN]₂[MBDTA]₂, the MBDTA radical is monomeric in its pure form⁵⁸ but adopts a diamagnetic pancake dimer when forming the cocrystal. Cocrystal formation has been argued based on a simple Born-Haber cycle; provided the enthalpy of sublimation of the cocrystal is greater than the sum of the sublimation enthalpies of the parent radicals then cocrystal formation is favored. Incorporation of intermolecular structure-directing interactions between different radicals assists cocrystal stabilization while choice of volatile radicals with low enthalpies of vaporization also assist cocrystal formation.
Their studies also showed that the TEMPO radical formed cocrystals with \((C_6F_5CNEEN)_2\) \((E = S, Se)\) of formula \([C_6F_5CNEEN]_2[TEMPO]\) with the TEMPO O atom forming supramolecular \(E\cdots O\) contacts between the DTDA or DSDA radical and TEMPO (Figure 1.27). Notably cocrystal formation with the less volatile \((PhCNEEN)_2\) dimers failed, consistent with the thermodynamic arguments proposed above. Further exploration of these structure-directing features and their competition with other supramolecular interactions will be explored in greater detail in Chapter 3.

**Figure 1.26** Molecular electrostatic potential of PhCNSSN (left) and MBDTA radicals (right) highlighting the \(\delta^+\) nature of the \(S-S\) bridge of PhCNSSN (purple) and the \(N^6\)-character of MBDTA (red). The two molecules are arranged to reflect the observed intermolecular close \(S\cdots N\) contacts between these two radicals.

**Figure 1.27**: Crystal structure of PhCNSSN + MBDTA cocrystal (left) and \(C_6F_5CNSeSeN + TEMPO\) cocrystal (right)
1.2.2 Porous Crystalline Materials

Crystalline materials which exhibit a porous architecture, i.e. a void space capable of containing other molecules, have the potential to be used in diverse applications ranging from molecular sieving, storage, chemical sensors, and in heterogeneous catalysis to name a few. Such porous materials have found applications in fields ranging from biology to materials chemistry. The variety of porous crystalline materials is large and is often subdivided into a range of different categories including zeolites, MOFs (metal organic frameworks), COFs (covalent organic frameworks), and HOFs (hydrogen-bonded organic frameworks). These materials often exhibit high surface areas, permanent or temporary porosity and often exhibit substantial thermal stability. The molecules contained within the void space of the framework (the ‘host’) are referred to as ‘guest’ molecules and may comprise solvent molecules, gas molecules or larger guest molecules whose shape and volume can be accommodated within the void space. Zeolites comprise a large family of both naturally occurring and synthetic aluminosilicates with rigid structures with microporous cavities (pore size less than 2 nm) whereas incorporation of organic linkers between metal ions in MOFs can lead to very large pore sizes with exceptionally large void spaces enabling for them to have a potentially higher adsorption capacity. Flexibility in the organic linkers can also give rise to flexible MOFs which offer the potential to undergo a unique “breathing” capability, which will be discussed in the coming sections. Among the different families of porous materials (zeolites, MOFs, COFs, HOFs etc.), this thesis will focus on metal organic frameworks and these are discussed in more detail in the next section.
1.2.3 Metal-Organic Frameworks

The term ‘metal-organic framework’ (MOF) was first implemented in 1995 by Omar Yaghi\textsuperscript{66} and has since been used interchangeably with porous coordination polymer. MOFs are materials constructed of strong bonds between a metal ion or cluster of metal ions, also referred to as a secondary building unit (SBUs) and a bridging ligand known as an organic linker (Figure 1.28).\textsuperscript{67}

![Formation of a metal-organic framework, adapted from [68]](image)

Figure 1.28: Formation of a metal-organic framework, adapted from [68]

The SBUs typically comprise robust metal-oxygen polyhedra consisting of divalent or trivalent metal cations including \( \text{Zn}^{2+} \), \( \text{Cu}^{2+} \), \( \text{Al}^{3+} \) and \( \text{Cr}^{3+} \) as well as heavier d-block metals such as \( \text{Zr}^{4+} \). The metals are typically ‘hard’ acids to complement the hard basicity of oxygen donors on the organic linkers such as hydroxide, oxide, phosphonate and carboxylate ligands (to name a few). Polynuclear cluster SBUs featuring carboxylates include tetrahedral \( \text{Zn}_4\text{O}(\text{OAc})_6 \), paddlewheel \( \text{Cu}_2(\text{OAc})_4 \) and triangular \( \text{M}_3\text{O}(\text{OAc})_6 \) functionalities. The linking of these SBUs by the organic linkers such as polycarboxylates leads to the three-dimensional MOF structure. The well-defined geometry (tetrahedral, square planar or trigonal etc.) of the SBU and the organic linker (often but not exclusively
linear) give rise to a number of default topologies which are formed as a result of this so-called ‘geometric principle of construction’ such that specific topologies can be targeted based on established SBUs.\textsuperscript{69} This concept is described as reticular chemistry and simply employs the idea of designing a material with a specific target in mind through bringing together the molecular building blocks (SBUs and linkers) in a premeditated ordered network. A classic example is MOF-5 (Figure 1.29). This material is based upon a basic zinc acetate ($\text{Zn}_4\text{O}(\text{OAc})_6$) SBU which act as an octahedral node (via the six carboxylate linkers) in which the acetates are replaced by 1,4-benzenedicarboxylate (BDC) units to link the $\text{Zn}_4\text{O}$ units together. Gas sorption measurements obtained on this material revealed 61% porosity, along with a Brunauer-Emmett-Teller (BET) surface area of 2320 m$^2$/g, which are significant findings as both are immensely increased over the previously studied zeolitic frameworks.\textsuperscript{70}

![Figure 1.29: MOF-5, built of Zn-O-C clusters bridged via chelating BDC units. Reproduced with permission from [71]](image-url)
The ‘isoreticular approach’ of MOF synthesis uses variations on the starting material to yield new materials from the parent compound without altering the fundamental topology of the material.\textsuperscript{72} For example, replacement of the linear 1,4-benzenedicarboxylate (BDC) spacer in MOF-5 by the linear $^2\text{O}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2^-$ ligand leads to an expanded version of MOF-5 with larger pores and 16 cubic MOFs derived from the parent MOF-5 have been prepared, highlighting the capability to form a wide array of topologically indistinguishable frameworks with functionally unique structures.\textsuperscript{72}

Additionally, post-synthetic modification of MOFs, or PSM synthesis, has become a growing area of interest. In the PSM process the pre-formed framework is functionalized through chemical reactions in order to modify the linker (or metal SBU), thereby altering the core framework post-synthetically.\textsuperscript{73} The ability to undertake such PSM processes is dependent upon the pore size to permit reagents to pass into the framework structure. The many applications that are possible with these frameworks are a direct result of their tailor-made functionalized framework and tunable pore sizes, which are dictated by the length of the organic linker and attached functional groups. The ability of MOFs to act as porous frameworks and uptake gases was established in the early 1990s, with many MOFs showing reversible gas sorption isotherms at low pressures and temperatures.\textsuperscript{74,75} The porous nature of many MOFs has attracted increasing interest in the past few decades with a diversity of applications, ranging from gas storage materials,\textsuperscript{65} sensors,\textsuperscript{76} drug delivery,\textsuperscript{77} and heterogenous catalysis,\textsuperscript{78} to developing coherent motion in molecular machines.\textsuperscript{79} Recent potential applications of these materials have included the use of
MOFs for applications involving supercapacitors, catalytic conversion, and even fuel cells.

1.2.4 Framework Flexibility

The rigidity of the MOF framework is strongly dependent upon the flexibility of the organic linkers and to a lesser degree the flexibility in coordination environment at the metal SBU. In 1998, the porosity of MOFs was classified into three categories, described as first, second and third generation MOFs (Figure 1.30):

First generation MOFs possess no permanent porosity and their frameworks irreversibly collapse upon removal of guest molecules.

Second generation MOFs reflect a much more stable and robust framework that retains its original porous structure even after guest removal.

Third-generation MOFs comprise flexible and dynamically porous materials, in which a structural transformation is observed following loss of guest molecules, but the process is reversible. Such third generation MOFs are often called soft porous crystals since they contain not only an extremely ordered overall network, but also some structural flexibility. The multi-stable nature of these systems enables them to display reversible transformability between states, permitting changes to both the shape and size of the pores of the framework to occur. The ability of third generation MOFs to distort their overall structure as a result of adsorption or desorption of various guest molecules is described as a ‘breathing effect,’ or gate-opening process, if the structural
transformation results in a large change in the internal volume of the pores of the framework. In particular, the MIL-88 series (MIL = Materials of Institut Lavoisier) is a remarkable example of a class of frameworks displaying this effect, where reports have shown the adsorption of various guests to cause the cell volume of the host framework to triple from its original size. Experiments have been conducted in an effort to maximize the use of this breathing property for practical applications, particularly in the health and life sciences field. Attempts to utilize the tunable and flexible nature of these frameworks were directed towards non-toxic Fe(III)-based MOFs, which were found to be effective carriers for controlled delivery of ibuprofen, as well as distributing anti-tumor drugs.

Figure 1.30: The three generations of metal-organic frameworks, adapted from [84]
1.2.5 The MIL-53 Series

The MIL-53 series of MOFs are third generation MOFs of formula \([M(OH)(BDC)]\) (BDC = benzene-1,4-dicarboxylate) where M is a trivalent metal ion \([M = Al, Cr, Fe, Ga, Sc, In, and V]\). To distinguish which metal ion is implemented, it is added to the framework name in parentheses, e.g. MIL-53(Al). The overall network of MIL-53 comprises corner-sharing \(MO_4(OH)_2\) octahedra linked through chelating BDC organic linkers and \(\mu_2-OH\) groups. The \(\mu_2-OH^-\) groups link \(M^{3+}\) ions together into linear chains in one dimension and the bridging \(BDC^{2-}\) anions cross-link these chains forming one-dimensional diamond-shaped rhombic channels. Despite the relative rigidity of the BDC linker (two torsional degrees of freedom) and the octahedral metal site, the MIL-53 series exhibits structural flexibility exhibiting reversible modification of the pore shape and size (Figure 1.31). This change in structure can be considered as a ‘wine-rack’ type mechanism in which there is conversion between a ‘collapsed’ or narrow-pore \((np)\) form and an ‘open’ or large pore \((lp)\) form.

![Figure 1.31: Breathing effect observed in MIL-53(Al, Cr) upon hydration and dehydration. Reproduced with permission from [93]](image-url)
MIL-53(Al) is central to work described later in this thesis, and is often prepared through hydrothermal synthesis,\textsuperscript{87,94} and initially contains a disordered array of BDC units and water molecules within the pores. Hydrogen bonding between host and guest leads to the narrow pore (\textit{np}) form of this framework. At elevated temperatures, the framework is dehydrated, and the absence of hydrogen-bonding guests allows the structure to relax to its large pore (\textit{lp}) form. As a result of the breathing nature of MIL-53(Al, Cr), interest has grown from the capacity to study these MOFs as potential adsorbents of carbon dioxide, methane, and hydrogen gas, particularly with the development of environmental health and a hydrogen economy.\textsuperscript{67} Studies have found MIL-53(Al, Cr) capable of adsorbing relatively large amounts of methane and carbon dioxide, which has also sparked the interest of utilizing these frameworks for further environmental applications, such as the sequestration of the greenhouse gas, CO\textsubscript{2}.\textsuperscript{95} The hydrated form of the MIL-53 framework was found to selectively adsorb CO\textsubscript{2} over CH\textsubscript{4}, and it was also reported that polar molecules in particular have an apparent effect on the overall flexibility of the framework, making it possible for the adsorption of varying greenhouse gases into the MIL-53 framework to be studied.\textsuperscript{67} In addition to the capability of adsorbing greenhouse gases, MIL-53(Al) also displays remarkable thermal stability, withstanding temperatures up to 500 °C.\textsuperscript{87} Due to its porous and flexible nature, numerous small molecules have successfully been included into the MIL-53(Al) framework, where the space group of the framework varies depending on the guest that has been included. The high temperature framework MIL-53(Al)-\textit{ht} adopts the orthorhombic \textit{Imma} space group, with parameters \(a = 6.608(1), b = 16.675(3), c = 12.813(2)\).\textsuperscript{87} Here the short crystallographic \(a\)-axis
corresponds to the Al-μ2-OH-Al chain direction and it is noteworthy that this parameter is relatively constant across all MIL-53(Al) structures, irrespective of guest. The space group as well as cell axes are modified as a result of adjusting the temperature or included guest molecules in the framework. Table 1 reflects the various reported space groups for MIL-53(Al) inclusion complexes. There is a common lowering of the overall crystal symmetry of the framework from orthorhombic to monoclinic, in an effort to accommodate potential guest molecules. This capability further emphasizes the flexible nature of this framework, not only at varying temperature but also following the inclusion of guest molecules directly into the pores of the framework.\textsuperscript{87}
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<td>(view down crystallographic c axis)</td>
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**Table 1.1: Reported space groups of MIL-53(Al) structures with various guests**
1.2.6 Radicals in Porous Crystalline Materials

The incorporation of guest molecules within porous coordination polymers offers the potential for novel materials with unique magnetic and electronic properties. In particular, MOFs incorporating paramagnetic materials such as radicals, exhibit the potential for one-dimensional conduction as well as the opportunity to probe low-dimensional magnetic phenomena and/or the opportunity (for paramagnetic or redox-active hosts) to probe electron-electron interactions between host and guest which might include magnetic interactions or even partial or complete (redox) charge transfer. In this way, MOFs incorporating radical species have the potential to be used in magnetic or electronic devices, molecular recognition, spin probes, and in chemical sensing. Studies by Faust and D’Alessandro have unveiled a number of modes of association for the various ways in which radical species can be included into the pores of a MOF. Their work has identified the first mode of radical incorporation known as a pendant radical, in which the radical guest is either terminally coordinated to the metal SBU or is appended to the organic linker (Figure 1.32). The second mode of radical association is referred to as a structurally integrated radical, where the radical is directly part of the organic linker. The final mode of radical association sees the radical not covalently bonded to the host framework, but rather acting as a discrete guest within the pores of the host framework.
1.2.7 Known Examples of Radicals in MOF Chemistry

The incorporation of radicals into the framework of MOFs is not well established. A recent review by Coronado in 2018 on the incorporation of magnetic functionalities into MOFs identified just 5 publications in which the radical was directly incorporated into the ligand of the MOF.\(^\text{104}\) Three of these studies were based on the work of Veciana who implemented the polychlorophenylmethyl tricarboxylic acid (ptmtcH\(_3\)) with d-block (Cu(II))\(^\text{105}\) or lanthanide ions ferromagnetic lanthanide-radical interactions.\(^\text{106}\) The simpler 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (Cl\(_2\)dhbq) ligand forms a crystalline honeycomb lattice with Fe(III) of formula (Me\(_2\)NH\(_2\))\(_2\)[Fe\(_2\)(Cl\(_2\)dhbq)\(_3\)]·2H\(_2\)O·6DMF in which solvent and dimethyl ammonium ions fill the pores.\(^\text{107}\) The solvated material exhibits
magnetic ordering below 80 K which is lowered upon desolvation to 26 K. The TCNQ radical anion has been extensively used as a bridging ligand but in only one example is the structure considered porous. The compound [{Ru$_2$(O$_2$CC$_6$H$_4$Cl)$_4$}$_2$TCNQ(OMe)$_2$]-CH$_3$Cl

(O$_2$CC$_6$H$_4$Cl = o-chlorobenzoate; TCNQ(OMe)$_2$ = 2,5-dimethoxy-7,7,8,8-tetracyanoquinodimethane) comprises two-dimensional layers of Ru$_2$(O$_2$CC$_6$H$_4$Cl)$_4$ paddlewheels, connected via TCNQ(OMe)$_2$ ligands. The compound is antiferromagnetic with $T_N = 75$ K. Removal of lattice CH$_3$Cl decreases the ordering temperature to 56 K but the structure can be resolvated by exposure to CH$_3$Cl vapour.$^{108}$ In all these cases the radical is structurally integrated into the MOF. Recent studies have described a pendant TEMPO radical based on UiO-68 which offers potential enhanced catalytic activity.$^{109}$

In contrast, inclusion of radicals as guests into porous crystalline materials has been slightly more extensively studied. Work conducted by Hulliger and Rawson examined the inclusion of thiazyl radicals within a porous non-covalent host framework, perhydrotriphenylene (PHTP) (Figure 1.33) through co-sublimation. Inclusion of the DTDA radical $p$-NCC$_6$H$_4$CNSSN within the PHTP framework revealed no evidence for magnetic communication between radicals within the channel due to the localized nature of the SOMO and dominant head-to-tail alignment of radicals within the channel.$^{110}$ Conversely EPR studies on the $\pi$-delocalized TTTA radical, C$_2$S$_3$N$_3$, incorporated within the channels of the PHTP host revealed the presence of exchange-coupled radicals within the host framework.$^{111}$ Kobayashi and coworkers also explored incorporation of radicals into non-covalent organic hosts and successfully included the nitronyl nitroxide radicals PhNN and $p$-NPNN (Figure 1.34) into CLPOT (2,4,6-tris(4-chlorophenoxy)-1,3,5-triazine)
nanochannels. EPR studies demonstrated the presence of spin-spin interactions between neighbouring $p$-NPNN molecules within the host nanochannels.\textsuperscript{112}
In 2011, work conducted by Poppl and coworkers illustrated the inclusion of nitroxide radicals into the framework $\text{Cu}_3(\text{BTC})_2$, also known as HKUST-1 (BTC$^\text{H}_3 = \text{benzene tricarboxylic acid, sym-C}_6\text{H}_3(\text{COOH})_3)$. EPR spectroscopy revealed that inclusion of the radical into the $\text{Cu}^{2+}$ framework generated an EPR silent ground state. Further analysis revealed ligand exchange is necessary, which affords the loss, or rather de-coordination, of at least one carboxylate oxygen.$^{113}$ In the same year, Potts and coworkers investigated the inclusion of two thiazyl radicals, benzodithiazolyl (BDTA) and methylbenzodithiazolyl (MBDTA), into the MIL-53(Al) host framework.$^{102}$ Structure solution from powder X-ray diffraction (Figure 1.35) found that the BDTA radical existed in its $\pi^* - \pi^*$ dimeric form within the pores of the framework, whereas the MBDTA radical retained its monomeric character within the pores as a direct result of the additional steric hindrance present in
this species. For both radicals, the inclusion complexes resulted in a change in the unit cell of the MIL-53(Al) framework upon inclusion (see Table 1). Additionally, the presence of the radicals within the pores resulted in the formation of new intermolecular interactions in the product inclusion complex, with hydrogen bonding occurring between the radical N and OH of the organic linkers of the framework, as well as $\pi$-$\pi$ interactions between the benzo-ring on the radical and the phenylene ring of the terephthalic acid from the host.\textsuperscript{102}

![Image of BDTA radical inclusion into MIL-53(Al)]

**Figure 1.35: Inclusion of BDTA radical into MIL-53(Al) via gas-phase diffusion, adapted from [102]**

As an extension of these studies, Cowley and coworkers explored the potential of incorporating thiazy1 radicals into porous materials. They incorporated the DTDA radical PhCNSSN into the zeolite faujasite (zeolite-Y).\textsuperscript{114} The red inclusion compound was found to be remarkably air sensitive and rapidly decolorized upon exposure to air. Elemental analysis revealed a high loading of radicals into the framework, but magnetic measurements indicated relatively low concentrations of radical within the zeolitic framework indicating that the majority of radicals form pancake-bonded dimers within the larger void spaces of the host lattice, whereas smaller pores held a preference for the
paramagnetic monomer form of the guest radical. More recently, Haynes studied the incorporation of DTDA radicals within a Cu metallocycle host (Figure 1.36).\textsuperscript{115} The bimetallic Cu metallocycle host has the formula $[\text{Cu}_2\text{L}_2\text{Cl}_4]$, comprising divalent Cu$^{2+}$ ions each bonded to two chloride anions and L is a bidentate ligand designed from imidazolyl groups attached by flexible methylene groups to an aromatic space moiety. The structure can be considered as a ‘molecular doughnut’ with accessible void space for guests and inclusion complexes formed with this host have found this host to be capable of adapting its cavity size via rotation of the imidazole rings to best fit a particular guest molecule.\textsuperscript{116}

Figure 1.36: Schematic of Cu metallocycle host (left), imidazolyl ligand of host (right) and crystal structure of PhCNSSN radical included into host (centre), adapted from [115]
The PhCNSSN radical guest was incorporated into the host via gas-phase diffusion. An observed compression of the Cu centre towards square planar was observed while simultaneously expanding along the Cu-Cu dimension and contracting along the phenylene···phenylene dimension to accommodate the radical guest. Subtle changes in the magnetic response were observed upon inclusion.

1.3 Thesis

This thesis focuses on developing new multi-component materials comprising thermally stable dithiadiazolyl (DTDA) and diselenadiazolyl (DSDA) radicals. Two approaches are employed; one comprising cocrystallization of DTDA and DSDA radicals with TEMPO and TEMPONE (Chapter 3) and the other based on inclusion chemistry using the MOF MIL-53(Al) (Chapter 2). The former chapter will focus on crystal engineering combinations of different radicals into new structures where the long-term objective is to prepare elusive organic ferrimagnets. The latter chapter extends previous studies of MIL-53(Al) host-guest chemistry to the new DTDA and DSDA guests PhCNEEN and C6F5CNEEN (E = S, Se), in particular examining how inclusion affects chemical reactivity of the guest molecules and how these could be developed into prototype chemical sensors for selected oxidants.
1.4 References


Chapter 2  Inclusion Chemistry of Main Group Radicals in MIL-53(Al)

2.1 Introduction

Porous inorganic-organic hybrid materials have attracted increasing interest in the past few decades with a range of applications including gas storage materials,\(^1\) sensors,\(^2\) drug delivery,\(^3\) heterogenous catalysis,\(^4\) and developing coherent motion in molecular machines.\(^5\) A range of different types of framework materials are also known and include well-known families such as metal-organic frameworks (MOFs),\(^6\) covalent organic frameworks (COFs),\(^7\) and hydrogen-bonded organic frameworks (HOFs).\(^8\) The redox behaviour of radicals has generated interest in their incorporation into such frameworks as paramagnetic struts in MOFs\(^9\) or as guest molecules within porous frameworks.\(^10\)

The many unique properties of dithiadiazolyl radicals have been well established, from their tendency to dimerize in the solid state\(^11\) to their interesting magnetic properties.\(^12\) Previous studies on the inclusion of dithiadiazolyl (DTDA) radicals in frameworks have focussed on the zeolitic alumino-silicate framework, faujasite, which was capable of accommodating diamagnetic dimers of the radical within the large cavities of the host,\(^10\) whereas inclusion complexes with the organic host PHTP suppresses dimerization, as a result of the decrease in cavity space.\(^13\) As an extension of these initial studies, new radical host-guest systems utilizing metal-organic framework (MOF) hosts offer great potential. From an electronic perspective there are many examples of isostructural MOFs comprising paramagnetic or diamagnetic metals, providing opportunities to examine both host-guest and guest-guest electronic interactions in a
systematic fashion. Recent studies have shown that the PhCNSSN radical could be incorporated into voids in the allegedly non-porous framework of a copper metallocycle through vacuum sublimation, suggesting the presence of a lattice breathing mode which temporarily opens up channels within the structure during host-guest generation.\textsuperscript{14} As an extension of these previous studies, this chapter consists of the inclusion and characterization of thiazyl and selenazyl radicals into the porous metal-organic framework host MIL-53(Al) via gas-phase sublimation.

2.2 Experimental

2.2.1 General Considerations

All reactions and resulting products were air and/or moisture sensitive and all reactions and manipulations were performed under inert conditions, with the use of a double manifold Schlenk line and MBraun LabMaster glove box. Filtrations were conducted under positive nitrogen pressure by means of cannula transfer, and solvents were obtained from a solvent purification system dried by molecular sieves, unless otherwise specified. MIL-53(Al) was synthesized with the use of a Biotage Initiator 1 microwave, with a synthetic methodology adapted from Loiseau \textit{et al.}\textsuperscript{15} and described below. Radicals \([\text{PhCNSSN}]_2,\textsuperscript{16} [\text{PhCNSeSeN}]_2,\textsuperscript{17} \text{[C}_6\text{F}_5\text{CNSSN}]_2,\textsuperscript{18} \text{and [C}_6\text{F}_5\text{CNSeSeN}]_2\textsuperscript{19} \) were prepared \textit{via} literature methods, with adaptations denoted below, and phase purity confirmed by PXRD.
2.2.2 Elemental Analysis (EA)

Elemental analyses were measured by combustion using a Perkin Elmer 2400 Series II CHNS/O Analyzer, operated in CHN mode. Samples of ca. 1.8-2.0 mg were sealed in aluminum capsules and weighed using a Perkin Elmer Ad-6 Autobalance located in a glove-bag under a nitrogen atmosphere.

2.2.3 Electron Pair Resonance (EPR) Spectroscopy

EPR spectra were obtained on a Bruker EMXplus X-band EPR spectrometer running at ca. 9.8 GHz, utilizing a highly sensitive cylindrical cavity fitted with a liquid nitrogen cryostat with a Eurotherm temperature control unit, along with a high precision microwave frequency counter. Both solid and solution samples were prepared in quartz tubes and solution simulations were made using Winsim, while anisotropic EPR spectra were simulated using PIP via the PIP4Win interface.

2.2.4 Differential Scanning Calorimetry (DSC)

DSC studies were performed on a Mettler Toledo DSC 822e. Samples of approximately 1.5 mg were hermetically sealed in pierced aluminum pans which were heated from 25 to 200 °C under a nitrogen atmosphere using a heating rate of 5 °C·min\(^{-1}\). Samples were then cooled back to 25 °C using a cooling rate of 5 °C·min\(^{-1}\). One minute isotherms were employed to stabilize the sample at each limiting low and high temperature.

2.2.5 Thermogravimetric Analysis (TGA)

TGA studies were conducted on (i) activated MIL-53(Al) (6.45 mg); (ii) PhCNSSN@MIL-53(Al) (8.51 mg); (iii) PhCNSeSeN@MIL-53(Al) (4.87 mg); (iv) C\(_6\)F\(_5\)CNSSN@MIL-53(Al) (4.487 mg), and (v) C\(_6\)F\(_5\)CNSeSeN@MIL-53(Al) (3.23 mg) as well as on (PhCNSSN)\(_2\) (4.24
mg), (PhCNSeSeN)$_2$ (4.22 mg), (C$_6$F$_5$CNSSN)$_2$ (3.20 mg) and (C$_6$F$_5$CNSeSeN)$_2$ (4.53 mg). The samples were maintained at 25 °C for 20 minutes prior to the heating cycle under a helium purged atmosphere from 25 to 500 °C with a heating rate of 5 °C·min$^{-1}$.

### 2.2.6 Powder X-Ray Diffraction (PXRD)

PXRD experiments on the air sensitive inclusion complexes were recorded on flame-sealed samples packed in 0.7 mm o.d. glass capillary tubes under nitrogen and were measured on a Bruker D8 Discover equipped with a Vantec-500 detector and GADDS software package and an Oxford Cryostream Plus variable temperature controller. PXRD profiles were obtained in the range 4.2° < 2θ < 40.0° and were recorded in 0.02° increments using Cu-K$_{α_1}$ radiation ($λ = 1.5418$ Å). The X-ray tube was operated at 40 kV and 40 mA with a collimated beam of 0.5 mm diameter. PXRD experiments on the synthesis and activation of MIL-53(Al) were undertaken on a PROTO AXRD Benchtop diffractometer with the XRDWIN software system operating at 30.0 kV and 20.0 mA. Measurements were obtained in the range 5.0° < 2θ < 50.0°, and were recorded in steps in the range 0.01 – 0.03 °. Approximately 25 mg of sample was packed on an amorphous PVC sample holder, and powder patterns were recorded at room temperature.

### 2.2.7 SQUID Measurements

Magnetic measurements were made on a sample of PhCNSSN@MIL-53(Al) (55.25 mg) and PhCNSeSeN@MIL-53(Al) (52.95 mg) from 1.8 – 300 K in an applied field of 1.0 T on a Quantum Design MPMS SQUID magnetometer (University of Zaragoza, Spain) by Prof. J. Campo and Dr. A. Arauzo.
2.2.8 Synthetic Methodology

2.2.8.1 Preparation of activated MIL-53(Al): Aluminum chloride hexahydrate (3.36 g, 13.88 mmol) and terephthalic acid (1.15 g, 6.94 mmol) were heated in distilled H₂O (15 mL) under microwave irradiation at 150 °C for 1 hr. The sample was filtered, rinsed with distilled H₂O (20 mL) and dried under dynamic vacuum at 200 °C for 4 days, forming MIL-53(Al)-as. Displacement of residual organic material in the channel structure was undertaken by microwave heating in DMF (10 mL) at 160 °C for 1 hr to generate MIL-53(Al)-DMF. The sample was filtered and washed with DMF (3 x 3 mL) and then the DMF was removed upon heating under dynamic vacuum at 150 °C for 3 days, yielding the activated MIL-53(Al)-ht whose PXRD profile was comparable to that found in the literature.¹⁵

EA: Calc. for C₈H₅O₅Al C 46.17%, H 2.42%, N 0.00%; Found C 45.83%, H 2.46%, N 0.00%.

IR (νmax/cm⁻¹): 1594 s (asymm. carboxylate), 1511m, 1409s (symm. carboxylate), 987vs, 837m, 752vs, 592vs, 472vs.

TGA (30 – 500 °C, 5 °C·min⁻¹): No mass loss to 500 °C.

2.2.8.2 Preparation of PhCNSSN@MIL-53(Al): [PhCNSSN]₂ (350 mg, 0.97 mmol) was sublimed under dynamic vacuum (90 °C, 10⁻² Torr) through a sample of activated MIL-53(Al) (350 mg, 1.68 mmol) supported on a glass sinter. Over the course of 5 hrs, the MIL-53(Al) changed colour from white to bright red, indicative of [PhCNSSN]₂ inclusion.

EA: Calc. for [C₈H₄O₄Al(OH)]·1/2C₇H₅N₂S₂: C 46.28%, H 2.54%, N 4.89%; Found C 45.61%, H 2.73%, N 4.93%.
IR ($\nu_{\text{max}}$/cm$^{-1}$): 1595s (asymm. carboxylate), 1508m 1410vs (symm. carboxylate), 1369m, 987s, 749vs, 653m, 590vs, 474vs, 445s

EPR (X-band, solid state, 298 K): $g_x = 2.0208$, $g_y = 2.0077$, $g_z = 2.0030$, $a_{Nx} = 0.5$, $a_{Ny} = 0.5$, $a_{Nz} = 14.5$ G.

HRMS (ASAP+, 200 °C) 181.9973 (M+H, calc. 181.9972).

2.2.8.3 Preparation of PhCNSeSeN@MIL-53(Al): [PhCNSeSeN]$_2$ (200 mg, 0.36 mmol) was sublimed under dynamic vacuum (100 °C, 10$^{-2}$ Torr) through a sample of activated MIL-53(Al) (200 mg, 0.96 mmol) supported on a glass sinter. A gradual colour change in the activated MIL-53(Al) was observed from white to bright purple over 5 hrs, indicative of [PhCNSeSeN]$_2$ inclusion.

EA: Calc. for [C$_8$H$_4$O$_4$Al(OH)]·1/5C$_7$H$_5$N$_2$Se$_2$: C 42.93%, 2.30%, 2.13%; Found C 42.46%, 2.70%, 2.17%

IR ($\nu_{\text{max}}$/cm$^{-1}$): 1569s (asymm. carboxylate), 1509m, 1411vs (symm. carboxylate), 993m, 752s, 590vs, 474vs

EPR (X-band, solid state, 298 K): $g_x = 2.0980$, $g_y = 2.0216$, $g_z = 1.9990$, $a_N = 5.73$ G, $a_{Se} = 81.6$ G.

HRMS: (ASAP+, 200 °C) 277.8863(M+H, calc. 277.8861)

2.2.8.4 Preparation of C$_6$F$_5$CNSSN@MIL-53(Al): [C$_6$F$_5$CNSSN]$_2$ (80 mg, 0.30 mmol) was sublimed under dynamic vacuum (40 °C, 10$^{-2}$ Torr) through a sample of activated MIL-53(Al) (80 mg, 0.38 mmol) supported on a glass sinter. A gradual colour change in the activated MIL-53(Al) was observed from white to bright orange-red over 5 hrs, indicative of [C$_6$F$_5$CNSSN]$_2$ inclusion.
IR ($\nu_{\text{max}}$/cm$^{-1}$): 1599s (asymm. carboxylate), 1412vs (symm. carboxylate), 989m, 751s

EPR (X-band, solid state, 298 K): $g_x = 2.0200$, $g_y = 2.0068$, $g_z = 2.0027$, $a_Nx = 0$ G, $a_Ny = 0$ G, $a_Nz = 14.1$ G.

HRMS: (ASAP+, 200 °C) 271.9496 (M+H, calc. 271.9506)

2.2.8.5 Preparation of C$_6$F$_5$CNSeSeN@MIL-53(Al): [C$_6$F$_5$CNSeSeN]$\_2$ (100 mg, 0.27 mmol) was sublimed under dynamic vacuum (95 °C, 10$^{-2}$ Torr) through a sample of activated MIL-53(Al) (100 mg, 0.48 mmol) supported on a glass sinter. A gradual colour change in the activated MIL-53(Al) was observed from white to deep purple over 5 hrs, indicative of [C$_6$F$_5$CNSeSeN]$\_2$ inclusion.

IR ($\nu_{\text{max}}$/cm$^{-1}$): 1597s (asymm. carboxylate), 1413vs (symm. carboxylate) 1000m, 750s

EPR (X-band, solid state, 298 K): $g_x = 2.098$, $g_y = 2.016$, $g_z = 2.002$.

2.2.8.6 Chlorination of Inclusion Compounds: Chlorination of each inclusion compound was achieved by placing each inclusion complex under a dynamic atmosphere of chlorine for 12 hrs, followed by a static flow of chlorine for a further 12 hrs. Through the course of the chlorination, PhCNSSN@MIL-53(Al) changed colour from bright red to deep yellow, PhCNSSeN@MIL-53(Al) changed colour from bright purple to pale yellow, while C$_6$F$_5$CNSSN@MIL-53(Al) and C$_6$F$_5$CNSSeN@MIL-53(Al) both changed colour to grey-yellow. Chlorination could also be achieved by placing a sample of the inclusion compound on a glass sinter over a small volume of SO$_2$Cl$_2$ (ca. 1 – 2 mL), sealing the system under static vacuum and heating to 55 °C. In all cases, the resulting chlorinated compounds were found to be EPR silent, consistent with complete oxidation of the included radicals.
**EA:** Calc. for 0.33PhCNSSNCl@MIL-53(Al) C 44.31%, H 2.40%, N 3.31%; Found C 42.88%, H 2.81%, N 3.29%

Calc. for 0.19PhCNSeSeNCl@MIL-53(Al) C 41.97%, H 2.25%, N 1.99%; Found C 38.00%, H 2.22%, N 1.98%

**2.2.8.7 Bromination of Inclusion Compounds:** Bromination of each inclusion compound was achieved by placing each inclusion compound under a bromine atmosphere (ca. 15 mL of bromine at room temperature) for ca. 8 hrs. During this time each inclusion complex changed colour to a deep red-brown. The resulting red-brown compounds were all found to be EPR silent, consistent with complete oxidation of each included radical.

**EA:** Calc. for 0.33PhCNSSNBr@MIL-53(Al) C 42.10%, H 2.28%, N 3.14%; Found C 39.95%, H 2.34%, N 3.01%

Calc. for 0.19PhCNSeSeNBr@MIL-53(Al) C 40.69%, H 2.18%, N 1.93%; Found C 40.70%, H 2.15%, N 0.58%

**2.2.8.8 Iodination of Inclusion Compounds:** A small sample (ca. 20 mg) of each inclusion compound was mounted on a glass sinter over a small quantity of iodine chips, sealed under static vacuum, and heated to 40 °C for 18 hrs. Over the course of the reaction, a colour change was observed for each inclusion complex to dark purple. Following iodination, each inclusion complex was found to be EPR active in the solid state, consistent with incomplete oxidation state of each radical in the framework.

**EA:** Calc. for 0.33PhCNSSN(1/3I)@MIL-53(Al): C 43.96%, H 2.38%, N 3.28%; Found C 42.88%, H 2.71%, N 3.29%
Calc. for 0.19PhCNSeSeN\textsubscript{3} C 33.69%, H 1.80%, N 1.60%; Found C 33.91%, H 2.00%, N 1.70%

**EPR:** PhCNSSN@MIL-53(Al): \(g_x = 2.0200, g_y = 2.0050, g_z = 2.0027\); \(a_{Nx} = 0\ G, a_{Ny} = 0\ G, a_{Nz} = 14.1\ G\).

PhCNSeSeN@MIL-53(Al): \(g_x = 2.0980, g_y = 2.0190, g_z = 1.9970\); \(a_{Nx} = 0\ G, a_{Ny} = 0\ G, a_{Nz} = 14.2\ G, a_{Sex} = 36\ G, a_{Sey} = 54\ G, a_{Sez} = 115\ G\).

\(\text{C}_6\text{F}_5\text{CNSSN@MIL-53(Al): } g_x = 2.02, g_y = 2.0067, g_z = 2.0027; a_{Nx} = 0\ G, a_{Ny} = 0\ G, a_{Nz} = 14.1\ G\).

\(\text{C}_6\text{F}_5\text{CNSeSeN@MIL-53(Al): } g_x = 2.098, g_y = 2.017, g_z = 1.996; a_{Nx} = 0\ G, a_{Ny} = 0\ G, a_{Nz} = 14.2\ G, a_{Sex} = 36\ G, a_{Sey} = 58\ G, a_{Sez} = 115\ G.\)

### 2.2.9 Structure Solution of PhCNSeSeN@MIL-53(Al) from PXRD Data

The unit cell was identified as Imma by comparison of the experimental powder profile with calculated peak positions based on previously reported structures. The unit cell parameters were then optimized through a Pawley refinement within Expo2014.\textsuperscript{22} A study of previous studies on MIL-53(Al) inclusion complexes in the Imma space group revealed that although the formula of the framework is Al(BDC)(OH), there are just 6 non-H atoms in the asymmetric unit with four of the six host atoms located on special positions; the \(\mu_2\)-OH is located on a special position (s.o.f. = 0.5), the crystallographically unique Al is on an inversion centre (s.o.f. = 0.25), the carboxyl C atom is on a special position (s.o.f. = 0.5), as is the C atom at the 1-position of the phenylene ring. In addition, the phenylene ring centroid is also located on a special position and a dummy atom (H with s.o.f. = 0) was included at this position for the purposes of structure solution. Structure solution within
DASH$^{23}$ implemented a rigid body search using the asymmetric unit (plus the dummy H atom) in which the Al was fixed to the known coordinates (0.25, 0.75, 0.25) and refined with the Al···π centroid (dummy H atom) vector restricted to align parallel to the (1 1 -1) direction such that the ring centroid would be located on a special position. This provided a satisfactory solution for the framework structure. Several of the atoms in the asymmetric unit were located just off their idealized special positions and the ‘correct’ site was determined by averaging the two sets of coordinates which were located at either side of the expected symmetry element. Having determined the framework structure, all six crystallographically independent non-H atoms of the host framework were fixed and a subsequent round of simulated annealing was employed using a model PhCNSeSeN molecule. The model permitted the coordinates and orientation of the molecule to be freely refined along with the torsion angle between phenyl and diselenadiazolyl rings. The site occupancy of the PhCNSeSeN radical was restricted to 0.05 to fit the experimentally determined composition, 0.2PhCNSeSeN@MIL-53(Al). The high symmetry of the Imma space group affords multiple symmetry elements (2$_1$ screw axis, inversion centres, glide and mirror planes) along the channel direction and all solutions revealed substantial disorder of the guest along the channel direction.
2.3 Results and Discussion

2.3.1 Synthesis of DTDA and DSDA Radicals

Four main group radicals, PhCNSSN, PhCNSeSeN and their fluorinated analogues C₆F₅CNSSN and C₆F₅CNSeSeN, were prepared according to the standard literature procedures (Scheme 2.1). For both DSDA derivatives, SeCl₂ was prepared *in situ* using a 1:1 mole ratio of SeCl₄ and elemental Se in Et₂O. The radicals were purified by vacuum sublimation and characterized by solution EPR and solid state PXRD to establish phase purity. Due to the decrease in volatility of the selenium analogues (in comparison to the sulfur derivatives), sublimation temperatures were much higher for the selenazyl radicals, ranging from 95 – 125 °C.

![Scheme 2.1: General Synthetic Route for DTDA and DSDA radicals (E = S, Se)](image)

2.3.2 Preparation of MIL-53(Al) via Microwave Synthesis

Initial reactivity studies utilized commercial MIL-53(Al) (Sigma Aldrich). While inclusion of radical guest species was successful, sample crystallinity was poor, reflected in broad, poorly resolved peaks in the PXRD profile. To circumvent this problem, MIL-53(Al) with
substantially higher crystallinity was prepared via a microwave-assisted synthesis (Scheme 2.2), adapted from the literature method.\textsuperscript{15} Removal of excess terephthalic acid from the initial “as-synthesised” material, MIL-53(Al)-as, was achieved by thermal annealing at 200°C under dynamic vacuum for 4 days. Microwave treatment of this sample in DMF and subsequent washing in DMF, followed by heating under dynamic vacuum for a further 3 days formed the activated, high temperature phase of MIL-53(Al)-ht. The changes in the PXRD profile after each step in the synthesis reflect the changes in the structure of the framework (Figure 2.1). The PXRD profile for the final activated form of the framework, MIL-53(Al)-ht, agreed well with the literature (Figure 2.2).

\[
\text{AlCl}_3 \cdot 6\text{H}_2\text{O} + \text{OH} \rightarrow \text{MIL-53(Al)-as}
\]

\[
\text{MIL-53(Al)-as} \rightarrow \text{MIL-53(Al)\cdot nDMF}
\]

\[
\text{MIL-53(Al)-ht} \rightarrow \text{MIL-53(Al)-ht}
\]

\[
\text{Scheme 2.2: Synthesis of MIL-53(Al)}
\]
MIL-53(Al)-as  'as prepared' initial sample of MIL-53(Al)
MIL-53(Al)-as+200°C  'as prepared' sample, followed heating at 200°C for 4d.
MIL-53(Al)-DMF  MIL-53(Al)-as+200°C, followed by microwave heating in DMF at 160°C for 1h.
MIL-53(Al)-ht  MIL-53(Al)-DMF after heating for 3d at 150°C

**Figure 2.1: Powder X-Ray Diffraction patterns at various stages of MOF synthesis**

**Figure 2.2: Comparison of experimental and predicted PXRD profiles for MIL-53(Al)-ht**
2.3.3 Inclusion of (PhCNSSN)$_2$ into MIL-53(Al)

Previous work successfully exploited the volatility of DTDA radicals to include them as guests into host frameworks via gas-phase diffusion. An optimized approach to loading radicals into these frameworks through such diffusion process is illustrated in Figure 2.3 in which the volatile radical is placed in the lower flask and the porous host framework is located on top of the glass sinter. The system, up to and including the host framework, is then immersed into a Kugelruhr, placed under vacuum and the system heated until the radical becomes volatile. The radical is initially trapped as a guest in the host framework but, once saturated, excess radical crystallizes above the host and the reaction is terminated.

![Diagram of inclusion process]

Figure 2.3: General setup used for inclusion chemistry, exemplified by inclusion of PhCNSSN into MIL-53(Al)
2.3.3.1 Progress of Inclusion: A small vial containing freshly sublimed black-green dichroic crystals of [PhCNSSN]$_2$ was sublimed into activated MIL-53(Al) at 90°C under dynamic vacuum. Over the course of five hours, the activated framework slowly changed colour from white to bright red (Figure 2.4), indicating inclusion of the PhCNSSN radical into the MIL-53(Al) lattice. The observed colour change in the MOF host, along with crystallization of [PhCNSSN]$_2$ on the glass walls above the host heralded saturation of the MIL-53(Al) framework.

![Figure 2.4: Progress of inclusion of PhCNSSN into the MIL-53(Al) framework](image)
2.3.3.2 PXRD Studies: Powder X-ray diffraction studies on the inclusion complex PhCNSSN@ MIL-53(Al) revealed the absence of any [PhCNSSN]$_2$ (which shows multiple features below 8°) and significantly more structural features than MIL-53(Al)-ht (Figure 2.5). The peak positions of the inclusion complex match very well those of the activated framework, albeit with significantly different intensities. This is consistent with the inclusion complex adopting a similar unit cell to the MIL-53(Al)-ht host but with the differing intensities reflect differing unit cell contents, consistent with the incorporation of the [PhCNSSN]$_2$ guest radical into the framework.

![Figure 2.5](image)

**Figure 2.5: PXRD patterns of PhCNSSN@MIL-53(Al) (bottom), MIL-53(Al)-ht (middle) and [PhCNSSN]$_2$ (top)**
The powder pattern of the inclusion complex was indexed on the orthorhombic space group Imma by initial comparison of peak positions with those predicted based on the different known structures of MIL-53(Al) inclusion complexes.\textsuperscript{15,23-26} The unit cell was then optimized using a Pawley refinement within DASH,\textsuperscript{23} which replicated all the major features of the experimental powder pattern, but also revealed a small number of unindexed low intensity features which were too weak to unambiguously index. It is notable that all MIL-53(Al) inclusion complexes exhibit a common 6.6 Å cell axis, corresponding to the channel direction. For the Imma space group this corresponds to the crystallographic $a$-axis. However, there is some variation in the crystallographic $b$ and $c$ axes which can be considered to correspond to an opening/closing breathing mode of the pores. The rigidity of the cross-braced (‘wine-rack’) framework means that a decrease in the crystallographic $b$-axis is reflected in a corresponding increase in the $c$-axis and vice versa. This is depicted in Figure 2.6 where the crystallographic $b$ and $c$ parameters follow a linear correlation. While the refined unit cell parameters for PhCNSSN@MIL53(Al) nicely fit this relationship, the parameters are at the extrema of previously reported structures which may suggest some build-up of strain within the lattice to accommodate the radical. In order to determine the structure of PhCNSSN@MIL53(Al), the position of the host framework within the unit cell was first determined and the site occupancy of the PhCNSSN molecule (0.27) estimated from the best fit to the peak intensities, providing a molecular composition of 0.27PhCNSSN@MIL-53(Al). Notably the framework contributes significantly to the (0 1 1) reflection at 8.8° whereas the guest contributes significantly to the (0 2 0) reflection at 10.4° (Figure 2.6). The site occupancy based on the fit to the PXRD
profile agrees well with the s.o.f. of 0.27 based on the elemental analysis data for a sample drawn from the same batch of PhCNSSN@MIL53(Al). The presence of multiple symmetry elements along the channel direction leads to substantial radical disorder along the channel direction.

Figure 2.6: (left) Correlation between crystallographic $b$ and $c$ axes for MIL-53(Al) inclusion complexes in the orthorhombic space group Imma; (right) packing of MIL-53(Al)-ht based on the unit cell of PhCNSSN@MIL-53(Al) viewed down the crystallographic $a$ axis, highlighting the (0 1 1) and (0 2 0) planes
2.3.3.3 High Resolution Mass Spectrometry (HRMS): High resolution mass spectra (Figure 2.8) on the PhCNSSN@MIL-53(Al) inclusion complex in ASAP+ mode revealed M+H ions at 181.9973 (calc. 181.9972) for the guest radical upon heating the inclusion complex to 200 °C, suggesting the radical guest becomes volatile at elevated temperatures, an observation subsequently confirmed via variable temperature-PXRD and TGA studies (see later). An additional feature at m/z = 104 can be assigned to protonated benzonitrile as a breakdown product [PhCN+H at 104.0502, calc. 104.0500].

Figure 2.7: PXRD patterns of the PhCNSSN inclusion complex (bottom), the simulated powder pattern of the inclusion complex from the solved structure (middle), and the simulated pattern of the solved empty pore MIL-53(Al)-ht framework (top)
2.3.3.4 EPR Spectroscopy: X-band EPR studies on the PhCNSSN@MIL-53(Al) inclusion complex were conducted at room temperature (Figure 2.9). The substantial line broadening points to a relatively high concentration of radicals within the host framework, while the anisotropy suggests limited molecular motion of the radicals within the framework on the EPR timescale. The simulation parameters (Table 2.1) obtained for this spectrum are comparable to values for the PhCNSSN radical found in the literature.27
Table 2.1: EPR simulation parameters for PhCNSSN@MIL-53(Al) in comparison with previously reported data on PhCNSSN measured in a frozen d₈-toluene matrix.

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2.3.3.5 Differential Scanning Calorimetry (DSC) Studies: DSC studies on [PhCNSSN]₂, pristine MIL-53(Al)-ht, and PhCNSSN@MIL-53(Al) were obtained in an effort to characterize the thermal behaviour of the inclusion complex. The DSC profile for [PhCNSSN]₂ (Figure 2.10) reveals a melt at 117 °C with subsequent recrystallization from the melt at 76 °C, in good agreement with literature data.¹⁶ MIL-53(Al)-ht reveals no significant thermal events upon heating to 200 °C, which also matches the known literature data for this framework.¹⁵ PhCNSSN@MIL-53(Al) similarly exhibits no significant
thermal change occurring across the range 30 – 200 °C, consistent with the absence of pristine [PhCNSSN]₂ on the surface of the framework.

![DSC profiles](image)

**Figure 2.10: DSC profiles of [PhCNSSN]₂ (top left), MIL-53(Al)-ht (top right), and PhCNSSN@MIL-53(Al) (bottom)**

2.3.3.6 **Thermogravimetric Analysis (TGA):** TGA analysis of the inclusion complex was studied in relation to the activated MIL-53(Al) host and (PhCNSSN)₂ guest to further probe its thermal stability. TGA data on activated MIL-53(Al) confirmed the known robustness of this framework, showing no mass loss to 500 °C (Figure 2.11). For (PhCNSSN)₂ mass loss (sublimation) starts below 100 °C with essentially complete mass loss by 300 °C, consistent with its known volatility. A subtle change in gradient is observed around 230 °C.
which may be attributed to the onset of a second process. The residual mass (ca. 10%) likely arises from some degree of decomposition competing with sublimation at elevated temperatures. For PhCNSSN@MIL-53(Al) mass loss begins around 150 °C, significantly higher than [PhCNSSN]₂, indicating an increased thermal stability of the radical as a result of inclusion into the MIL-53(Al) framework. Although mass loss is incomplete by 500 °C, the weight loss of 21% provides a lower limit to the loading of radical into the framework of ca. 0.33PhCNSSN@MIL-53(Al), in agreement with elemental analysis and fitting of the PXRD profile.

Figure 2.11: TGA profile for [PhCNSSN]₂ (black), PhCNSSN@MIL-53(Al) (red), and MIL-53(Al)-ht (grey)
2.3.3.7 SQUID Analysis: SQUID dc magnetometry measurements on PhCNSSN@MIL-53(Al) (55.25 mg) were made from 1.8 – 300 K in an applied field of 1.0 T. The molecular weight of the inclusion complex was estimated through a combination of elemental analysis, PXRD fitting of the radical site occupancy factor, and TGA data as approximately 0.33PhCNSSN@MIL-53(Al) (MW = 806 g mol⁻¹ per radical). Data points in the vicinity of 50 K were omitted due to O₂ contamination. PhCNSSN@MIL-53(Al) exhibits Curie-Weiss behaviour with C = 0.033 emu⋅K⋅mol⁻¹, corresponding to just 9% of that expected for an S = ½ paramagnet (0.375 emu⋅K⋅mol⁻¹) (Figure 2.12), indicating the majority of PhCNSSN radicals form π*-π* dimers within the channels of the host framework. The Weiss constant (+0.66 K) indicates negligible interactions between these magnetically dilute S = ½ spins.

Figure 2.12: Temperature dependence of (left) 1/χ and (right) χT for PhCNSSN@MIL-53(Al)
2.3.3.8 Variable Temperature PXRD Studies: A sample of PhCNSSN@MIL-53(Al) was heated on a PROTO AXRD temperature stage from room temperature to 400 °C with PXRD patterns collected at 25 °C intervals. A stack plot is shown in Figure 2.13 and reveals a decrease in the (0 2 0) reflection at 10.4° and an enhancement of the (0 1 1) reflection around 8.8°, consistent with the elimination of the radical guest from within the host framework. Sequential fitting of each PXRD profile to the Imma cell reveal an unusual evolution in the cell parameters between room temperature and 225 °C (Table 2.2, Figure 2.14), which is also clearly manifested in the temperature dependence of the position of the (0 2 0) reflection as well as peaks around 15 and 17.5°. The temperature dependence of the unit cell parameters and cell volume clearly reveal a structural change in the range 100 – 200 °C, with a maximum cell volume at 175 °C, before the MOF returns to its closed pore geometry. The temperature window for this structural change follows the observed TGA data well, where the onset of PhCNSSN elimination from the host lattice occurs around 150 °C. This suggests that loss of radical is accompanied by an opening of the framework structure, with the structure collapsing down again after elimination of the radical from the framework. Additionally, the inclusion complex changes colour upon heating to 400 °C from bright red to white, also consistent with the loss of all PhCNSSN that was loaded within the framework, leaving behind pristine MIL-53(Al).
Table 2.2: Unit cell parameters for PhCNSSN@MIL-53(Al) based on the Imma space group, along with the refined profile residuals for temperatures in the range 25 – 250 °C.

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Figure 2.13: Variable temperature PXRD profiles for PhCNSSN@MIL-53(Al) from room temperature to 400°C
2.3.3.9 Chemical Removal of Radical Guest: Addition of solvents in which the radical is soluble leads to rapid leaching of the radical from the MIL-53(Al) lattice, suggesting guest···solvent interactions are at least comparable with host···guest interactions, although entropy likely plays a contributing role in this process. Solution EPR studies were undertaken on a sample of PhCNSSN@MIL-53(Al) suspended in CH₂Cl₂. This afforded an EPR spectrum comprising an isotropic 1:2:3:2:1 pentet \( (g = 2.0102, a_N = 5.12 \text{ G}) \), consistent with free PhCNSSN in solution rather than immobilized within the host lattice (Figure 2.15).

Figure 2.14: (left) Temperature dependence of the unit cell parameters of PhCNSSN@MIL-53(Al) upon heating; (right) correlation of crystallographic \( b \) and \( c \) axes upon heating (red circles) in relation to known cells for the Imma setting of MIL-53(Al) inclusion compounds (open circles)
2.3.4 Inclusion of [PhCNSeSeN]$_2$ in MIL-53(Al)

2.3.4.1 Progress of Inclusion: The inclusion of [PhCNSeSeN]$_2$ into the MIL-53(Al) framework was carried out in a similar fashion to the inclusion of PhCNSSN, with an observable colour change of the host from white to bright purple upon heating to 100 °C under dynamic vacuum for five hours (Figure 2.16).
2.4.3.2 PXRD Studies: PXRD analysis of PhCNSeSeN@MIL-53(Al) reveals the absence of any [PhCNSeSeN]$_2$ based on a comparison with predicted PXRD patterns (Figure 2.17). The powder pattern for this inclusion complex was indexed on the orthorhombic space group Imma, comparable to MIL-53(Al)-ht, by an initial comparison of peak positions with those predicted based on the different known structures of the MIL-53(Al) inclusion complexes.
Notably the impurity peak at $9.5^\circ$ and other weak high angle reflections are diagnostic of the monoclinic Cc phase of MIL-53(Al) and this tentative assignment is supported by VT PXRD studies described later. The unit cell parameters of PhCNSeSeN@MIL-53(Al) were optimized using a Pawley refinement starting from a known Imma cell within Expo2014 (Figure 2.18). The coordinates of the host lattice were determined using a simulated annealing process within DASH, and a second round of simulated annealing undertaken to locate the radical guest within the lattice, fixing the site occupancy of the guest PhCNSeSeN molecule to fit the chemical composition based on analytical data. The structure derived from this simulated annealing is shown in Figure 2.19.

Figure 2.17: PXRD patterns of PhCNSeSeN@MIL-53(Al) (bottom), MIL-53(Al)-ht (middle), and [PhCNSeSeN]$_2$ (top)
Figure 2.18: Pawley refinement of PhCNSeSeN@MIL-53(Al) with Miller indices for low angle reflections assigned. Features attributable to the impurity Cc space group are marked with an asterisk (*) [Experimental (+), simulation (---) and difference (bottom)].

Figure 2.19: Structure of PhCNSeSeN@MIL-53(Al) determined from simulated annealing of the PXRD profile.
2.3.4.3 High Resolution Mass Spectrometry (HRMS): High resolution mass spectrometry studies on the PhCNSeSeN@MIL-53(Al) inclusion complex in ASAP+ mode revealed M+H ions upon heating the inclusion complex to 200 °C, suggesting the radical guest becomes labile at elevated temperatures, an identical observation to that seen previously for the PhCNSSN@MIL-53(Al) inclusion complex. Not only can the [PhCNSeSeN+H]^+ ion be assigned based on the accurate mass (277.8863, calc. 277.8861) but also through the isotope distribution pattern (Figure 2.20).

![HRMS spectrum](image1.png)

**Figure 2.20:** (top) HRMS spectrum (ASAP+, 200 °C) of PhCNSeSeN@MIL-53(Al): ([PhCNSeSeN+H] calc. 277.8861); (bottom) computed isotope distribution pattern for [PhCNSeSeN+H]
2.3.4.4 EPR Spectroscopy: The EPR spectra of PhCNSeSeN@MIL-53(Al) exhibits a rhombic EPR spectrum with an even greater level of g-tensor anisotropy when compared to PhCNSSN@MIL-53(Al). This is expected for the inclusion of heavier p-block elements in which the spin-orbit coupling constant scales as $Z^4$ and gives rise to greater deviations from the free electron value, $g_e (g_e = 2.0023)$.\textsuperscript{27} Notably the second derivative plot of the PhCNSeSeN@MIL-53(Al) complex clearly reveals hyperfine coupling to two equivalent $^{14}$N nuclei (Figure 2.21). Both the hyperfine couplings and g-tensor parameters obtained for the inclusion complex (Table 2.3) are comparable to the literature values for the PhCNSeSeN radical\textsuperscript{17} and point to inclusion of the radical within the host framework through vacuum sublimation.

![Figure 2.21: Room temperature X-band solid state EPR spectra of PhCNSeSeN@MIL-53(Al): (left) first derivative spectrum; (right) second derivative EPR spectrum](image)

The spectrum of PhCNSeSeN@MIL-53(Al) is much sharper than that observed for the PhCNSSN inclusion complex, which indicates a lower radical concentration since dipolar coupling (which scales as $r^3$)\textsuperscript{28} is a significant contributor to the EPR linewidth. The EPR parameters are comparable to those previously reported for PhCNSeSeN.\textsuperscript{17}
2.3.4.5 DSC Studies: The DSC profile for [PhCNSeSeN]₂ (Figure 2.22; top left) reveals an endothermic melting at 187°C, consistent with the literature data for this main group radical.²⁹ MIL-53(Al)-ht again exhibits no significant thermal events upon heating to 200°C, and the selenium inclusion complex similarly exhibits the same thermal stability across the range 30 – 275 °C, consistent with the absence of pristine [PhCNSeSeN]₂.

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Table 2.3: Simulation parameters for the EPR Spectrum of PhCNSeSeN@MIL-53(Al) and comparison with those reported for a frozen solution of PhCNSeSeN.

Figure 2.22: DSC profiles of [PhCNSeSeN]₂ (top left), MIL-53(Al)-ht (top right), and PhCNSeSeN@MIL-53(Al) (bottom right)
**2.3.4.6 TGA Analysis:** To further probe the thermal stability of PhCNSeSeN@MIL-53(Al), TGA studies were conducted. (PhCNSeSeN)_2 commences mass loss at 180 °C, consistent with vaporization of the radical. Mass loss continued up to 440 °C in a stepped fashion suggesting one or more thermal processes alongside vaporization. The residual mass (10%) suggests some thermal degradation at elevated temperatures to form less volatile species. MIL-53(Al) shows negligible mass loss to 500 °C. For the inclusion complex, PhCNSeSeN@MIL-53(Al), there is no mass loss until ca. 240 °C, somewhat higher than PhCNSSN@MIL-53(Al), suggesting stronger host-guest interactions in the selenium analog. By 500 °C mass loss is still incomplete at 22%. Nevertheless, this provides a lower limit for radical loading from which a stoichiometry of 0.2PhCNSeSeN@MIL-53(Al) can be estimated, in good agreement with elemental analysis data. The inclusion complex changes colour upon heating to 400 °C from bright purple to white, also consistent with the loss of all [PhCNSeSeN]_2 that was loaded within the framework, leaving behind pristine MIL-53(Al)-ht.

![Figure 2.23: TGA profile for MIL-53(Al)-ht (top), PhCNSeSeN@MIL-53(Al) (middle), and [PhCNSeSeN]_2 (bottom)](image-url)
2.3.4.7 SQUID Analysis: Magnetic measurements were made on a sample of PhCNSeSeN@MIL-53(Al) (52.95 mg) from 1.8 – 300 K in an applied field of 1.0 T. Chemical formulae of 5 MIL-53(Al) : 1 PhCNSeSeN were employed for data analysis (MW = 1315.57 g mol\(^{-1}\)) based on elemental analysis and TGA data. A diamagnetic correction was applied to give the best fit to Curie-Weiss behaviour up to 250 K. A plot of \(\frac{1}{\chi}\) vs T (Figure 2.24) similarly shows the sample obeys Curie-Weiss behaviour with \(C = 0.131\) emu·K·mol\(^{-1}\) and \(\Theta = -0.93\) K. These values correspond to ca. 35% of the spins being monomeric, a significant increase over the PhCNSSN inclusion complex, although the Weiss constant again indicates a lack of significant magnetic communication between the residual paramagnetic centres.

![Figure 2.24](image-url)
2.3.4.8 Variable Temperature PXRD Studies: A sample of PhCNSeSeN@MIL-53(Al) was heated on a PROTO AXRD temperature stage from room temperature to 400 °C with PXRD patterns collected at 25 °C intervals. In contrast to PhCNSSN@MIL-53(Al), the temperature dependence of the PXRD profiles and unit cell parameters show no significant structural change in the range 150 – 275 °C. This suggests that radical loss is not accompanied by a change in pore conformation. It is noteworthy that the impurity phase (monoclinic Cc phase of MIL-53(Al)), reflected in the low intensity peak at 9.5° (as well as additional low intensity high angle reflections) disappears on heating above 250 °C. This is in agreement with the conversion of the MIL-53(Al)-lt phase to MIL-53(Al)-ht previously described by Loiseau.\textsuperscript{15}

Figure 2.25: Variable temperature PXRD profiles for PhCNSeSeN@MIL-53(Al) from room temperature to 400°C
2.3.4.9 **Chemical removal of radical guest:** The PhCNSeSeN@MIL-53(Al) inclusion complex was suspended in both CH$_2$Cl$_2$ and THF. Unlike PhCNSSN@MIL-53(Al) where the radical is extracted from the framework structure, reflected in the observation of an isotropic EPR spectrum, PhCNSeSeN@MIL-53(Al) continues to exhibit a classical anisotropic spectrum, consistent with the retention of the radical within the framework, suggesting that host···guest interactions are stronger than guest···solvent interactions (Figure 2.26).

![EPR spectra](image)

**Figure 2.26:** Room temperature X-band solution EPR spectrum of PhCNSeSeN in CH$_2$Cl$_2$ (left) and PhCNSeSeN@MIL-53(Al) suspended in CH$_2$Cl$_2$ (right)

2.3.5 **Inclusion of [C$_6$F$_5$CNSSN]$_2$ into MIL-53(Al)**

**2.3.5.1 Progress of Inclusion:** In order to extend initial reactivity studies, the phenyl derivatives PhCNSSN and PhCNSeSeN were replaced by more volatile perfluorophenyl derivatives which are more volatile and offer alternative sets of host···guest intermolecular interactions. The inclusion of [C$_6$F$_5$CNSSN]$_2$ into MIL-53(Al) was carried out
in a similar fashion, with an observable colour change of the host from white to bright orange-red upon heating to just 40 °C under dynamic vacuum for five hours (Figure 2.27).

2.4.5.2 PXRD Studies: As with PhCNSSN@MIL-53(Al) and PhCNSeSeN@MIL-53(Al), the peak positions in the PXRD profile for C$_6$F$_5$CNSSN@MIL-53(Al) matches very well that of the MIL-53(Al)-ht phase (Imma) but offers differing peak intensities, consistent with different unit cell contents between the activated host framework and that of the inclusion complex with [C$_6$F$_5$CNSSN]$_2$ now within the pores of the framework (Figure 2.28).

Figure 2.27: Progress of inclusion of C$_6$F$_5$CNSSN into the MIL-53(Al) host
2.3.5.3 High Resolution Mass Spectrometry (HRMS): HRMS spectra of the C₆F₅CNSSN@MIL-53(Al) inclusion complex in ASAP+ mode revealed M+H ions at 271.9496 (calc. 271.9501) upon heating the inclusion complex to 200 °C (Figure 2.30), suggesting the radical guest becomes labile at elevated temperatures, an identical observation to that seen with the previous inclusion complexes.
2.3.5.4 EPR Spectroscopy: Room temperature solid state EPR studies were conducted on the \( \text{C}_6\text{F}_5\text{CNSSN} \) inclusion complex, and again reveal an intense rhombic symmetry and substantial line broadening, both features which point to a high concentration of radical loading within the host framework. There is again a great deal of anisotropy seen in this spectra, comparable to that seen previously, further suggesting little radical motion within the framework on the EPR timescale, and simulation parameters (Table 2.4) are in good agreement with literature values of the radical alone, consistent with the incorporation of the \( \text{C}_6\text{F}_5\text{CNSSN} \) radical into the MIL-53(Al) framework.\(^{18}\)

![Figure 2.30: Room temperature X-band Solid State EPR spectrum of \( \text{C}_6\text{F}_5\text{CNSSN}@\text{MIL-53(Al)} \)](image)

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\(^{18}\)
Table 2.4: EPR simulation parameters for C₆F₅CNSSN@MIL-53(Al) in comparison with previously reported data on C₆F₅CNSSN measured in a frozen d₈-toluene matrix.

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2.3.5.5 TGA Analysis: Thermal gravimetric analysis of the C₆F₅CNSSN@MIL-53(Al) inclusion complex reveals substantially higher thermal stability than the pristine radical (where mass loss begins around 40 °C). Mass loss for C₆F₅CNSSN@MIL-53(Al) commences around 110 °C (in good agreement with changes in the VT-PXRD profile, vide infra) and mass loss slows above 340 °C. By 500 °C there is a total mass loss of 20.5%, providing a lower limit for the radical loading of 0.2C₆F₅CNSSN@MIL-53(Al).

Figure 2.31: TGA profile for MIL-53(Al)-ht (top), C₆F₅CNSSN@MIL-53(Al) (middle), and [C₆F₅CNSSN]₂ (bottom)
2.3.5.6 Variable Temperature PXRD Studies: A sample of C$_6$F$_5$CNSSN@MIL-53(Al) was heated on a PROTO AXRD temperature stage from room temperature to 400 °C and PXRD patterns were collected at 25 °C intervals. The temperature dependence of the PXRD profile reveals notable structural changes in the range 125 – 225 °C, reflected in the emergence of new reflections at ca. 9.5°, 16.5°, 21° and 23.5° etc. These are comparable with the impurity peaks in PhCNSeSeN@MIL-53(Al) and attributed to formation of quantities of MIL-53(Al)-lt (monoclinic Cc). At temperatures above 250 °C these features disappear, leaving only the MIL-53(Al)-ht phase (orthorhombic Imma), consistent with previous studies.$^{15}$

Figure 2.32: Variable temperature PXRD profiles for C$_6$F$_5$CNSSN@MIL-53(Al) on heating from room temperature to 400 °C
2.3.5.7 Chemical removal of the radical guest: Solution EPR studies were undertaken on a suspension of C$_6$F$_5$CNSSN@MIL-53(Al) in CH$_2$Cl$_2$. This revealed an isotropic 1:2:3:2:1 pentet (g = 2.0098, a$_N$ = 5.10 G), consistent with leaching of C$_6$F$_5$CNSSN from the host lattice, comparable with PhCNSSN@MIL-53(Al).

![Figure 2.33: Room temperature X-band Solution EPR spectra of C$_6$F$_5$CNSSN in CH$_2$Cl$_2$ (left) and C$_6$F$_5$CNSSN@MIL-53(Al) following suspension in CH$_2$Cl$_2$ (right)](image)

2.3.6 Inclusion of [C$_6$F$_5$CNSeSeN]$_2$ into MIL-53(Al)

2.3.6.1 Progress of Inclusion: The inclusion of C$_6$F$_5$CNSeSeN into MIL-53(Al) was carried out using the established methodology, with an observable colour change of the host from white to deep purple upon heating the radical to 95 °C under dynamic vacuum (Figure 2.34).
2.3.6.2 PXRD Studies: PXRD studies on $C_6F_5CNSeSeN@MIL-53(Al)$ revealed similar trends to those observed for other DTDA and DSDA radical inclusion complexes examined in this series, specifically formation of an orthorhombic phase (Imma) as the major component, with cell parameters comparable to MIL-53(Al)-ht based on peak positions. Again, the peak intensities differ significantly, consistent with incorporation of the radical guest into the channel structure.

Figure 2.34: Progress of inclusion of $C_6F_5CNSeSeN$ into the MIL-53(Al) framework
2.3.6.3 High Resolution Mass Spectrometry (HRMS): HRMS spectra of the C$_6$F$_5$CNSeSeN@MIL-53(Al) inclusion complex in ASAP+ mode revealed M+H ions at 366.8314 (calc. 366.8140) upon heating the inclusion complex to 200 °C (Figure 2.36), suggesting the radical guest has become volatile at elevated temperatures, an identical observation to that seen with the previous inclusion complexes.

Figure 2.35: PXRD patterns of C$_6$F$_5$CNSeSeN@MIL-53(Al) (bottom), MIL-53(Al)-ht (middle), and [C$_6$F$_5$CNSeSeN]$_2$ (top)

Figure 2.36: HRMS spectrum (ASAP+, 200°C) of C$_6$F$_5$CNSeSeN@MIL-53(Al)
2.3.6.4 EPR Spectroscopy: Room temperature solid state EPR studies were conducted on C₆F₅CNSeSeN@MIL-53(Al). The spectrum exhibits near axial symmetry (Table 2.5) with substantial line broadening masking hyperfine coupling (Figure 2.36). The latter points to a high concentration of radical loading within the host framework. The g-tensor anisotropy is comparable with that seen for PhCNSeSeN observed previously, further suggesting little radical motion within the framework on the EPR timescale.

![Simulation and Experimental EPR Spectra](image)

**Figure 2.37:** Room temperature X-band solid state EPR spectrum of C₆F₅CNSeSeN@MIL-53(Al)
TGA Analysis: Thermal gravimetric analysis of the $C_6F_5CNSeSeN@MIL-53(Al)$ inclusion complex reveals thermal stability in the host-guest complex where mass loss commences around 200 °C in relation to the pristine radical (130 °C). By 500 °C there is a total weight loss of 34%, corresponding to a chemical formula of ca. $0.3C_6F_5CNSeSeN@MIL-53(Al)$.

### Table 2.5: Simulation parameters for the EPR Spectrum of $C_6F_5CNSeSeN@MIL-53(Al)$ and comparison with those reported for a frozen solution of $C_6F_5CNSeSeN$

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*2.3.6.5 TGA Analysis: Thermal gravimetric analysis of the $C_6F_5CNSeSeN@MIL-53(Al)$ inclusion complex reveals thermal stability in the host-guest complex where mass loss commences around 200 °C in relation to the pristine radical (130 °C). By 500 °C there is a total weight loss of 34%, corresponding to a chemical formula of ca. $0.3C_6F_5CNSeSeN@MIL-53(Al)$.*
Variable Temperature PXRD Studies: A sample of C₆F₅CNSeSeN@MIL-53(Al) was heated on a PROTO AXRD temperature stage from room temperature to 400 °C, and PXRD patterns were collected at 25 °C intervals. Unlike C₆F₅CNSSN@MIL-53(Al) which shows the marked emergence of a second phase on warming, thermal treatment of C₆F₅CNSeSeN@MIL-53(Al) reveals the predominant nature of the orthorhombic Imma phase across the entire temperature range, albeit with changes in peak intensities consistent with removal of guest molecules upon heating (Figure 2.38). In this context it is noteworthy that both DSDA inclusion complexes show relatively simple behaviour with the dominant process being elimination of the radical from the Imma cavity, whereas the two DTDA inclusion complexes show more complex responses reflected in the emergence of new phases as well as unexpected pore opening-closing mechanisms.

Figure 2.38: TGA profile for MIL-53(Al)-ht (top), C₆F₅CNSeSeN@MIL-53(Al) (middle), and [C₆F₅CNSeSeN]₂ (bottom)
2.3.6.7 **Chemical removal of radical guest:** The \( \text{C}_6\text{F}_5\text{CNSeSeN} \) radical is known to have a much better solubility in organic solvents than \( \text{PhCNSeSeN} \). The stabilization of \( \text{C}_6\text{F}_5\text{CNSeSeN} \) in solution therefore offered the potential for chemical leaching of this radical from the host-guest complex. Indeed, solution EPR studies on a suspension of \( \text{C}_6\text{F}_5\text{CNSeSeN}\@\text{MIL-53(Al)} \) in \( \text{CH}_2\text{Cl}_2 \) revealed an isotropic broad singlet (\( g = 2.0377 \)) consistent with leaching of \( \text{C}_6\text{F}_5\text{CNSeSeN} \) from the host lattice (Figure 2.39).
2.3.7 Reactivity of radical guests inside the framework

Early work by Banister and co-workers illustrated that the PhCNSSN radical undergoes halogenation to form the halide salts [PhCNSSN]Cl (yellow), [PhCNSSN]Br (red), and [PhCNSSN]I (purple). While chlorination and bromination lead to diamagnetic salts via 1e⁻ oxidation of the radical, the iodide salts tend to retain their paramagnetism, suggesting incomplete radical oxidation in the presence of this milder oxidant. Structural studies by Oakley revealed that [PhCNSSN]I should be better viewed as the mixed valence tri-iodide salt, [PhCNSSN]₃[I₃] and higher polyiodides have been isolated such as [PhCNSSN][I₃].

Given the highly colored nature of the inclusion complexes, we were interested to explore whether (i) the radicals exhibited similar reactivity pathways while contained within a framework structure and (ii) if so, whether there were marked color changes which could potentially be used as sensors for strong oxidizers.

Figure 2.40: Room temperature X-band Solution EPR spectra of C₆F₅CNSeSeN in CH₂Cl₂ (left) and C₆F₅CNSeSeN@MIL-53(Al) following suspension in CH₂Cl₂ (right)
**2.3.7.1 Chlorination and Bromination:** Treatment of each inclusion complex with chlorine gas resulted in a colour change from bright red to pale yellow (Figure 2.40), and EPR studies on the chlorinated samples revealed complete quenching of the radical signal following chlorination. Similar behaviour was also observed when using SO$_2$Cl$_2$ as the oxidant. Similar treatment with bromine vapour led to a colour change to a burgundy-red (Figure 2.41), with a similar quenching of the EPR spectrum. Elemental analysis on samples after halogenation revealed compounds of composition [PhCNSSN]X@MIL-53(Al) (X = Cl, Br).

**2.3.7.2 Iodination:** In all cases iodination led to a colour change to a deep purple but incomplete quenching of the EPR signal, consistent with the formation of a charge-transfer salt within the pores of the host framework. For PhCNSSN@MIL-53(Al) elemental analysis pointed towards incomplete oxidation and formation of [PhCNSSN]I@MIL-53(Al) whereas PhCNSeSeN@MIL-53(Al) afforded the tri-iodide, [PhCNSSN]$_3$I@MIL-53(Al).
Figure 2.41: (top) Progress of chlorination of PhCNSSN@MIL-53(Al), following exposure to chlorine gas for ca. 12 hours; (middle) progress of bromination of PhCNSeSeN@MIL-53(Al) over 18h; (bottom) progress of iodination of PhCNSeSeN@MIL-53(Al) using iodine chips with the reaction vessel maintained at 40°C
2.3.7.3 PXRD Studies: Notably halogenation leads to marked changes in the experimental powder patterns, consistent with the incorporation of additional heavy atoms within the MIL-53(Al) framework (Figure 2.41). For PhCNSSN@MIL-53(Al) halogenation appears to occur with retention of the Imma (MIL-53(Al)-ht) setting, whereas PhCNSeSeN@MIL-53(Al) affords quantities of both the MIL-53(Al)-ht and MIL-53(Al)-lt phases (diagnostic reflections at 9.5°).

**Figure 2.42: PXRD patterns following halogenation of (top) PhCNSSN@MIL-53(Al) and (bottom) PhCNSeSeN@MIL-53(Al)**
2.3.7.4 EPR Studies of Iodination: Figure 2.42 illustrates the EPR spectra of the inclusion complexes following iodination, revealing the retention of paramagnetism after iodination. A comparison of EPR spectra before and after iodination reveal narrower linewidths and sharper spectra after iodination, reflecting a decrease in dipolar broadening consistent with partial oxidation of some radicals in the channel structure. Simulation parameters are presented in Tables 2.6 – 2.9.

Figure 2.43: Room temperature X-band Solid State EPR spectra of (top left) PhCNSSN@MIL-53(Al), (top right) PhCNSeSeN@MIL-53(Al), (bottom left) C₆F₅CNSSN@MIL-53(Al), and (bottom right) C₆F₅CNSeSeN@MIL-53(Al) following iodination
### Table 2.6: EPR simulation parameters for PhCNSSN@MIL-53(Al) following iodination in comparison with previously reported data on PhCNSSN measured in a frozen $d_8$-toluene matrix.

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### Table 2.7: Simulation parameters for the EPR Spectrum of PhCNSeSeN@MIL-53(Al) following iodination and comparison with those reported for a frozen solution of PhCNSeSeN.

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### Table 2.8: EPR simulation parameters for C$_6$F$_5$CNSSN@MIL-53(Al) following iodination in comparison with previously reported data on C$_6$F$_5$CNSSN measured in a frozen $d_8$-toluene matrix.

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### Table 2.9: Simulation parameters for the EPR Spectrum of C$_6$F$_5$CNSeSeN@MIL-53(Al) following iodination and comparison with those reported for a frozen solution of C$_6$F$_5$CNSeSeN.

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2.4 Conclusions

In this chapter, the successful inclusion of four radicals as guests into the porous host framework MIL-53(Al) has been described. Radical inclusion was readily identified by a colour change of the MOF host to bright red (PhCNSSN), purple (PhCNSeSeN), orange-red (C₆F₅CNSSN) and deep-purple (C₆F₅CNSeSeN). The loadings of the radicals into the channel structure range from 0.2 – 0.5 radicals per MIL-53(Al) unit based on a combination of TGA and elemental analysis data. Notably a calculation of the void space in the structure of MIL-53(Al) (1.2 Å probe radius)³¹ revealed a void volume per unit cell of 646 Å³. Based on this available void space and the estimated volume of PhCNSSN (191 Å³),¹⁰ the maximum occupancy of PhCNSSN molecules is ca. 3.4 PhCNSSN units per unit cell, providing an upper ratio of 3.4 PhCNSSN : 4 MIL-53(Al) or 0.85:1. The experimentally determined loadings of radicals within the channels (0.2 – 0.5 : 1) correspond to packing efficiencies of 24 – 59%, at the lower end in relation to simple close-packed lattices (52% for simple cubic, 68% for bcc and 74% for ccp).³² EPR studies show that the radicals are static within the channels on the EPR timescale at ambient temperature while SQUID data on both PhCNSSN@MIL-53(Al) and PhCNSeSeN@MIL-53(Al) reflect some degree of spin-pairing (dimerization) within the channels. Attempted structure solution from powder data revealed the host structure but the presence of a range of symmetry elements within the channel structure afforded severe disorder of the guests within the channel structure. TGA studies revealed that in all cases incorporation of the radical into the MIL-53(Al) framework led to an increase in thermal stability of the radicals suggesting host···guest interactions are stronger than the guest···guest interactions within the pristine radicals.
themselves. With the exception of PhCNSeSeN@MIL-53(Al), radicals could be leached from the pores using common organic solvents suggesting that a combination of entropy coupled with strong solvent···radical interactions can overcome the host···guest interactions. VT-PXRD studies reveal that for the DSDA host-guest complexes PhCNSeSeN@MIL-53(Al) and $C_6F_5CNSeSeN@MIL-53(Al)$, loss of radical from the framework does not occur with any substantial change in the host-lattice. Conversely the DTDA radicals appear to follow more complex behaviour. For $C_6F_5CNSSN@MIL-53(Al)$ loss of radical from the channels is initially accompanied by structural collapse to the monoclinic Cc phase (MIL-53(Al)-lt) of the host framework which then transforms back to the (empty) MIL-53(Al)-ht form at elevated temperatures. For PhCNSSN@MIL-53(Al), which has the highest radical loading within the series, the thermal evolution of the VT-PXRD data indicate a ‘wine-rack’ style pore opening/closing mechanism within the Imma space group accompanying radical loss.

The current study also provides the first examination of radical reactivity within the host framework. Both DTDA and DSDA radicals are known to be redox active and preliminary halogenation studies on PhCNSSN@MIL-53(Al) and PhCNSeSeN@MIL-53(Al) reveal that the radicals are capable of being oxidized within the host framework to form the corresponding PhCNSSN$^+$ and PhCNSeSeN$^+$ cations with the corresponding halide counterion incorporated into the lattice based on changes to the PXRD profile and elemental analysis data. Complete oxidation was confirmed by the absence of an EPR signal on chlorination and bromination. In contrast the milder oxidant I$_2$ led to incomplete oxidation. Halogenation is accompanied by significant colour changes depending on the
type of halogen used. Unfortunately, the rate of oxidation within the pore channels at ambient conditions is slow making them unsuitable fast-response sensors for oxidants.

Future work for this project consists of unravelling the variations in the thermal degradation pathways between systems containing seemingly similar guest molecules. A working hypothesis is that the more volatile DTDA radicals are more readily removed from the channels, permitting collapse of the structure to the MIL-53(Al)-lt phase in relation to the DSDA host-guest complexes. In addition, PhCNSSN@MIL-53(Al) has the highest radical loading within the series and perhaps has to adopt a ‘wine-rack’ opening/closing mechanism in order to liberate radicals from the framework. Additional studies on the C₆F₅CNSSN and C₆F₅CNSeSeN inclusion complexes could include structure solution and refinement from their PXRD profiles, although it is likely that they too adopt disordered structures.

MIL-53(Al) is just one member of the MIL-53 series and other MIL-53 derivatives are known which contain paramagnetic frameworks, including MIL-53(Fe) and MIL-53(Cr). Magnetic data on the inclusion complexes to date indicate that the remaining radicals within the channel structure act as near perfect $S = \frac{1}{2}$ paramagnets. Incorporation of these radicals into MIL-53(Fe) or MIL-53(Cr) would permit the examination of electronic interactions between host and guest.
2.5 References


Chapter 3 Crystal Engineering of Thiazyl-Based Radical-Radical Co-Crystals

3.1 Introduction

Dithiadiazolyl radicals have been extensively studied for the use as building blocks for conducting and magnetic materials.\textsuperscript{1,2} The well-established localized nature of the SOMO, which is largely invariant to substituent make these systems particularly interesting to study from a crystal engineering point of view. Specifically the nature of the R substituent has rather minimal effect on the electronic properties of the DTDA ring while permitting the solid state architecture to be modified.\textsuperscript{2,3} The symmetry of the SOMO permits a range of $\pi^*-\pi^*$ dimer bonding modes to be realized but the cis-oid $\pi^*-\pi^*$ motif is by far the most common.\textsuperscript{4} Attempts to suppress dimerization have sparked a significant area of research, as inhibiting this extremely favourable process is the first stepping stone to exploit the full magnetic potential of these systems. Success in this area has tended to arise from utilizing steric effects to suppress the cis-oid $\pi^*-\pi^*$ dimerization mode. In some cases, this has been successful\textsuperscript{5,6} but in other instances has simply favored formation of twisted dimer motifs such as the adamantyl dithiadiazolyl.\textsuperscript{7} The use of perfluorophenyl substituents leads to large twist angles between Ar\textsubscript{F} and DTDA rings to minimize intramolecular $\delta^+\text{N}\cdots\text{F}^{-}\beta$ repulsions\textsuperscript{8} making the perfluoroaryl ring bulky with respect to cis-dimerization and several $\text{p-XC}_6\text{F}_4\text{CNSSN}$ derivatives remain monomeric in the solid state ($X = \text{Br, I, CN, C}_6\text{F}_4\text{CN, NO}_2$).\textsuperscript{8-12} Notably among these derivatives dimerization appears suppressed through a combination of perfluorination (destabilizing the cis-oid dimer) while simultaneously incorporating significant structure-directing groups such as $\text{S}_2\cdots\text{NC}$- and $\text{S}_2\cdots\text{O}_2\text{N}$- or sigma-hole type $\text{N}\cdots X$ ($X = \text{Br, I}$) interactions. More recent studies
have focused on hetero-dimer structures where complementarity of functional groups such as the use of aryl/perfluoroaryl interactions has been used to promote cocrystal formation, e.g. \([\text{C}_6\text{F}_5\text{CNSN}][\text{PhCNSN}]\) and \([\text{NC}_5\text{F}_4\text{CNSN}][\text{PhCNSN}]\) (Figure 3.1).\(^\text{13,14}\)

![Figure 3.1: Crystal structures of DTDA-based cocrystals; (left)[PhCNSN][C\(_6\)F\(_5\)CNSN]; (right) [PhCNSN][NC\(_5\)F\(_4\)CNSN].](image)

The formation of cocrystals comprising two different radicals has some potential in the field of organic magnetism. While a range of organic ferromagnets have been reported, approaches to design organic ferrimagnets have been challenging. Conventional wisdom has sought to combine two separate building blocks; radical A containing an \(S = 1\) (or greater) spin ground state diradical, and radical B containing an \(S = \frac{1}{2}\) radical. In the presence of antiferromagnetic exchange coupling between these radicals through the lattice then ferrimagnetism is expected with a non-zero magnetic moment given by:\(^\text{15}\)

\[
M = |g_A S_A - g_B S_B| \quad \text{Eq. 3.1}
\]

However, there are a number of challenges to this approach. Firstly, the number of stable diradicals with a thermally robust \(S = 1\) ground state (i.e. well thermally isolated from \(S = 0\) excited states) are few. In addition, approaches to favor cocrystal formation rather than
phase separation adds an additional layer of complexity into the process. An early success in this area is Sugawara’s work on cocrystal formation between the 3,5-dinitrophenyl nitronyl nitroxide radical \((S = \frac{1}{2})\) with the 1,3-bis(nitronyl nitroxide) benzene triplet diradical \((S = 1)\) (Figure 3.2).\(^\text{16}\) Unfortunately this compound did not exhibit ferrimagnetism but showed the potential for cocrystallizing two different radical species.

![Cocrystallization of a multi-spin system by Sugawara et al., adapted from [14]](image)

A few years after Sugawara’s report, Inoue\(^\text{17}\) described an organic ferrimagnet in which they exploited strong intramolecular antiferromagnetic and ferromagnetic interactions between three \(S = \frac{1}{2}\) spins to form a molecule with an overall \(S = \frac{3}{2}\) spin ground state below 50 K. Much weaker inter-molecular ferromagnetic interactions between \(S = \frac{1}{2}\) ground state molecules led to magnetic ordering at very low temperature \((T_c = 0.28 \text{ K})\).\(^\text{17}\)
An alternative approach to designing organic ferrimagnets was recently proposed by Rawson, based on co-crystal formation between $S = \frac{1}{2}$ radicals.\textsuperscript{15} Provided the g-values for the two radicals are different then Eq. 3.1 simplifies to $M = \frac{1}{2} |g_A - g_B|$.\textsuperscript{15} While g-values for organic radicals are typically close to the free electron value ($g = 2.0023$), the incorporation of heavier $p$-block radicals leads to larger g values due to enhanced spin-orbit coupling which scales as $Z^4$.\textsuperscript{18} Thus approaches to combine heavier $p$-block radicals with more conventional organic radicals could lead to values of $|g_A - g_B|$ which could give rise to measurable bulk moments. For example DSDA, DTDA, DTA and TEMPO radicals exhibit g-values around 2.040, 2.010, 2.005 and 2.003 respectively.\textsuperscript{19-22} As proof-of-principle a series of radical-radical cocrystals were reported.\textsuperscript{15} The structures of the 2:2 cocrystal [PhCNSSN]\textsubscript{2}[MBDTA]\textsubscript{2} and the 2:1 cocrystal [C\textsubscript{6}F\textsubscript{5}CNSSN]\textsubscript{2}[TEMPO] are shown in Figure 3.3. The corresponding DSDA derivative, [C\textsubscript{6}F\textsubscript{5}CNSeSeN]\textsubscript{2}[TEMPO] adopts a similar structure to [C\textsubscript{6}F\textsubscript{5}CNSSN]\textsubscript{2}[TEMPO].\textsuperscript{15}

![Figure 3.3: Crystal structures of (left) [PhCNSSN]\textsubscript{2}[MBDTA]\textsubscript{2}; (right) [C\textsubscript{6}F\textsubscript{5}CNSSN]\textsubscript{2}[TEMPO]](image)

In all three cases a simple thermodynamic approach coupled with an understanding of the electrostatics of each system were used to favour cocrystallization and will be discussed in the following section.
3.1.2 Thermodynamics of cocrystal formation

Previous work by Robinson et al. illustrated the basic thermodynamic aspects of cocrystal formation through co-sublimation. A simple Born-Haber cycle reveals the energetics are simply dictated by the relative enthalpies of sublimation of the two parent radicals (‘energy in’) vs the enthalpy of sublimation of the cocrystal (‘energy out’) (Figure 3.4). Unfortunately, this cycle cannot be used in a predictive fashion as the enthalpy of vaporization for the cocrystal can only be measured once the cocrystal is formed! Nevertheless, it is conceptually helpful in identifying key factors required for cocrystal formation. For example, radicals with low enthalpies of sublimation (volatile) should favour cocrystal formation, while cocrystals which exhibit potentially robust supramolecular synthons should facilitate increases in the lattice enthalpy of the cocrystal.

Figure 3.4: Thermodynamic approach applied to cocrystal design, adapted from Ref. [14]
Previous work on DTDA radicals has shown the propensity for the DTDA disulfide bond to form strong $\delta^+S_2 \cdots E^\delta-$ interactions.\textsuperscript{23} These are manifested in multiple cyano-functionalized DTDA radicals where chain-forming electrostatic $\delta^+S_2 \cdots NC^\delta-$ interactions are almost invariably observed.\textsuperscript{10,11,24} Nitro substituents are also known to effectively create similar $\delta^+S_2 \cdots O_2N^\delta-$ interactions.\textsuperscript{12} In the absence of structure-directing groups, these interactions are replaced by $\delta^+S_2 \cdots \pi^\delta-$ and/or $\delta^+S \cdots N^\delta-$ contacts.\textsuperscript{23} The incorporation of other electrostatic interactions was therefore a good target to attempt cocrystal formation. The molecular electrostatic potential map (MEP) provides a convenient interpretation of the charge distribution on the molecular surface.\textsuperscript{25} Initial work by Nascimento \textit{et al.} successfully utilized the electrostatic potential map to identify that the volatile radical TEMPO would be a good potential building block for cocrystal formation with DTDA radicals since it bears a large partial negative charge on the N-O group (Figure 3.5).\textsuperscript{15} This could assist cocrystal stabilization through an $S_2 \cdots O-N$ interaction. In addition, this interaction would bring regions of spin density on both radicals into close proximity which may facilitate efficient through-space magnetic interactions. The crystal structure of $[C_6F_5CNSSN]_2[TEMPO]$ (Figure 3.3) clearly shows the presence of such electrostatically favorable contacts.
3.1.3 Chapter Overview

On the basis of the preliminary studies by Nascimento, a family of DTDA and DSDA radical-radical cocrystals were targeted. The radical $[\text{C}_6\text{F}_5\text{CNSSN}]_2$ as well as $[\text{p-ClC}_6\text{F}_4\text{CNSSN}]_2$ are known to form cis-oid dimers in the solid state but selected other members of the series $\text{p-XC}_6\text{F}_4\text{CNSSN}$ do not dimerize ($X = \text{Br}, \text{I}, \text{NC}, \text{NO}_2, \text{NCC}_6\text{F}_4$) and may favor 1:1 cocrystals of formula $[\text{Ar}_5\text{CNSSN}]\text{[TEMPO]}$. In this Chapter the structures of cocrystals formed between $\text{p-XC}_6\text{F}_4\text{CNSSN}$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{CN}$) and TEMPO are described. In addition, the related cocrystals formed between $\text{p-XC}_6\text{F}_4\text{CNSeSeN}$ ($X = \text{F}, \text{Br}$) and TEMPO are isolated and characterized. As an extension of those studies cocrystals comprising the TEMPONE radical with $[\text{C}_6\text{F}_5\text{CNSSN}]_2$ or $[\text{C}_6\text{F}_5\text{CNSeSeN}]_2$ are reported. In the TEMPONE radical there are two electronegative groups (C=O vs N-O) which can compete to form close contacts with the disulfide or diselenide bridge on the DTDA or DSDA rings respectively. The charge distribution and spin density for TEMPONE are presented in Figure 3.6.
3.2 Experimental

3.2.1 General Considerations

All reactions undertaken in this Chapter were completed under an atmosphere of nitrogen or argon with the use of solvents dried over molecular sieves. Analytical and spectroscopic techniques were conducted in the same manner as described in Chapter 2 (PXRD and EA measurements), with additional techniques specific to this project described below. Lithium bis(trimethylsilyl) amide, triphenyl antimony, tetrafluoroterephthalonitrile and benzonitrile were all purchased from Sigma-Aldrich and used as received. Pentafluorobenzonitrile and TEMPO were purchased from Oakwood Chemical, where pentafluorobenzonitrile was used as received, and TEMPO was sublimed under vacuum to remove minor impurities prior to use. TEMPONE was purchased from Cayman Chemicals and was also used as received. Nitriles \( p\text{-ClC}_6\text{F}_4\text{CN} \), \( p\text{-BrC}_6\text{F}_4\text{CN} \), and \( p\text{-IC}_6\text{F}_4\text{CN} \) were synthesized according to the literature.\(^{22}\) The DTDA radicals \( p\text{-XC}_6\text{F}_4\text{CNSSN} \) were prepared according to the literature methods\(^{15}\) and the DSDA radical, \( [\text{C}_6\text{F}_5\text{CNSeSeN}]_2 \), was also prepared according to the literature method.\(^{18}\) Phase purity of
DTDA and DSDA radicals were confirmed by PXRD against computed PXRD patterns based on single crystal data, as well as by EPR spectroscopy.

3.2.2 Molecular Electrostatic Potential Maps

Molecular electrostatic potential maps were computed using the UB3LYP functional and 6-31G* basis set within Jaguar. Single point (1SCF) calculations were implemented using the crystallographically determined geometry. Rainbow plots of the electrostatic potential plotted on the electron density surface are illustrated in this chapter for C$_6$F$_5$CNSSN, TEMPO, and TEMPONE (Figures 3.5 and 3.6).

3.2.3 Single Crystal X-ray Diffraction (SCXRD)

Single crystal X-ray diffraction analysis was completed on a Bruker D8 Venture equipped with an Oxford Cryostream. Data were collected using the APEX-3 software and an absorption correction applied using SADABS. All structures were solved by intrinsic phasing and refined against $F^2$ using the SHELXTL package.

3.3 Synthetic Methodology

3.3.1 Preparation of [C$_6$F$_5$CNSSN]$_2$[TEMPO]

The radicals [C$_6$F$_5$CNSSN]$_2$ (100 mg, 0.369 mmol) and TEMPO (29 mg, 0.183 mmol) were stirred together in CH$_2$Cl$_2$ (12 mL) for ca. 2 hrs. The solvent was removed in vacuo. A cold finger was added to the Schlenk and evacuated in an ice bath for 2 hours. The reaction mixture was sublimed under static vacuum in a 25 °C oil bath with 0 °C isopropanol circulating through the cold finger for 48 hours, resulting in the formation of dark green-black blocks on the cold finger, which were determined to be [C$_6$F$_5$CNSSN]$_2$[TEMPO] by X-ray diffraction (44 mg, 34%).
EA: Calc. for C_{23}H_{18}F_{10}N_{5}OS_{4} C 39.54%, H 2.60%, N 10.02%; Found C 38.95%, H 2.20%, N 10.16%

EPR (X-band, 183 K, CH_{2}Cl_{2}) 53% C_{6}F_{5}CNSSN (g = 2.010, a_{N} = 5.03 G, a_{F} = 1.53 G); 47% TEMPO (g = 2.0062, a_{N} = 15.67 G)

3.3.2 Preparation of [p-ClC_{6}F_{4}CNSSN]_{2}[TEMPO]

The radicals [p-ClC_{6}F_{4}CNSSN]_{2} (140 mg, 0.487 mmol) and TEMPO (38 mg, 0.243 mmol) were stirred together in CH_{2}Cl_{2} (10 mL) for ca. 2 hrs. The solvent was removed \textit{in vacuo}. A cold finger was added to the Schlenk and evacuated in an ice bath for 2 hrs. The reaction mixture was sublimed under static vacuum at 40°C for 3 days, resulting in the formation of dark purple-black crystalline material on the cold finger which was determined to be [p-ClC_{6}F_{4}CNSSN]_{2}[TEMPO] by X-ray diffraction (58 mg, 33%).

EA: Calc. for C_{23}H_{18}F_{10}Cl_{2}N_{5}OS_{4}: C 37.76%, H 2.48%, N 9.57%; Found C 37.80%, H 2.46%, N 9.38%

EPR (X-band, 298 K, CH_{2}Cl_{2}) 72% p-ClC_{6}F_{4}CNSSN (g = 2.010, a_{N} = 5.07 G); 28% TEMPO (g = 2.0058, a_{N} = 15.47 G)

3.3.3 Preparation of [p-BrC_{6}F_{4}CNSSN]_{2}[TEMPO]

The radicals p-BrC_{6}F_{4}CNSSN (80 mg, 0.241 mmol) and TEMPO (19 mg, 0.121 mmol) were stirred together in CH_{2}Cl_{2} (12 mL) for ca. 2 hrs. The solvent was removed \textit{in vacuo}, and a cold finger was added to the Schlenk and evacuated in an ice bath for 2 hrs. Sublimation was carried out in a 45°C oil bath with -2°C isopropanol circulating through
the cold finger. After 5 days, dark purple blocks began forming on the cold finger. The
product was identified as the 2:1 cocrystal [p-BrC₆F₄CNSSN]₂[TEMPO] by x-ray diffraction
(23 mg, 23%).

EA: Calc. for C_{23}H_{18}F₈Br₂N₅O₄: C 33.67%, H 2.21%, N 8.54%; Found C 32.40%, H 2.63%, N
8.23%

EPR (X-band, 298 K, CH₂Cl₂) 22% p-BrC₆F₄CNSSN (g = 2.010, a_N = 4.89 G); 78% TEMPO (g =
2.0061, a_N = 15.44 G)

3.3.4 Preparation of [p-IC₆F₄CNSSN]₂[TEMPO]

The radicals p-IC₆F₄CNSSN (70 mg, 0.185 mmol) and TEMPO (14 mg, 0.0925 mmol),
were stirred together in CH₂Cl₂ (10 mL) for ca. 2 hrs. The solvent was removed in vacuo. A
cold finger was added to the Schlenk and evacuated in an ice bath for ca. 2 hrs. Sublimation
was carried out at 60 °C with 10 °C isopropanol circulating the cold finger for
3 days, after which time dark purple blocks began forming on the cold finger which were
identified as the 2:1 cocrystal [p-IC₆F₄CNSSN]₂[TEMPO] by X-ray diffraction (17 mg, 20%).

EA: Calc. for C_{23}H_{20}F₈I₂N₅O₄: C 30.21%, H 1.98%, N 7.66%; Found C 31.04%, H 2.56%, N
6.81%.

EPR (X-band, 298 K, CH₂Cl₂) 75% p-IC₆F₄CNSSN (g = 2.010, a_N = 5.22 G); 25% TEMPO (g =
2.0057, a_N = 15.88 G)

3.3.5 Preparation of [p-NCC₆F₄CNSSN]₂[TEMPO]

The radicals p-NCC₆F₄CNSSN (100 mg, 0.359 mmol) and TEMPO (28 mg, 0.180
mmol) were stirred together in CH₂Cl₂ (15 mL) for ca. 2 hrs. The solvent was removed in
vacuo. A cold finger was added to the Schlenk and evacuated in an ice bath for ca. 2hrs.
Sublimation was carried out at 60 °C for 4 days, after which time dark red blocks were deposited onto the cold finger. The product was identified as the 2:1 cocrystal, \([\rho \text{-NCC}_6\text{F}_4\text{CNSSN}]_2[\text{TEMPO}]\) by X-ray diffraction (50 mg, 23%).

**EA:** Calc. for C\(_{23}\)H\(_{18}\)F\(_8\)N\(_7\)O\(_4\): C 42.13%, H 2.55%, N 13.76%; Found C 41.52%, H 3.12%, N 12.67%.

**EPR (X-band, 298 K, CH\(_2\)Cl\(_2\))** 76% p-NCC\(_6\)F\(_4\)CNSSN (g = 2.01, a\(_N\) = 15.65 G); 24% TEMPO (g = 2.0057, a\(_N\) = 4.98 G)

### 3.3.6 Preparation of [C\(_6\)F\(_5\)CNSeSeN]\(_2\)[TEMPO]

The radicals [C\(_6\)F\(_5\)CNSeSeN]\(_2\) (100 mg, 0.274 mmol) and TEMPO (21 mg, 0.137 mmol) were stirred together in DCM (15 mL) for \(ca.\) 2 hrs. The solvent was removed \textit{in vacuo}. A cold finger was added to the Schlenk and evacuated in an ice bath for \(ca.\) 2 hrs. Sublimation was carried out at 52 °C with 0 °C isopropanol circulating in the cold finger. After 2 days, a mixture of a dark purple material and dark black blocks formed on the cold finger, both of which were determined by X-ray diffraction to be the 2:1 cocrystal [C\(_6\)F\(_5\)CNSeSeN]\(_2\)[TEMPO] (35 mg, 29%).

**EA:** Calc. for C\(_{23}\)H\(_{18}\)F\(_{10}\)N\(_5\)O\(_4\)C 31.17%, H 2.05%, N 7.90%; Found C 30.92%, H 2.43%, N 7.71%

**EPR (X-band, 298 K, CH\(_2\)Cl\(_2\))** 27% C\(_6\)F\(_5\)CNSeSeN (g = 2.039); 73% TEMPO (g = 2.006, a\(_N\) = 15.08 G)

### 3.3.7 Preparation of [p-BrC\(_6\)F\(_4\)CNSeSeN]\(_2\)[TEMPO]

The radicals [p-BrC\(_6\)F\(_4\)CNSeSeN]\(_2\) (100 mg, 0.235 mmol) and TEMPO (18 mg, 0.118 mmol) were stirred together in CH\(_2\)Cl\(_2\) (15 mL) for \(ca.\) 2 hrs. The solvent was removed \textit{in vacuo}.
vacuo. A cold finger was added to the Schlenk and evacuated in an ice bath for 2 hrs. Sublimation was carried out at 60 °C with -5 °C isopropanol circulating the cold finger. After 24 hours, small red blocks began to form on the cold finger. Sublimation was continued under these conditions for an additional 3 days to yield the cocrystal \([p\text{-BrC}_6\text{F}_4\text{CNSeSeN}]_2[\text{TEMPO}]\) (45 mg, 38%).

**EA:** Calc. for \(C_{23}H_{18}F_8N_5OSe_4\text{Br}_2\) C 27.40%, H 1.80%, N 6.95%; Found C 27.89%, H 0.88%, N 6.10%.

**EPR (X-band, 298 K, CH\(_2\)Cl\(_2\))** 41% \(p\text{-BrC}_6\text{F}_4\text{CNSeSeN}\) \((g = 2.038)\); 59% TEMPO \((g = 2.005, a_N = 14.88 \text{ G})\)

### 3.3.8 Preparation of \([\text{C}_6\text{F}_5\text{CNSSN}]_2[\text{TEMPONE}]\)

The radicals \([\text{C}_6\text{F}_5\text{CNSSN}]_2\) (100 mg, 0.369 mmol) and TEMPO (31 mg, 0.184 mmol) were stirred together in CH\(_2\)Cl\(_2\) (10 mL) for ca. 2 hrs. The solvent was removed in vacuo. A cold finger was added to the Schlenk and evacuated in an ice bath for 2 hrs. Sublimation was carried out under static vacuum at 40 °C with 5 °C isopropanol circulating the cold finger. After 48 hours, dark red blocks formed near the top of the cold finger which proved to be \([\text{C}_6\text{F}_5\text{CNSSN}]_2\) by SCXRD. A second attempt of the experiment on the same scale but changing the isopropanol temperature to 0 °C resulted in the formation of the cocrystal \([\text{C}_6\text{F}_5\text{CNSSN}]_2[\text{TEMPONE}]\).

**EPR (X-band, 298 K, CH\(_2\)Cl\(_2\))** 57% \(\text{C}_6\text{F}_5\text{CNSSN}\) \((g = 2.0098, a_N = 5.15 \text{ G})\); 43% TEMPO \((g = 2.0053, a_N = 14.67 \text{ G})\)

### 3.3.9 Preparation of \([\text{C}_6\text{F}_5\text{CNSeSeN}]_2[\text{TEMPONE}]\)
The radicals \([C_6F_5CNSeSeN]_2\) (100 mg, 0.274 mmol) and TEMPONE (23 mg, 0.137 mmol) were stirred together in \(CH_2Cl_2\) (10 mL) for ca. 2 hrs. The solvent was removed \textit{in vacuo}. A cold finger was added to the Schlenk and evacuated in an ice bath for 2 hrs. Sublimation was carried out at 50 °C under dynamic vacuum for ca. 36 hrs, after which time a dark purple residue formed at the bottom of the cold finger and dark fan-shaped crystals formed towards the middle of the cold finger. The product was found to be the 2:1 \([C_6F_5CNSeSeN]_2[\text{TEMPONE}]\) cocrystal (65 mg, 53%).

\textbf{EPR (X-band, 298 K, CH\(_2\)Cl\(_2\))} 52\% \(C_6F_5CNSeSeN\) \((g = 2.0397)\); 48\% TEMPONE \((g = 2.0051, \ a_N = 14.33 \text{ G})\)

\textbf{3.4 Results and Characterization}

\textbf{3.4.1 Preparation of Starting Materials}

While pentafluorobenzonitrile and tetrafluorophthalonitrile were commercially available, the starting materials \(p-XC_6F_4CN\) \((X = \text{Cl, Br, I})\) were synthesized by Dr. Elodie Heyer according to the procedure described by Birchall and coworkers.\(^{22}\) The DTDA and DSDA radicals were prepared according to the literature methods from the corresponding nitriles.\(^{8,10,13,19,32}\) A key step in the synthesis of the DTDA and DSDA radicals was an appropriate choice of reducing conditions, as the Ar\(_f\)CNSSN radicals tend to be low-melting and often form oils with common solvents. Haynes' solvent-free method\(^{14}\) was employed. Heating a mixture of the chloride salt with SbPh\(_3\) to 70 °C affords molten SbPh\(_3\) which simultaneously acts as solvent and reductant, generating the radical as a dark paste. Subsequent vacuum sublimation permitted the \(p-XC_6F_4CNSSN\) radical to be isolated from the side-product, Ph\(_3\)SbCl\(_2\).
3.4.2 Preparation of cocrystals

The radicals ArF-CNSSN or ArF-CNSeSeN and TEMPO or TEMPONE were mixed in CH$_2$Cl$_2$ and the solvent then removed *in vacuo*. The crude reaction mixture was then sublimed onto a cold finger and the stoichiometry of the cocrystal determined by single crystal X-ray diffraction. In some cases, a range of stoichiometries were employed, such as 1:1 stoichiometry with the DTDA:TEMPO derivatives and 4:1 stoichiometry with DTDA:TEMPO derivatives, in an effort to identify if cocrystals with other stoichiometries could be obtained. In all cases only one cocrystal was obtained upon sublimation. After identifying the correct stoichiometry, reactions were repeated using appropriate ratios of each reagent. Previous work on cocrystal formation between [PhCNSSN]$_2$ and MBDTA, indicated that cocrystal formation was achieved after mixing in CH$_2$Cl$_2$, prior to sublimation.$^{15}$ The initial oily nature of the mixtures formed by mixing the two radicals precluded such an examination.

3.4.3 Characterization of [C$_6$F$_5$CNSSN]$_2$[TEMPO]

3.4.3.1 Single Crystal X-ray Diffraction: The [C$_6$F$_5$CNSSN]$_2$[TEMPO] cocrystal was found to crystallize in the monoclinic space group $Cc$ with one C$_6$F$_5$CNSSN and half a TEMPO molecule in the asymmetric unit. As seen in Figure 3.7, the crystal structure consists of two DTDA radicals which adopt a *cis-oid* dimer motif and one TEMPO radical. The intra-dimer S···S contacts at 2.974(1) Å are comparable with ‘normal’ intra-dimer S···S
distances observed in cis-oid DTDA dimers (2.9 – 3.1 Å). The perfluoroaryl ring plane and the DTDA ring plane are twisted by 34.29° and there is a slight inclination of the two DTDA ring planes of 14.26° to accommodate the steric bulk of the perfluoroaryl ring.

Figure 3.7: Crystal structure of [C₆F₅CNSSN]₂[TEMPO] highlighting S···S and S···O contacts. Thermal ellipsoids drawn at the 50% probability level.

The DTDA dimer interacts in a ‘head-to-head’ fashion with the N-O group of the TEMPO radical, forming a set of tetrafurcated δ⁺S···Ο⁻ contacts with an S₄ centroid..Ο distance of 2.282 Å and S···Ο distances of 2.906 and 2.923 Å. Similar types of multi-centre interactions have previously been observed in related systems such as the mixed valence chloride salt [F₃CCNSSN]₃Cl.³³
3.4.3.2 Powder X-Ray Diffraction Studies: Powder X-ray diffraction confirms the bulk phase purity of the cocrystal sample. Figure 3.8 depicts a comparison of the experimentally obtained PXRD profile for \([C_6F_5CNSSN]_2[\text{TEMPO}]\) in relation to the simulated powder pattern based on the single crystal structure determination. The powder profile of \([C_6F_5CNSSN]_2\) is included for comparison and reveals no contamination of the DTDA starting material. It should be noted that TEMPO is polymorphic with three reported phases: Cm, Fdd2 and I-42d.\(^{34-36}\) Given the multiple phases of this radical, it was not included in the PXRD plot. Nevertheless, it is clear that the experimental and computed PXRD profiles for \([C_6F_5CNSSN]_2[\text{TEMPO}]\) show excellent agreement confirming the phase purity of this material.

![Figure 3.8: Experimental (bottom) and simulated (middle) PXRD patterns of \([C_6F_5CNSSN]_2[\text{TEMPO}]\) and pristine \([C_6F_5CNSSN]_2\) (top)](image)

3.4.3.3 EPR Spectroscopy: EPR spectroscopy was used to confirm the presence of both radicals present in the cocrystal. A small sample of \([C_6F_5CNSSN]_2[\text{TEMPO}]\) cocrystals was dissolved in dry \(CH_2Cl_2\), to afford an EPR active solution (Figure 3.9). At room temperature this comprised an overlapping pentet and triplet spectrum. Upon cooling, resonances
sharpened and at 183 K the DTDA EPR spectrum revealed a pentet of triplets. Simulation of the spectrum recorded at 183 K afforded a 1:2:3:2:1 pentet of triplets ($\text{C}_6\text{F}_5\text{CNSSN}$: $g = 2.010$, $a_N = 5.03$ G, $a_F = 1.53$ G) overlapping with a 1:1:1 triplet (TEMPO: $g = 2.0062$, $a_N = 15.67$ G) ($R^2 = 0.994$). The simulation revealed a DTDA:TEMPO ratio of 1.13:1, somewhat lower than the 2:1 ratio expected from the cocrystal stoichiometry (2:1). However, DTDA radicals are well-known to dimerize in solution and dimerization is favored at lower temperatures, so only the contribution from monomeric DTDA radicals is observed.

Figure 3.9: X-band solution EPR spectrum of $[\text{C}_6\text{F}_5\text{CNSSN}]_2[\text{TEMPO}]$ observed at 183 K
3.4.4 Characterization of \([p-CIC_6F_4CNSSN]_2[TEMPO]\)

3.4.4.1 Single Crystal X-Ray Diffraction: The \([p-CIC_6F_4CNSSN]_2[TEMPO]\) cocrystal was found to crystallize in the monoclinic space group \(P2_1/c\) (Figure 3.10). In contrast to \([C_6F_5CNSSN]_2[TEMPO]\) which contains one DTDA radical and a half-molecule of TEMPO in the asymmetric unit, \([p-CIC_6F_4CNSSN]_2[TEMPO]\) adopts a lower symmetry structure with three complete radical molecules in the asymmetric unit. These comprise a \([p-CIC_6F_4CNSSN]_2\) cis-oid dimer and one disordered TEMPO radical. The DTDA dimer bears asymmetric intradimer \(S\cdots S\) contacts of 3.034(1) and 2.970(1) Å, typical of intra-dimer \(S\cdots S\) contacts in DTDA radicals (2.9 – 3.1 Å) and comparable to that observed in pristine \([p-CIC_6F_4CNSSN]_2\). The perfluoroaryl and DTDA ring planes exhibit torsion angles of 37.18° and 28.72° respectively whose average (32.95°) is similar to that observed in \([C_6F_5CNSSN]_2[TEMPO]\) (34.29°). The angle between the two DTDA ring planes is 12.08°. The cis-oid DTDA dimer forms four asymmetric \(S\cdots O\) contacts in the range 2.787(3) – 3.264(3) Å, generating a similar supramolecular motif to that observed in \([C_6F_5CNSSN]_2[TEMPO]\). While this \(S_4\cdots O\) motif is common, the orientation of the TEMPO molecule with respect to the cis-oid dimer varies with twist angles between the \(C_2NO\) plane and each DTDA ring plane of 53.84° and 54.74° (cf 66.91° for \([C_6F_5CNSSN]_2[TEMPO]\)).
3.4.4.2 Powder X-Ray Diffraction Studies: A comparison of the predicted and experimental PXRD profile for \([p-CIC_6F_4CNSSN]_2[TEMPO]\) is shown in Figure 3.11, as well as the computed PXRD pattern for \([p-CIC_6F_4CNSSN]_2\). There is excellent agreement between peak positions and intensities, taking into account small shifts in peak positions based on thermal expansion expected between the single crystal data measured at 170(2) K and the PXRD profile which was measured at room temperature.
3.4.4.3 EPR Spectroscopy: A sample of \([p-\text{ClC}_6\text{F}_4\text{CNSSN}]_2[\text{TEMPO}]\) was suspended in dry \(\text{CH}_2\text{Cl}_2\) and the resulting room temperature EPR spectrum presented in Figure 3.12, comprising an overlapping 1:2:3:2:1 pentet \((g = 2.010, a_N = 5.07 \text{ G})\) and 1:1:1 triplet \((g = 2.0058, a_N = 15.47 \text{ G})\). Variable-temperature EPR studies revealed the emergence of additional hyperfine coupling to \(^{19}\text{F}\) at low temperatures \((a_F = 1.79 \text{ G})\) (Figure 3.13).
Figure 3.12: Room temperature solution X-band EPR spectrum of \([p-\text{ClC}_6\text{F}_4\text{CNSSN}]_2[\text{TEMPO}]\)

Figure 3.13: Variable Temperature solution EPR Spectra of \([p-\text{ClC}_6\text{F}_4\text{CNSSN}]_2[\text{TEMPO}]\) from 190 K to room temperature
3.4.5 Characterization of \([p-\text{BrC}_6\text{F}_4\text{CNSSN}]_2[\text{TEMPO}]\)

While both \([\text{C}_6\text{F}_5\text{CNSSN}]_2\) and \([p-\text{ClC}_6\text{F}_4\text{CNSSN}]_2\) form cis-oid dimers, \(p-\text{BrC}_6\text{F}_4\text{CNSSN}\) is monomeric in the solid state,\(^8\) forming supramolecular chains linked through \(\text{N} \cdots \text{Br}\) sigma hole interactions. It was therefore of interest to examine whether \(p-\text{BrC}_6\text{F}_4\text{CNSSN}\) (or \(p-\text{IC}_6\text{F}_4\text{CNSSN}\) or \(p-\text{NCC}_6\text{F}_4\text{CNSSN}\)) adopted a similar structure to \([\text{C}_6\text{F}_5\text{CNSSN}]_2[\text{TEMPO}]\) or \([p-\text{ClC}_6\text{F}_4\text{CNSSN}]_2[\text{TEMPO}]\) in which the radical is forced to dimerize to adopt a tetrafurcated \(S_4 \cdots O\) interaction or whether \(p-\text{BrC}_6\text{F}_4\text{CNSSN}\) retains its monomeric structure and maybe adopts a 1:1 cocrystal stoichiometry.

3.4.5.1 Single Crystal X-Ray Diffraction: Crystallographic studies on the cocrystal formed from \(p-\text{BrC}_6\text{F}_4\text{CNSSN}\) and TEMPO proved to be isomorphous with \([p-\text{ClC}_6\text{F}_4\text{CNSSN}]_2[\text{TEMPO}]\), crystallizing in the monoclinic space group \(P2_1/c\), with three molecules in the asymmetric unit; a cis-oid \((p-\text{BrC}_6\text{F}_4\text{CNSSN})_2\) dimer linked to TEMPO via a tetrafurcated set of \(S_4 \cdots O\) contacts (Figure 3.14). In contrast to \([p-\text{ClC}_6\text{F}_4\text{CNSSN}]_2[\text{TEMPO}]\) there was no evidence for any crystallographic disorder in the TEMPO molecule.

![Figure 3.14: Crystal structure of \([p-\text{BrC}_6\text{F}_4\text{CNSSN}]_2[\text{TEMPO}]\). Thermal ellipsoids for non-H atoms displayed at 50% probability.](image-url)
Within the cis-oid DTDA dimer, the intra-dimer S⋯S distances are both 2.979(2) Å. slightly smaller than those observed in the pristine radical alone. The perfluoroaryl and DTDA ring planes exhibit slight torsion, with torsion angles of 22.18° and 31.58°, respectively, while the two DTDA ring planes are inclined at 11.51°. In a similar fashion to both [C₆F₅CNSSN]_2[TEMPO] and isomorphous [p-CIC₆F₄CNSSN]_2[TEMPO], this cocrystal forms a set of tetrafurcated S₄⋯O contacts which fall in the range 2.787(4) – 3.134(4) Å.

![Diagram of crystal packing](image)

**Figure 3.15: Crystal packing of [p-BrC₆F₄CNSSN]_2[TEMPO] to form supramolecular chains**

Each formula unit is linked through a web of intermolecular close contacts, of which the bromine forms a notable C-Br⋯F interaction (Br⋯F at 3.152(3) and 3.342(3) Å) with near linear C-Br⋯F angles of 171.6(2) and 174.9(2)° and links molecules parallel to the crystallographic b-axis (Figure 3.15). While the geometry is typical of that formed for a sigma-hole interaction, the distances are close to the sum of the van der Waals radii (3.30 Å), suggesting that it may not contribute significantly to the total lattice enthalpy.
3.4.5.2 Powder X-Ray Diffraction Studies: PXRD was again used as an analytical tool to assess the phase purity of the bulk cocrystal. Figure 3.16 illustrates the experimentally obtained and simulated powder profiles for the \([p-\text{BrC}_6\text{F}_4\text{CNSSN}]_2[\text{TEMPO}]\) cocrystal, as well as the powder pattern of the pristine DTDA radical alone. The peak profiles for the cocrystal are relatively broad, indicating slightly poor crystallinity. Nevertheless, the low angle data in particular point to phase pure material with no evidence for contamination with the DTDA radical.

![Figure 3.16: Experimental (bottom) and simulated (middle) PXRD patterns of \([p-\text{BrC}_6\text{F}_4\text{CNSSN}]_2[\text{TEMPO}]\) and pristine \(p-\text{BrC}_6\text{F}_4\text{CNSSN}\) (top)](image)

3.4.5.3 EPR Spectroscopy: EPR spectroscopy was again used as a means to confirm the identity of the radicals present in this cocrystal system. Room-temperature EPR spectra (Figure 3.18) reveal an overlapping 1:1:1 triplet \((g = 2.0061, a_N = 15.44 \text{ G})\) indicative of the TEMPO radical with a 1:2:3:2:1 pentet \((g = 2.0097, a_N = 4.89 \text{ G})\), indicative of the \(p-\text{BrC}_6\text{F}_4\text{CNSSN}\) component.
Figure 3.17: Room temperature X-band solution EPR spectrum of [p-BrC₆F₄CNSSN]₂[TEMPO]

3.4.6 Characterization of [p-IC₆F₄CNSSN]₂[TEMPO]

The p-IC₆F₄CNSSN radical is also monomeric in the solid state and isomorphous with p-BrC₆F₄CNSSN (space group Aba2), forming supramolecular chains linked through N···I sigma hole interactions. In p-BrC₆F₄CNSSN, cocrystal formation afforded a cis-oid dimer with S···O interactions to the TEMPO radical at the expense of losing the N···I sigma hole interactions. It was therefore of interest to examine cocrystal formation between p-IC₆F₄CNSSN and TEMPO.

3.4.6.1 Single Crystal X-Ray Diffraction: The [p-IC₆F₄CNSSN]₂[TEMPO] cocrystal was found to crystallize in the monoclinic space group P2₁/n, with three molecules in the asymmetric unit again consisting of one cis-oid dimer of the DTDA radical and one TEMPO radical, linked through a tetrafurcated set of S···O contacts (Figure 3.18).
The intra-dimer S···S contacts within the cis-oid dimer (3.0020(7) and 3.0115(8) Å) fall within the normal range observed for DTDA cis-oid dimers. The angle between the two DTDA ring planes is 21.97°, significantly larger than observed in previous cocrystals of this type. The opening up of the angle between the two ring planes reduces the effectiveness of the orbital overlap, reducing the strength of the π-π bonding interaction. Notably this does not appear driven by the steric bulk of the iodo groups since the I···I separation (4.6041(4) Å) is significantly larger than the sum of the van der Waals radii (4.30 Å). Instead it may occur as a result of the large angle between perfluoroaryl and DTDA ring planes (48.85° and 47.69°) which enhances the steric bulk of the substituent. The corresponding angles for other cocrystals are less than 38° (Table 3.1).
<table>
<thead>
<tr>
<th>Compound</th>
<th>ds···S/Å</th>
<th>DTDA/DTDA angle/°</th>
<th>ArF/DTDA angle/°</th>
<th>ds···O/Å</th>
</tr>
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<tbody>
<tr>
<td>[C₆F₅CNSSN]₂[TEMPO]</td>
<td>2.974(1)</td>
<td>14.26</td>
<td>34.29</td>
<td>2.9061</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.9234</td>
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<tr>
<td>[p-ClC₆F₄CNSSN]₂[TEMPO]</td>
<td>2.970(1)</td>
<td>12.08</td>
<td>28.72, 37.18</td>
<td>2.807(3)</td>
</tr>
<tr>
<td></td>
<td>3.034(1)</td>
<td></td>
<td></td>
<td>2.787(3)</td>
</tr>
<tr>
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<td></td>
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<td>3.264(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.131(4)</td>
</tr>
<tr>
<td>[p-BrC₆F₄CNSSN]₂[TEMPO]</td>
<td>2.979(2)</td>
<td>11.51</td>
<td>22.18, 31.58</td>
<td>3.134(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.052(4)</td>
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<td></td>
<td></td>
<td>2.922(4)</td>
</tr>
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<td>2.787(4)</td>
</tr>
<tr>
<td>[p-IC₆F₄CNSSN]₂[TEMPO]</td>
<td>3.0020(7)</td>
<td>21.97</td>
<td>47.69, 48.85</td>
<td>2.822(2)</td>
</tr>
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<td></td>
<td>3.0115(8)</td>
<td></td>
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<td>3.014(2)</td>
</tr>
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<td>3.035(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.941(2)</td>
</tr>
<tr>
<td>[p-NCC₆F₄CNSSN]₂[TEMPO]</td>
<td>3.0195(7)</td>
<td>36.28</td>
<td>42.19, 66.59</td>
<td>2.832(2)</td>
</tr>
<tr>
<td></td>
<td>3.0281(7)</td>
<td></td>
<td></td>
<td>2.849(2)</td>
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<td></td>
<td>2.914(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.790(2)</td>
</tr>
</tbody>
</table>

Table 3.1: Selected geometric parameters for the [ArF-CNSSN]₂[TEMPO] supramolecular motif

The strain incorporated into the system to accommodate the S···S interaction is manifested in a ‘bowing’ of the DTDA molecule. The bowing angle can be calculated as the angle between the iodine, phenylene ring, and carbon of the heterocyclic ring, and this dimer species possesses bowing angles of 173.62° and 176.11° degrees, while an unstrained aromatic ring would have an idealized angle of 180°. This indicates that in this system there is some build-up of strain within the cis-oid dimers.¹⁹
While $p$-BrC$_6$F$_4$CNSSN sacrificed C-Br···N sigma-hole interactions to form the cocrystal, the packing of [p-IC$_6$F$_4$CNSSN]$_2$[TEMPO] retains the C-I···N sigma-hole interactions (Figure 3.19). These sigma-hole interactions are well within the sum of the van der Waal radii of I and N (3.53 Å) and possess near linear C-I···N angles of 172.58° and 167.97°, consistent with the sigma-hole directionality often seen with these types of interactions. These link DTDA radicals parallel to the crystallographic b-axis.

Figure 3.19: Solid state packing of [p-IC$_6$F$_4$CNSSN]$_2$[TEMPO] highlighting supramolecular S···O and C-I···N contacts.

3.4.6.2 Powder X-Ray Diffraction Studies: PXRD was utilized to assess the phase purity of the bulk sublimed material. Figure 3.20 illustrates the experimentally obtained and simulated powder profiles for the [p-IC$_6$F$_4$CNSSN]$_2$[TEMPO] cocrystal, as well as the powder pattern of the pristine DTDA radical alone. Again, the bulk material exhibits relatively broad PXRD profiles indicative of small crystalline particles. Nevertheless, taking
into account the broadness, comparison of these powder profiles reveals the bulk
cocrystal is in fact phase pure and is not contaminated with $p$-$IC_6F_4CNSSN$.

**Figure 3.20:** Experimental (bottom) and simulated (middle) PXRD patterns of $[p$-$IC_6F_4CNSSN]_2[TEMPO]$ and pristine $p$-$IC_6F_4CNSSN$ (top)

### 3.4.6.3 EPR Spectroscopy:

EPR studies on this cocrystal system revealed the presence of an intense 1:1:1 triplet corresponding to the TEMPO radical ($a_N = 15.88$ G), along with an overlapping pentet consistent with the $p$-$IC_6F_4CNSSN$ radical component ($a_N = 5.22$ G) (Figure 3.21).
3.4.7 Characterization of [p-NCC₆F₄CNSSN]₂[TEMPO]

While p-NCC₆F₄CNSSN is known to be polymorphic,¹⁰ neither form dimerizes in the solid state. In addition, both phases exhibit the robust S₂···NC supramolecular synthon²³ and cocrystal formation would necessitate cleavage of this interaction in order to form the ubiquitous S₂···O-N contacts to TEMPO. The ability to form a cocrystal between p-NCC₆F₄CNSSN and TEMPO therefore provides a qualitative probe of the relative strengths of the S₂···NC vs S₂···O-N interactions. Cocrystallization studies revealed formation of a 2:1 cocrystal, [p-NCC₆F₄CNSSN]₂[TEMPO]:

3.4.7.1 Single Crystal X-Ray Diffraction: The 2:1 cocrystal of [p-NCC₆F₄CNSSN]₂[TEMPO] was found to crystallize in the triclinic space group P̅I. The crystal structure comprises a formal cis-oid p-NCC₆F₄CNSSN dimer linked to one TEMPO radical through a set of intermolecular S···O contacts (Figure 3.22).
Despite the superficial similarities to other cocrystals in this series, the geometry of the interactions is rather different suggesting substantial compromise to accommodate the S₄⋯O interaction. The cis-oid [p-NCC₆F₄CNSSN]₂ dimer exhibits intradimer S⋯S contacts of 3.0195(7) and 3.0281(7)Å, comparable with other DTDA dimers. However, the torsion angles between the perfluoroaryl planes and DTDA ring planes are 42.19 and 65.59°, substantially larger than those seen previously in these cocrystal systems. Normally the DTDA ring planes are close to planarity, maximizing the π*-π* orbital overlap but in this case the rings are inclined at 36.28°, substantially larger than any other derivative in this series (Table 3.1). While the S⋯O contacts between DTDA S atoms and the TEMPO O atom are similar to others in this series, the orientation of the TEMPO molecule with respect to the DTDA dimer is markedly different. Perspective views of the five cocrystals in this series are presented in Figure 3.23 and an angle θ defined as (90 – ϕ) where ϕ is the angle between the two planes containing (i) the two C atoms of the DTDA
cis-oid dimer and the TEMPO O atom and (ii) the two C atoms alpha to the NO group and the TEMPO O atom. When the TEMPO ring plane is co-parallel to the DTDA ring planes then $\theta = 0^\circ$, whereas $\theta = 90^\circ$ reflects the TEMPO and DTDA ring planes being mutually perpendicular.

Figure 3.23 clearly reveals that the $S_4 \cdots O$ interaction is quite severely distorted for $[p\cdot CLC_6F_4CNSSN]_2[TEMPO]$ with the TEMPO O atom distinctly offset from the $S_4$ centroid.
Notably all \([p-XC_6F_4CNSSN]_2[TEMPO]\) cocrystals \((X = F, \text{Cl}, \text{Br}, \text{I})\) exhibit TEMPO planes near perpendicular \((\theta \sim 90^\circ)\) to the DTDA ring planes whereas \([p-NCC_6F_4CNSSN]_2[TEMPO]\) adopts an alternative conformation. While the preference for the former arrangement may be a range of packing forces, an orbital contribution may also play some small part.

Figure 3.24 shows the idealized orbital interactions for \(\theta = 0\) and \(90^\circ\). In the former case the TEMPO SOMO is essentially non-bonding with respect to the HOMO (and LUMO) of the cis-oid DTDA \(\pi^*-\pi^*\) dimer. In the latter case, which is dominant in this series, the TEMPO SOMO is in phase with the DTDA \(\pi^*-\pi^*\) HOMO. While this orbital interaction is likely weak, it may contribute significantly within the context of the multiple weak non-covalent interactions which are characteristic of supramolecular chemistry.

An examination of the environment of the cyano group, reveals a complete absence of structure-directing \(S_2\cdots\text{NC}\) interactions but a lateral close contact between the CN group and a DTDA heterocyclic N atom is observed which is similar to that seen in \(\alpha-p-\)
NCC₆F₄CNSSN radical. The C⋯N closest contact is 3.192(4) Å and the N⋯S contact is 3.365(4) Å. The corresponding distances in α-p-NCC₆F₄CNSSN are 3.235(3) and 3.407(3) Å.

![Chemical structure and diagram](image)

Figure 3.25: Lateral CN⋯S-N interactions in (left) [p-NCC₆F₄CNSSN]₂[TEMPO] and (right) α-p-NCC₆F₄CNSSN.

### 3.4.7.2 Powder X-Ray Diffraction Studies

PXRD was utilized to assess the phase purity of the bulk cocrystal. Figure 3.26 illustrates the experimentally obtained and simulated powder profiles for the [p-NCC₆F₄CNSSN]₂[TEMPO] cocrystal. Comparison of these powder profiles reveals the bulk cocrystal appears phase pure, with no evidence for contamination with the DTDA radical p-NCC₆F₄CNSSN.
Figure 3.26: Experimental (bottom) and simulated (middle) PXRD patterns of $[\text{p-NCC}_6\text{F}_4\text{CNSSN}]_2[\text{TEMPO}]$ and pristine $\beta$-$\text{p-NCC}_6\text{F}_4\text{CNSSN}$ (top)

3.4.7.3 EPR Spectroscopy: EPR measurements on the $[\text{p-NCC}_6\text{F}_4\text{CNSSN}]_2[\text{TEMPO}]$ cocrystal in dry CH$_2$Cl$_2$ reveal again the presence of an intense 1:1:1 triplet diagnostic of TEMPO ($g = 2.0057$, $a_N = 15.65$ G), as well as a second overlapping 1:2:3:2:1 pentet ($g = 2.0100$, $a_N = 4.98$ G) corresponding to the DTDA component.

Figure 3.27: Room temperature solution X-band EPR spectrum of $[\text{p-NCC}_6\text{F}_4\text{CNSSN}]_2[\text{TEMPO}]$
3.4.8 Characterization of \([C_6F_5CNSeSeN]_2[TEMPO]\)

As an extension of the work on DTDA cocrystals with TEMPO, the reactivity of perfluoroaryl DSDA radicals with TEMPO was explored. Specifically, the potential for the perfluorophenyl DSDA radical (C\(_6\)F\(_5\)CNSeSeN) to cocrystallize with TEMPO was examined. Reaction of C\(_6\)F\(_5\)CNSeSeN with TEMPO in an identical fashion to the perfluoroaryl DTDA series described in sections 3.4.1 – 3.4.5.

3.4.8.1 Single Crystal X-Ray Diffraction: Sublimation afforded the 2:1 cocrystal, \([C_6F_5CNSeSeN]_2[TEMPO]\) which crystallizes in the triclinic space group \(P\bar{1}\). Figure 3.28 illustrates the crystal structure which exhibits three molecules in the asymmetric unit; a cis-oid DSDA dimer and one TEMPO radical. The DSDA dimer exhibits asymmetric intra-dimer Se…Se contacts of 3.1330(8) and 3.1895(7) Å, slightly shorter than the symmetric contacts observed in pristine \([C_6F_5CNSeSeN]_2\).\(^{19}\) The angles formed between perfluoroaryl and DTDA ring planes are 39.01° and 42.13° for the two crystallographically independent radical while the angle formed between the two DSDA rings is 17.78° (cf. \([C_6F_5CNSSN]_2[TEMPO]\) at 14.26°). The cis-oid dimer interacts with TEMPO through a set of tetrafurcated \(\delta^+\text{Se} \cdots \text{O}^\ominus\) contacts in the range 2.897(5) – 3.348(4) Å with the TEMPO O atom displaced away from the Se\(_4\) centroid. The \(\theta\) angle between the DSDA dimer and the TEMPO ring plane is 25.47°, similar in geometry to \([p-NCC_6F_4CNSSN]_2[TEMPO]\).
Figure 3.28: (left) Crystal structure of $[\text{C}_6\text{F}_5\text{CNSeSeN}]_2[\text{TEMPO}]$ with thermal ellipsoids for non-H atoms displayed at 50% probability; (centre and right) detail of the Se$_4$···O interactions.

The displacement of the TEMPO O atom would appear to be a consequence of other packing forces. Specifically, the well-established set of lateral Se-N contacts$^{19}$ (2.914(6) and 3.024(6) Å) bring two dimers close together such that the stericos of the perfluoroaryl ring displaces the TEMPO radical from the centroid of the Se$_4$ centroid (Figure 3.29).

Figure 3.29: Intermolecular Se···N contacts in $[\text{C}_6\text{F}_5\text{CNSeSeN}]_2[\text{TEMPO}]$.

### 3.4.8.2 Powder X-Ray Diffraction Studies:
PXRD again verified the phase purity of the bulk sublimed material. Figure 3.30 illustrates the experimentally obtained and simulated powder profiles for the $[\text{C}_6\text{F}_5\text{CNSeSeN}]_2[\text{TEMPO}]$ cocrystal, as well as the powder pattern
of the pristine DSDA radical alone. Comparison of these powder profiles reveals the bulk cocystal is in fact phase pure, and there is no contamination from the DSDA radical alone apparent through analysis of the PXRD profiles.

**Figure 3.30:** Experimental (bottom) and simulated (middle) PXRD patterns of $[C_6F_5CNSeSeN]_2[TEMPO]$ and pristine $C_6F_5CNSeSeN$ (top)

### 3.4.8.3 EPR Spectroscopy:

EPR spectroscopy was again used as a mean of confirming the identity of the cocystal. A small amount of the $[C_6F_5CNSeSeN]_2[TEMPO]$ was dissolved in CH$_2$Cl$_2$ to reveal an intense 1:1:1 triplet ($g = 2.006$, $a_N = 15.48$ G) indicative of the TEMPO radical, along with a broad singlet ($g = 2.039$), corresponding to the DSDA component. While DSDA radicals provide well-resolved anisotropic EPR spectra (see Chapter 2), the increased anisotropy in selenium systems, which scales as $Z^4$, leads to line broadening, which in turn affects the EPR signal so that hyperfine coupling to N or Se is not detectable in standard isotropic solution spectra. Simulation of the EPR spectrum ($R^2 = 0.9977$) afforded a 0.67:1 $C_6F_5CNSeSeN$:TEMPO ratio, significantly lower than the expected 2:1 ratio from crystallographic studies. However, this can be rationalized as previous studies.
have shown that even at low concentrations DSDAs show a strong propensity to dimerize. This leads to reduced quantities of monomeric $C_6F_5CNSeSeN$ in solution.

Figure 3.31: Room temperature X-band solution EPR spectrum of $[C_6F_5CNSeSeN]_2[TEMPO]$

In order to further probe the magnitude at which the DSDA dimers are in fact dimerizing, a variable temperature solution EPR experiment was undertaken on this cocrystal system. Figure 3.32 illustrates a variable temperature EPR plot across the range 183 – 273 K. At low temperatures, there is only one feature present; the 1:1:1 triplet corresponding to TEMPO, with no features evident for the $C_6F_5CNSeSeN$ radical. This suggests that all DSDA present in the sample has dimerized below 220 K. As the temperature is gradually increased, the dimers are able to dissociate and a broad low field resonance, expected for the DSDA component, becomes visible.
3.4.9 Characterization of \([p\text{-BrC}_6\text{F}_4\text{CNSeSeN}]_2[\text{TEMPO}]\)

Structural studies on \([C_6\text{F}_5\text{CNSeSeN}]_2\) reveal it forms a cis-oid dimer\(^{10}\) but \([p\text{-ClC}_6\text{F}_4\text{CNSeSeN}]_2\) and \([p\text{-BrC}_6\text{F}_4\text{CNSeSeN}]_2\) exhibit an unusual edge-to-face \(\pi-\pi\) interaction,\(^{19}\) potentially indicating that the cis-oid dimer is a less stable conformation.

While attempts to prepare \([p\text{-ClC}_6\text{F}_4\text{CNSeSeN}]_2[\text{TEMPO}]\) were inconclusive with no crystal suitable for X-ray diffraction isolated during the lifetime of this thesis, crystals of \([p\text{-BrC}_6\text{F}_4\text{CNSeSeN}]_2[\text{TEMPO}]\) could be isolated.

3.4.9.1 Single Crystal X-Ray diffraction: \([p\text{-BrC}_6\text{F}_4\text{CNSeSeN}]_2[\text{TEMPO}]\) crystallizes in the monoclinic space group \(P2_1/c\) with the ubiquitous three molecules in the asymmetric unit, comprising one cis-oid \((p\text{-BrC}_6\text{F}_4\text{CNSeSeN})_2\) dimer and one TEMPO radical (Figure 3.33). The \textit{cis-oid} DSDA dimer exhibits intra-dimer Se\(\cdots\)Se contacts of 3.066(2) and 3.224(2) Å. Nonetheless, cocrystallization and the strength of the Se\(\cdots\)O contact sees the DSDA dimer
in the classical *cis-oid* dimer in this cocrystal system. The angles between the two crystallographically independent sets of perfluoroaryl and DSDA ring planes are 59.16° and 74.32°. These large twist angles increase the steric bulk of the perfluoroaryl group and the two DSDA ring planes are inclined at 30.37°, comparable to \([p\text{-}NCC_6F_4CNSSN]_2[TEMPO]\) (36.28°). The DSDA dimer forms a set of asymmetric \(\text{Se}_4 \cdots \text{O}\) contacts of 2.968(7), 2.972(8), 3.285(6), and 3.071(6) Å, comparable to those observed in other DTDA/DSDA-TEMPO cocrystal systems. The \(\theta\) angle for this system is 52.48°, reflecting the TEMPO radical plane lying close to an \(\text{Se}_4\) diagonal.

![Figure 3.33](image)  
*(left)* Crystal structure of \([p\text{-}BrC_6F_4CNSeSeN]_2[TEMPO]\) with thermal ellipsoids for non-H atoms displayed at 50% probability; *(centre and right)* detail of the \(\text{Se}_4 \cdots \text{O}\) interactions.
The packing of \([p-\text{BrC}_6\text{F}_4\text{CNSeSeN}]_2[\text{TEMPO}]\) exhibits multiple lateral Se···N contacts between DSDA rings with Se···N contacts in the range 2.851(8) – 3.241(8) Å (Figure 3.34) with three of the four crystallographically independent DSDA N atoms forming such contacts.

Figure 3.34: Packing of \([p-\text{BrC}_6\text{F}_4\text{CNSeSeN}]_2[\text{TEMPO}]\) highlighting intermolecular Se···N and Se···O contacts.

3.4.9.2 EPR Spectroscopy: Room temperature solution EPR studies conducted on the \([p-\text{BrC}_6\text{F}_4\text{CNSeSeN}]_2[\text{TEMPO}]\) cocrystal reveal an intense 1:1:1 triplet \((a_N = 14.88 \text{ G})\) corresponding to the TEMPO component, with an additional second low field feature comprising a broad singlet diagnostic of the DSDA component. Simulation of this EPR spectrum \((R^2 = 0.998)\) reveals a relative DSDA:TEMPO ratio of 0.71:1, much lower than the expected 2:1 ratio, which can be attributed to the strong propensity for DSDA radicals to dimerize in solution.\(^{19,40}\)
The last few sections have clearly identified that cocrystal formation is successful for a wide range of perfluoroaryl DTDA and DSDA radicals with TEMPO. All these derivatives exhibit an $E_4\cdots\cdot\cdot\cdot O$ tetrafurcated interaction between a cis-oid DTDA or DSDA radical dimer and the TEMPO O. As an extension of these initial studies we examined TEMPONE which offers both N-O and C=O functionality to act as templating agents. These studies were aimed to examine the competition between $E_4\cdots\cdot\cdot\cdot O\cdot N$ and $E_4\cdots\cdot\cdot\cdot O=C$ interactions and, if $E_4\cdots\cdot\cdot\cdot O=C$ is also a supramolecular synthon, to see if TEMPONE can support cis-oid dimers at both N-O and C=O functionalities affording 4:1 cocrystals.

In the first two experiments, $[C_6F_5CNSSN]_2$ and $[C_6F_5CNSeSeN]_2$ were cosublimed with TEMPONE. A range of stoichiometries ranging from 1:1 to 4:1 were employed but only
cocrystals of formula [C₆F₅CNSSN]₂[TEMPONE] and [C₆F₅CNSeSeN]₂[TEMPONE] were isolated.

3.4.10.1 Single Crystal X-Ray Diffraction: [C₆F₅CNSSN]₂[TEMPONE] crystallizes in the triclinic space group P̅1, with three molecules in the asymmetric unit consisting of one DTDA cis-oid dimer and one TEMPONE radical with a tetrafurcated S₄⋯O-N interaction comparable to previously characterized DTDA/TEMPO derivatives. The DTDA dimer exhibits unexceptional intra-dimer S⋯S contacts of 2.9600(8) and 3.0411(9) Å. The angles between perfluoroaryl and DTDA ring planes in the two crystallographically independent DTDA molecules are 48.52° and 46.77°. This leads to an angle of 21.26° between the two DTDA radicals (cf 14.26° for [C₆F₅CNSSN]₂[TEMPO]). The cis-oid DTDA dimer forms a tetrafurcated S₄⋯O interaction to the N-O group of the TEMPONE radical with S₄⋯O contacts of 2.873(1), 2.896(2), 2.917(1) and 3.019(1) Å. The θ angle

Figure 3.36: (left) Crystal structure of [C₆F₅CNSSN]₂[TEMPONE]. Thermal ellipsoids for non-H atoms displayed at 50% probability; (right) detail of the S₄⋯O contact between the cis-oid DTDA dimer and the TEMPONE radical.
is 87.75°, offering an almost idealized bonding interaction between the HOMO of the cis-oid dimer and the TEMPONE SOMO (Figure 3.24). The C=O group which is not involved in a tetrafurcated interaction instead forms a centrosymmetric interaction with a second carbonyl group (C⋯O at 3.191(3) Å) (Figure 3.37).

![Figure 3.37: Supramolecular assembly of [C₆F₅CNSSN]₂[TEMPONE] units via carbonyl⋯carbonyl interactions.]

### 3.4.10.2 Powder X-Ray Diffraction Studies:
PXRD was used to verify the phase purity of the bulk sublimed material. Figure 3.38 illustrates the experimentally obtained and simulated powder profiles for the [C₆F₅CNSSN]₂[TEMPO] cocrystal, as well as the powder patterns for the starting materials, [C₆F₅CNSSN]₂ and TEMPONE. While there are some minor discrepancies in peak positions and intensities, the powder profile suggests that the bulk material is phase pure.
**3.4.10.3 EPR Spectroscopy:** Figure 3.39 illustrates the solution X-band EPR spectrum of this cocrystal system, which revealed the expected overlapping of a dominant 1:1:1 triplet ($g = 2.0053$, $a_N = 14.67$ G) corresponding to the TEMPONE radical and an overlapping 1:2:3:2:1 pentet ($g = 2.0098$, $a_N = 5.15$ G) corresponding to the $C_6F_5CNSSN$ component. Simulation of the EPR spectrum parameters ($R^2 = 0.991$) results in a relative ratio of 1.30:1 DTDA: TEMPONE, lower than the expected 2:1 ratio. This is common for such cocrystal complexes given the propensity for DTDA and DSDA radicals to dimerize in solution.
3.4.11 Characterization of [C₆F₅CNSeN]₄[TEMPONE]

3.4.11.1 Single Crystal X-Ray Diffraction: As an extension of the TEMPONE studies, the next step was to observe the effect of substituting selenium for sulfur in this cocrystal system. [C₆F₅CNSeN]₄[TEMPONE] was found to crystallize in the triclinic space group P̅1, isomorphous with [C₆F₅CNSSN]₂[TEMPONE]. The DSDA dimer exhibits intra-dimer Se…Se contacts of 3.2456(4) and 3.0664(4) Å. The angles between the two crystallographically independent perfluoroaryl and DTDA ring planes are 49.41° and 53.30°. The two DSDA ring planes form an angle of 20.63°. The cis-oid DSDA dimer exhibits Se…O contacts of 3.016(2), 3.014(2), 2.999(2), and 3.105(2) Å to the TEMPONE nitroxide O atom.
3.4.11.2 Powder X-Ray Diffraction Studies: PXRD was used to confirm the phase purity of the bulk cocrystal. Figure 3.41 illustrates the experimentally obtained and simulated powder profiles for the \([C_6F_5CNSeSeN]_2[TEMPO]\) cocrystal, as well as the computed powder pattern for \([C_6F_5CNSeSeN]_2\) and TEMPONE. Comparison of these powder profiles reveal the phase purity of the sublimed material.

Figure 3.40: Crystal structure of \([C_6F_5CNSSN]_2[TEMPO]\). Thermal ellipsoids for non-H atoms displayed at 50% probability.

Figure 3.41: Experimental (bottom) and simulated (middle-grey) PXRD patterns of \([C_6F_5CNSeSeN]_2[TEMPO]\) and pristine \([C_6F_5CNSeSeN]_2\) (middle-top) and TEMPONE (top)
3.4.11.3 EPR Spectroscopy: EPR spectroscopy conducted on the [C₆F₅CNSeSeN]₂[TEMPONE] cocrystal reveals an intense 1:1:1 triplet ($a_N = 14.33$ G) corresponding to the TEMPONE component and a second broad singlet ($g = 2.0397$) observed slightly downfield from the triplet, diagnostic of the C₆F₅CNSeSeN component (Figure 3.42). Additionally, simulation of the EPR spectrum ($R^2 = 0.999$) afforded a relative DSDA:TEMPONE ratio of 1.06:1, which corresponds to approximately 50% of the DSDA radicals present as dimers.

Figure 3.42: Room temperature X-band EPR spectrum of [C₆F₅CNSeSeN]₂[TEMPONE]
3.5 Conclusions

In this Chapter two new classes of radical-radical cocrystals have been prepared through the exploitation of a simple thermodynamic approach, comprising [DTDA]$_2$[TEMPO(NE)] and [DSDA]$_2$[TEMPO(NE)]. In total 9 new cocrystals have been isolated and structurally characterized. In all cases the DTDA or DSDA radicals adopt a cis-oid dimer motif which forms tetrafurcated E$_4$⋯O-N interactions with either TEMPO or TEMPONE. For [p-XC$_6$F$_5$CNSSN]$_2$[TEMPO] (X = F, Cl, and Br), PXRD studies on the material before and after sublimation, indicate cocrystallization commences upon solvent removal, prior to vacuum sublimation.

The repeated appearance of this interaction, even when competing with established supramolecular synthons such as S$_2$⋯NC, reflects the robust nature of this intermolecular interaction. It should be noted that [PhCNSSN]$_2$ and [PhCNSeSeN]$_2$ fail to form cocrystals with TEMPO under the conditions employed, suggesting the lattice enthalpies of these two radicals are too high in relation to their fluorinated analogues. Energetically it is noteworthy that the enthalpy of fusion for [PhCNSSN]$_2$ is 57.6 kJ·mol$^{-1}$ whereas the corresponding $\Delta H_{\text{ fus}}$ for [C$_6$F$_5$CNSSN]$_2$ is 36.1 kJ·mol$^{-1}$, suggesting relatively subtle changes in vaporization enthalpy may affect whether cocrystal formation is observed or not. In many cases cold finger temperatures below zero were often required to isolate cocrystals, suggesting that low temperatures (when entropic contributions are minimized) are required to favor cocrystal formation. This is consistent with cocrystal formation being marginally enthalpically favorable. It is clear that cocrystal formation in these systems reflects very subtle energetics and small contributions of even just a few
kJ·mol$^{-1}$ may prove significant in term of making the overall thermodynamic aspects of cocrystal formation favorable. The fact that $p$-NCC$_6$F$_4$CNSSN sacrifices the well-established robust S$_2$···NC supramolecular synthon$^{23}$ to form S$_4$···O interactions speaks to the strength of this new architectural building block.

Initial cocrystallization attempts began with the hypothesis of forming 1:1 systems with E$_2$···O-N interactions and both building blocks retain their paramagnetism. The persistent experimental observation of a 2:1 cocrystal is retrospectively unsurprising since it combines the strong enthalpic preference for DTDA and DSDA radicals to form π*-π* dimers as well as the structure directing favorable E$_4$···O interaction, each of which contribute substantially to the total lattice enthalpy. In this context it is noteworthy that the radical-radical cocrystal [PhCNSSN][S$_3$N$_2$]Cl forms a similar tetrafurcated S$_4$···Cl interaction.$^{41}$ Identification of favorable interactions of this type offer the potential for further approaches to cocrystal formation in DTDA and DSDA chemistry.

EPR spectroscopy proved useful for identifying the presence and identity of the individual radical components in each cocrystal system. In solution the observed EPR spectra reflect a superposition of the two individual radicals present. However, the propensity of the DTDA and particularly DSDA radicals to dimerize in solution means that EPR cannot be reliably implemented to determine the chemical composition. In future, detailed VT-EPR studies could be used to estimate dimerization enthalpies for DTDA and/or DSDA radicals using another radical as an internal standard. This is clearly seen in the variable temperature studies completed on the [C$_6$F$_5$CNSeSeN]$_2$[TEMPO] system, where there is no signal present for the DSDA component below 220 K.
3.6 References


28. APEX-3, Bruker AXS, Madison, Wisconsin, USA.

29. SADABS, Bruker AXS Inc., Madison, Wisconsin, USA.


Chapter 4  Conclusions and Future Work

Chapter 1 of this thesis outlined some of the unusual physical properties associated with paramagnetic organic molecules and the inter-relationship between their structure and function. The work presented in Chapters 2 and 3 of this thesis has focused on the use of dithiadiazolyl and diselenadiazolyl radicals as just two examples of thermally stable radicals as possible building blocks for the construction of novel multi-component materials.

In Chapter 2 the inclusion chemistry of four stable main-group radicals (\([\text{PhCNSSN}]_2, [\text{PhCNSeSeN}]_2, [\text{C}_6\text{F}_5\text{CNSSN}]_2, \text{and} [\text{C}_6\text{F}_5\text{CNSeSeN}]_2\) into the porous framework MIL-53(Al) has been explored via gas phase diffusion. In all cases, inclusion of the radical guest into the porous framework was found to result in enhanced thermal stability of each radical. PXRD studies revealed they all adopt the orthorhombic Imma space group, also known as the MIL-53(Al)-ht phase. High radical loadings up to 0.5 molecules of guest per MIL-53(Al) unit were observed (cf a maximum computed loading of 0.85 based on the void space with 100% packing efficiency). Magnetic measurements reveal the majority of radicals form diamagnetic \(\pi^*\text{-}\pi^*\) dimers within the channels while EPR spectra reflect limited molecular motion within the channels on the EPR timescale at ambient temperature. Variable-temperature PXRD studies coupled with TGA measurements revealed elimination of the radical from the channels at elevated temperatures but with distinct release mechanisms which appear sensitive to the guest: PhCNSSN@MIL-53(Al) exhibited the highest radical loadings and guest elimination appeared linked to a wine-rack ‘breathing’ mode of the host lattice. For \(\text{C}_6\text{F}_5\text{CNSSN}@\text{MIL-}\)
53(Al) radical elimination occurs at lower temperatures and a build-up of the monoclinic MIL-53(Al)-\textit{lt} phase is observed on removal of the guest, followed by the established transformation\textsuperscript{1} to the orthorhombic MIL-53(Al)-\textit{ht} phase at elevated temperatures. Conversely the more thermally robust DSDA derivatives appear to predominantly follow a simpler mechanism in which diffusion of the radical retains the MIL-53(Al)-\textit{ht} phase. Despite population of the channel structure with radical guests, treatment with halogens (Cl\textsubscript{2}, Br\textsubscript{2} and I\textsubscript{2}) led to radical oxidation, indicating mobility of the halogens within the channels despite the presence of the radical guests. MIL-53(Al) is a suitable diamagnetic host for preliminary inclusion studies. However, it is just one member of a larger series of closely related paramagnetic frameworks with MIL-53(Fe) and MIL-53(Cr) providing promising alternative host frameworks in which to explore magnetic interactions between paramagnetic hosts and guests. In this context, the development of a simple synthetic pathway for the preparation of crystalline phase-pure MIL-53(Al) as part of this thesis may prove advantageous.

Supramolecular chemistry incorporates a range of non-covalent interactions to help control aspects of solid-state structure of molecule-based species. Within organic chemistry a large number of supramolecular synthons are well-established, of which hydrogen-bonding\textsuperscript{2} the six-fold phenyl embrace,\textsuperscript{3} \( \pi \)-stacking between electron-rich and electron-poor aromatics,\textsuperscript{4} and sigma-hole interactions\textsuperscript{5} provide just some examples. The application of such interactions to facilitate formation of radical-radical cocrystals is limited, although examples of hydrogen-bonded nitronyl nitroxide radical pairs are known\textsuperscript{6} as well as \( \pi \ldots \pi \) interactions in two pairs of DTDA radical cocrystals.\textsuperscript{7} The work in
Chapter 3 of this thesis provides a unique study in which the radical units themselves act as the supramolecular synthons. These studies clearly identify that the N-O unit of nitroxide radicals forms a robust supramolecular synthon with cis-oïd π−π dimers of DTDA and DSDA radicals through a tetrafurcated set of $\delta^+\ldots\delta^-$ contacts, with a set of nine crystal structures all revealing this motif. The TEMPONE radical was also used to provide a competing site for a potential tetrafurcated C=O...E$\delta^+$ contact but structural studies show a persistent preference for the nitroxide group. A simple qualitative thermodynamic analysis of cocrystal formation was used to explain the propensity for volatile perfluoroaryl DTDA and DSDA radicals to participate in cocrystal formation whereas the simpler (non-fluorinated) aryl derivatives were less volatile and led to phase separation. In all these cocrystals the DTDA and DSDA radicals adopt the cis-oïd π−π dimer motif, effectively quenching paramagnetism in this unit.

Attempts were made to cocrystallize dithiadiazolyl and diathiazolyl radicals together, as there have been reports in the literature of this success. However, attempts of obtaining X-ray diffraction quality crystals were unsuccessful to the extreme sensitivity noted with this experiment. However, following mixing of the $\text{C}_6\text{F}_5\text{CNSSN}$ and MBDTA radicals in a 1:1 ratio in CH$_2$Cl$_2$ and removing the solvent in vacuo in an identical fashion to that done for the previously reported cocrystal systems appears to have formed a cocrystal as seen in the obtained EPR spectrum. The EPR spectrum consists of a superposition of a triplet and pentet, consistent with cocrystallization of a DTDA and DTA radical.
Additionally, PXRD studies reveals that the powder profile of the product does not match either the MBDTA or C₆F₅CNSSN radicals on their own, nor does it appear to be a mixture of peaks from each individual powder pattern, which also points toward cocrystal formation. Since EPR spectroscopy confirms cocrystal formation, and PXRD studies reveal the formation of a new material, future work will consist of repeating these experiments so that X-ray diffraction quality material may be obtained.

Figure 4.2: PXRD patterns of [C₆F₅CNSSN][MBDA] (bottom), MBDTA radical (middle) and [C₆F₅CNSSN]₂ (top)
Future work implementing sterically encumbered DTDA/DSDA radicals which disfavour cis-oid $\pi-\pi$ dimerization should suppress formation of this motif and afford a simpler bifurcated 1:1 adduct with two E...O contacts. This would permit an examination of through-space magnetic exchange between the two $S = \frac{1}{2}$ DTDA (or DSDA) and TEMPO-based radicals. The ability to establish robust structural synthons which also provide effective magnetic communication may facilitate formation of new organic ferrimagnets.

In summary the work presented in this thesis provides new insight into two areas of contemporary supramolecular chemistry; host-guest interactions in metal-organic frameworks and co-crystal formation. The use of redox-active radicals in these systems provides additional techniques (SQUID magnetometry and EPR spectroscopy) to probe host-guest interactions, while the identification of robust supramolecular synthons for radical-radical cocrystal studies is an important step towards the generation of new organic ferrimagnets.
4.1 References


APPENDICES

Appendix 1  Permission Requests

A1.1 Permission Request for Chapter 1 Figure 1.29

Title: Impact of Preparation and Handling on the Hydrogen Storage Properties of Zn4O(1,4-benzenedicarboxylate)3 (MOF-5)

Author: Steven S. Kaye, Anne Dailly, Omar M. Yaghi, et al

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Nov 1, 2007

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If credit is given to another source for the material you requested, permission must be obtained from that source.
A1.2 Permission Request for Chapter 1 Figure 1.31

Title: Very Large Breathing Effect in the First Nanoporous Chromium(III)-Based Solids: MIL-53 or CrIII(OH){O2C−C6H4−CO2}·{HO2C−C6H4−CO2H}x·H2Oy

Author: Christian Serre, Franck Millange, Christelle Thouvenot, et al.

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Nov 1, 2002

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Appendix 2  
Supplementary Crystallography Information

A2.1 Crystal data and structure refinement for [C₆F₅CNSSN]₂[TEMPO]

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A2.2 Crystal data and structure refinement for \([p\text{-ClC}_6F_4\text{CNSSN}]_2\text{[TEMPO]}\]

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196
A2.3 Crystal data and structure refinement for \([p\text{-BrC}_6\text{F}_4\text{CNSSN}]_2\text{[TEMPO]}\)

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Identification Code mo_HEMANpIC6F4DTEMPO_0m_a

Empirical Formula C23H18F8I2N5O4

Formula weight 914.46

Temperature 170(2) K

Crystal system Monoclinic

Space group P21/n

a/Å 8.3625(5)
b/Å 14.4160(7)
c/Å 25.1628(12)
α/° 90
β/° 93.636
γ/° 90

Volume/ Å³ 3027.4(3)

Z 4

Density calc mg/m³ 2.006

Absorption coefficient/mm⁻¹ 2.432

F(000) 1764

Crystal size/mm³ 0.325 x 0.190 x 0.140

Radiation MoKα (λ = 0.71073)

2θ range for data collection/° 2.891 to 29.184

Index ranges -11 ≤ h ≤ 11, -19 ≤ k ≤ 19, -34 ≤ l ≤ 34

Reflections collected 90861

Independent reflections 8179 [R(int) = 0.0315]

Data/restraints/parameters 8179/0/392

Goodness-of-fit on F² 1.041

Final R indices [I>2σ (I)] R₁ = 0.0233, wR₂ = 0.0490

Final R indices (all data) R₁ = 0.0329, wR₂ = 0.0526

Largest diff. peak/hole/e Å⁻³ 0.769/-1.054
### A2.5 Crystal data and structure refinement for [p-NCC₆F₄CNSSN]₂[TEMPO]

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<td>Absorption coefficient/mm⁻¹</td>
<td>0.409</td>
</tr>
<tr>
<td>F(000)</td>
<td>722</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.450 x 0.120 x 0.077</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
</tr>
<tr>
<td>2θ range for data collection/°</td>
<td>3.153 to 2.447</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -18 ≤ l ≤ 18</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>72156</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>6031 [R(int) = 0.0487]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>6031/0/410</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.138</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>R₁ = 0.0342, wR₂ = 0.0804</td>
</tr>
<tr>
<td>Final R indices (all data)</td>
<td>R₁ = 0.0491, wR₂ = 0.0882</td>
</tr>
<tr>
<td>Largest diff. peak/hole/e Å⁻³</td>
<td>0.262/-0.335</td>
</tr>
</tbody>
</table>
A2.6 Crystal data and structure refinement for \([\text{C}_6\text{F}_5\text{CNSeSeN}]_2[\text{TEMPO}]\)

**Identification Code**  
DSDA_TEMPO_a

**Empirical Formula**  
\(\text{C}_{23}\text{H}_{18}\text{F}_{10}\text{N}_5\text{OSe}_4\)

**Formula weight**  
886.26

**Temperature**  
170(2) K

**Crystal system**  
Triclinic

**Space group**  
P\(\overline{1}\)

**a/Å**  
7.5591(3)

**b/Å**  
13.324(5)

**c/Å**  
15.8480(6)

**\(\alpha^\circ\)**  
111.179(2)

**\(\beta^\circ\)**  
93.272(2)

**\(\gamma^\circ\)**  
105.509(2)

**Volume/Å\(^3\)**  
1413.06(10)

**Z**  
2

**Density\(_{\text{calc}}\) mg/m\(^3\)**  
2.083

**Absorption coefficient/mm\(^{-1}\)**  
7.109

**F(000)**  
850

**Crystal size/mm\(^3\)**  
0.140 x 0.060 x 0.010

**Radiation**  
MoK\(\alpha\) (\(\lambda = 0.71073\))

**2\(\theta\) range for data collection/\(^\circ\)**  
3.035 to 65.357

**Index ranges**  
-8 \(\leq h \leq 8\), -15 \(\leq k \leq 15\), -18 \(\leq l \leq 18\)

**Reflections collected**  
21629

**Independent reflections**  
4812 [R(int) = 0.0714]

**Data/restraints/parameters**  
4812/0/392

**Goodness-of-fit on F\(^2\)**  
1.044

**Final R indices [I>2\(\sigma\) (I)]**  
\(R_1 = 0.0397\), \(wR_2 = 0.0904\)

**Final R indices (all data)**  
\(R_1 = 0.0623\), \(wR_2 = 0.1010\)

**Largest diff. peak/hole/e Å\(^3\)**  
0.688/-0.610
A2.7 Crystal data and structure refinement for \([p-\text{BrC}_6\text{F}_4\text{CNSeSeN}]_2[\text{TEMPO}]\)

Identification Code  
LW_NS_pBrC6F4DSDA_TEMPO_coxtal

Empirical Formula  
C_{23}H_{16}Br_{2}F_{8}N_{5}OSe_{4}

Formula weight  
1006.07

Temperature  
170(2) K

Crystal system  
Monoclinic

Space group  
P2_1/c

\(a/\text{Å}\)  
11.1500(8)

\(b/\text{Å}\)  
19.6825(14)

\(c/\text{Å}\)  
15.0730(11)

\(\alpha/\degree\)  
90

\(\beta/\degree\)  
110.815(2)

\(\gamma/\degree\)  
90

Volume/\text{Å}^3  
3092.0(4)

\(Z\)  
4

Density\text{calc} \text{mg/m}^3  
2.161

Absorption coefficient/mm\(^{-1}\)  
7.406

\(F(000)\)  
1908

Crystal size/mm\(^3\)  
0.109 x 0.115 x 0.202

Radiation  
MoK\(\alpha\) (\(\lambda = 0.71073\))

\(2\theta\) range for data collection/\degree  
2.998 to 18.907

Index ranges  
-10 \(\leq h \leq 10\), -17 \(\leq k \leq 17\), -13 \(\leq l \leq 13\)

Reflections collected  
36517

Independent reflections  
4468 [R(int) = 0.0323]

Data/restraints/parameters  
4468/0/392

Goodness-of-fit on \(F^2\)  
1.079

Final R indices [I>2\(\sigma\) (I)]  
\(R_1 = 0.0496, wR_2 = 0.1015\)

Final R indices (all data)  
\(R_1 = 0.0952, wR_2 = 0.1198\)

Largest diff. peak/hole/e \text{Å}^3  
0.385/-0.604
### A2.8 Crystal data and structure refinement for [C₆F₅CNSSN]₂[TEMPONE]

**Identification Code**
LW_NS_C6F5DTDA_TEMONE_0m

**Empirical Formula**
C₂₃H₁₈F₁₀N₅O₂S₄

**Formula weight**
886.26

**Temperature**
170(2) K

**Crystal system**
Triclinic

**Space group**
P\(\overline{1}\)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a/\AA)</td>
<td>8.2483(4)</td>
</tr>
<tr>
<td>(b/\AA)</td>
<td>11.5621(5)</td>
</tr>
<tr>
<td>(c/\AA)</td>
<td>15.1116(7)</td>
</tr>
<tr>
<td>(\alpha/\degree)</td>
<td>90.896(2)</td>
</tr>
<tr>
<td>(\beta/\degree)</td>
<td>105.020(2)</td>
</tr>
<tr>
<td>(\gamma/\degree)</td>
<td>92.380(2)</td>
</tr>
<tr>
<td>Volume/(\AA^3)</td>
<td>1386.92</td>
</tr>
</tbody>
</table>

**Z**
2

**Density \(_{calc}\) g/cm\(^3\)**
1.707

**Absorption coefficient/mm\(^-1\)**
0.444

**F(000)**
712

**Crystal size/mm\(^3\)**
0.040 x 0.060 x 0.246

**Radiation**
MoK\(\alpha\) (\(\lambda = 0.71073\))

**2\(\theta\) range for data collection/\(\degree\)**
2.992 to 25.416

**Index ranges**
-9 \(\leq h \leq 9\), -13 \(\leq k \leq 13\), -18 \(\leq l \leq 18\)

**Reflections collected**
59608

**Independent reflections**
5090 [R(int) = 0.0237]

**Data/restraints/parameters**
5090/0/401

**Goodness-of-fit on F\(^2\)**
1.051

**Final R indices [I>2\(\sigma\) (I)]**
\(R_1 = 0.03114\), w\(R_2 = 0.0672\)

**Final R indices (all data)**
\(R_1 = 0.0470\), w\(R_2 = 0.0733\)

**Largest diff. peak/hole/e \(\AA^{-3}\)**
0.232/-0.272
### A2.9 Crystal data and structure refinement for \([\text{C}_6\text{F}_5\text{CNSeSeN}]_2[\text{TEMPONE}]\)

<table>
<thead>
<tr>
<th>Identification Code</th>
<th>LW_NS_C6F5DSDA_TEMONE_coxtal_0m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>(\text{C}<em>{23}\text{H}</em>{16}\text{F}_{10}\text{N}_5\text{O}_2\text{Se}_4)</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>886.26</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>150(2) K</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>(\text{P}\overline{1})</td>
</tr>
<tr>
<td>(a/\text{Å})</td>
<td>8.2594(4)</td>
</tr>
<tr>
<td>(b/\text{Å})</td>
<td>11.5470(5)</td>
</tr>
<tr>
<td>(c/\text{Å})</td>
<td>15.3824(7)</td>
</tr>
<tr>
<td>(\alpha/°)</td>
<td>88.462(2)</td>
</tr>
<tr>
<td>(\beta/°)</td>
<td>74.864(1)</td>
</tr>
<tr>
<td>(\gamma/°)</td>
<td>86.695(2)</td>
</tr>
<tr>
<td><strong>Volume/\text{Å}^3</strong></td>
<td>1413.68(11)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
</tr>
<tr>
<td><strong>Density_{calc} g/cm^3</strong></td>
<td>2.115</td>
</tr>
<tr>
<td><strong>Absorption coefficient/mm^1</strong></td>
<td>5.290</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>862</td>
</tr>
<tr>
<td><strong>Crystal size/mm^3</strong></td>
<td>0.109 x 0.171 x 0.416</td>
</tr>
<tr>
<td><strong>Radiation</strong></td>
<td>MoK(\alpha) ((\lambda) = 0.71073)</td>
</tr>
<tr>
<td><strong>2(\theta) range for data collection/°</strong></td>
<td>3.032 to 26.445</td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>(-10 \leq h \leq 10, -14 \leq k \leq 14, -19 \leq l \leq 19)</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>64254</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>5102 [R(int) = 0.0146]</td>
</tr>
<tr>
<td><strong>Data/restraints/parameters</strong></td>
<td>5818/0/461</td>
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<tr>
<td><strong>Goodness-of-fit on (F^2)</strong></td>
<td>1.209</td>
</tr>
<tr>
<td><strong>Final R indices [I&gt;2(\sigma) (I)]</strong></td>
<td>(R_1 = 0.0262, wR_2 = 0.0630)</td>
</tr>
<tr>
<td><strong>Final R indices (all data)</strong></td>
<td>(R_1 = 0.0332, wR_2 = 0.0679)</td>
</tr>
<tr>
<td><strong>Largest diff. peak/hole/e \text{Å}^3</strong></td>
<td>0.470/-1.074</td>
</tr>
</tbody>
</table>
VITA AUCTORIS

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