New Directions in Inorganic Polymer and Materials Chemistry

Studies of Metal Germanium Sulfides, Ferrocene-Containing Materials, and Mesoporous Silica – Poly(ferrocenylsilane) Composites

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy (Ph.D.)

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to my Parents and Weird Al

"...I’m talking about a specific, extra type of integrity that is not lying, but bending over backwards to show how you’re maybe wrong, that you ought to have when acting as a scientist. And this is our responsibility as scientists, certainly to other scientists, and I think to laymen."

- Richard P. Feynman, "Surely You're Joking, Mr. Feynman!"

A novel condensation polymerization of \([Ge_4S_{10}]^{\text{+}}\) clusters in the presence of acid gave a high-temperature, high-pressure polymorph of GeS\(_2\). Characterization by Rietveld refinement and Raman spectroscopy revealed that the structure contains \([Ge_4S_{10}]\) clusters intact and linked into two interpenetrating diamond-like lattices.

The first examples of mesostructured metal germanium sulfides were prepared and characterized. These materials display hexagonal symmetry akin to MCM-41. Moreover, the channel diameters may be modified by varying the surfactant employed in the preparation. A liquid crystal templating mechanism in formamide has been proposed as the source of the mesoscopic organization of the materials.

Investigations into the spirocyclic \([1]\text{silaferrocenophanes}\) has expanded into several fields. Using these ferrocenophanes as precursors, a variety of new materials and molecular chemistry has been developed. Among these, we have discovered convenient routes to ferrocenylchlorosilanes, ferrocenylsilanols, ferrocenylsiloxanes, poly(ferrocenylsilane) thermosets and gels, and shaped magnetic ceramics.

\([1]\text{Silaferrocenophanes}\) have been incorporated into the well-ordered channels of MCM-41 and subsequently pyrolyzed to yield a superparamagnetic mesostructured ceramic. An investigation of the magnetic properties of the material revealed that the ceramic contains superparamagnetic iron nanoparticles, which are capped with an iron silicate coating and confined to the channels of mesoporous silica.
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anal analysis
br broad
"Bu butyl
c.a. circa
calc’d calculated
cf. compare with
Cp cyclopentadienyl
CP cross-polarization
CPM cetylpyridinium
CTA cetyltrimethylammonium
CTABr cetyltrimethylammonium bromide
CV cyclic voltammetry
d doublet
DSC differential scanning calorimetry
e.g. for example
EI electron impact
eq equivalents
e.s.d. estimated standard deviation
Fc ferrocenyl
fc 1,1’-ferrocenediyl
FT Fourier transform
FW formula weight
h hours
IR infrared
J coupling constant
m medium
M+ molecular ion
MAS magic angle spinning

xviii
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>max</td>
<td>maximum</td>
</tr>
<tr>
<td>MCM</td>
<td>Mobil composition of matter</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>min</td>
<td>minutes</td>
</tr>
<tr>
<td>mp</td>
<td>melting point</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>ODA</td>
<td>octadecyltrimethylammonium</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>PXRD</td>
<td>powder X-ray diffraction</td>
</tr>
<tr>
<td>ref.</td>
<td>reference</td>
</tr>
<tr>
<td>ROP</td>
<td>ring-opening polymerization</td>
</tr>
<tr>
<td>s</td>
<td>singlet (NMR)</td>
</tr>
<tr>
<td>s</td>
<td>strong (IR, Raman, UV-vis)</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SQUID</td>
<td>superconducting quantum interference device</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>TBTPB</td>
<td>tetrakis(3,5-bis(trifluoromethyl)phenyl)borate</td>
</tr>
<tr>
<td>TDT</td>
<td>tetradecyltrimethylammonium</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>Tg</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
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<td>tetrahydrofuran</td>
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<td>TMEDA</td>
<td>N,N,N',N'-tetramethylethylenediamine</td>
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<tr>
<td>UV-vis</td>
<td>ultraviolet - visible</td>
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<tr>
<td>w</td>
<td>weak</td>
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CHAPTER 1

Introduction

1.1 Preamble

Until recently, polymer and inorganic materials chemistry were two distinct and mature fields. Now they are being integrated to create exciting classes of hybrid polymer-solid state materials that have intriguing properties. I would like to summarize a few recent contributions that illustrate the new direction materials chemists are pursuing.

In reality, polymer-solid state composite materials are not new at all - for millions of years, nature has orchestrated the growth of inorganic media at the interface of polysaccharides, proteins, and glycoproteins. Bones, teeth, shells, and other inorganic biominerals are formed in the presence of these structure-directing macromolecules. Nature’s polymer-inorganic materials technology, which has been recognized this century in the biomineralization community, is now emerging in various forms in biomimetic inorganic chemistry and polymer-inorganic materials.

Many advances have taken advantage of the microphase separation observed in diblock and triblock copolymers. Materials chemists have utilized these morphologies to template inorganic phases by the hydrolytic condensation of metal alkoxides, thereby forming a metal oxide cast of the block copolymer mesophase. The template can be removed from the composite to yield a mesoporous material. In a novel twist, mesoporous polymers were prepared by first crosslinking a polymer around silica nanospheres then dissolving the silica in aqueous HF. Block copolymers have been
observed to undergo microphase separation on freshly cleaved mica. Chemists have used these nanoscale patterns as lithographic masks for making periodical arrays of inorganic materials, such as silicon nitride.\textsuperscript{5}

Various polymers, both conducting and insulating, have been intercalated into layered inorganic hosts, such as metal oxides and metal sulfides.\textsuperscript{6} These materials are of interest as battery cathode materials. Nanocrystalline inorganics, such as titania and alumina, enhance the conductivity of poly(ethyleneoxide) - lithium salt composites.\textsuperscript{7} The inorganic crystals function as plasticizers, allowing the polymer to maintain a glassy state at ambient temperature. These composites display room-temperature lithium ion conductivity and are attractive as electrolytes for solid state batteries.

Polymer-inorganic laminates have been prepared by exfoliating layered inorganic materials into single sheet colloid particles in solution and then reassembling the colloids in the presence of polymers.\textsuperscript{8} Alternatively, hydrolytic condensation of a silicon alkoxide possessing a terminally-bonded, polymerizable headgroup in the presence of a templating surfactant and a free radical initiator creates layered polymer-silica composites.\textsuperscript{9} Indentation measurements indicated that their hardness approaches that of the nacre of abalone shell.

This preamble is intended to highlight some current activity in the field of polymer-inorganic materials chemistry. Exciting, imaginative research is occurring at the boundary of these two subdisciplines. Hybrid materials may express the chemical and physical properties of both components, allowing the development of materials that display the morphologies, flexibility, and insulating properties of the polymer combined
with the hardness, conductivity, and optical properties of inorganic materials. We can look forward to a carnival of new materials emerging from this symbiosis.

1.2 Inorganic Materials

1.2.1 Motivation

Historically, man has depended on natural materials for survival. For example, bones, animal hides, wood, stones, and shells were important for hunting and for providing clothing and shelter to humans. The ability to smelt metals and make glass were simple modifications to fit their needs. In this century, there has been a materials revolution. For the first time, we possess the theoretical understanding, experimental technique and processing skill required to design material compositions to meet our needs.

Nearly every area of our society now depends on materials we have designed, particularly the military and the automotive, aviation, and electronics industries. Today, materials are not only required to sustain life, but also to meet our society's demands for faster, lighter, stronger, and more sophisticated technologies. Advanced materials control the economy, set the pace for communication, and may even solve the energy shortages of the future. Synthetic materials are everywhere.

Until recently, most materials have been built using a top-down approach, which is reliant on high-precision physical techniques (e.g. machining, carving, etching). It is becoming increasingly desirable to build materials from the atom up, using chemical synthesis. This approach, which was probably initiated with the discovery of synthetic
polymers, is now used to create high temperature superconductors, fibre optics, molecular magnets, high performance plastics, advanced ceramics, and other materials that are permeating the marketplace. New materials are desired for improving current technology, and as a source of inspiration for new technology.

1.2.2 Rational Design of Materials

As a demonstration of our theoretical understanding, many materials can now be designed with a computer. Once the desired attributes are known, atoms can be assembled on the computer screen to create the target material. We can calculate various physical properties of the material, for example, its conductivity, magnetic moment, and colour, even though the material has never been synthesized!

Hoffman et al. predicted that a material composed of interpenetrating diamond-like networks of SiO$_2$ and BeF$_2$ would be extremely hard and potentially useful in many applications (e.g. drilling, cutting, jeweller’s tools, engine components). However, the synthesis of this material appears to be extremely challenging. There are many other examples of materials that would have interesting properties, but are still synthetically not plausible (the pursuit of β-C$_3$N$_4$ is another good case).

Developing synthetic routes to new materials will be an important area of research in the future. There are several approaches that have been explored recently as synthetic routes to new and interesting materials. Polymers that incorporate transition metals are attracting attention as they may combine the processibility and flexibility of polymers with the interesting electronic, magnetic, and optical properties associated with transition metals. Pyrolysis of polymers, particularly metal-containing polymers, may yield
materials with properties unavailable from traditional routes. Supramolecular assembly of building blocks is another underdeveloped area of materials chemistry that may be useful for preparing new materials. Inorganic or organic-inorganic composites with controlled architecture may have improved or unique properties compared with composites prepared by mixing and baking. An elegant example is the organic-inorganic laminate reported by Brinker et al. that mimics nacre. The rational synthesis of new materials is a maturing area that requires close attention if we are to make progress in the field of materials science.

1.3 Inorganic Polymers

1.3.1 Brief History

The incorporation of inorganic elements into the backbones of polymers is expected to give materials with interesting properties. Although organic polymers have exploded in the marketplace and are used for everything from plastic car bodies and toothbrushes to telephones and explosives, inorganic polymers have made a much slower advance. Polysiloxanes 1 ([R₂SiO]ₙ, silicones) and polyphosphazenes 2 ([R₂PN]ₙ) are the only two examples of inorganic polymers that are now commercial as a virtue of their unique properties. The preparation of well-characterized, high-molecular weight inorganic polymers has been hindered by the lack of viable synthetic routes to these materials.
1.3.2 Transition-Metal Containing Polymers

Transition metal containing polymers, in particular, are expected to possess intriguing properties.\textsuperscript{12} A variety of organic polymers have been prepared with metal-containing substituents, but there are relatively few examples of well-defined polymers with transition metals in the backbone due to limitations of synthetic routes to these materials. This synthetic difficulty emerges when one realizes that the three typical routes that have been used to prepare organic polymers (condensation polymerization (i), addition polymerization of olefins (ii), and ring-opening of strained cyclic monomers (iii)) are not easily adapted to inorganic species.\textsuperscript{15}
Condensation polymerization has been used extensively in the preparation of linear inorganic polymers. However, this method suffers from the stringent stoichiometric control required for the starting materials. The degree of polymerization is directly associated to the ratio of monomers introduced into the synthesis.\textsuperscript{16} As it is often difficult to prepare inorganic monomers in 99.9+ % purity, only low-molecular weight polymers have been obtained by this route.

Addition polymerization of olefins represents another common synthetic route to high molecular weight organic polymers. Unfortunately, the difficulty of preparing unsaturated inorganic analogues has precluded inorganic polymer synthesis by this route.

However, ring-opening polymerization of strained inorganic rings is a well-known route to inorganic polymers. The prevalence of rings in inorganic chemistry and
the chain-growth mechanism for ring-opening polymerization makes this an attractive route to high-molecular weight polymers.\textsuperscript{17} Still, there are few examples of well-defined metal-containing rings that will undergo ring-opening polymerization.

1.3.3 Gels

Swellable gels are materials of intense interest where metal-containing polymers could make a large impact. As a consequence of their ability to exhibit controlled swelling and contraction, gels are attracting attention for drug delivery, chemomechanical actuators, artificial muscles, and chemical sensors.\textsuperscript{18} Osada \textit{et al.} reported an electrically-driven polymer gel that moved along a ratchet at speeds up to 25 cm min\textsuperscript{-1}.\textsuperscript{19} Irie synthesized a polyacrylamide gel with triphenylmethane leucocyanides that exhibited reversible photostimulated bending in an electric field.\textsuperscript{20} One could envisage a polymer gel that would undergo rapid volume changes upon oxidation change of a species inside the gel. In fact, Yoshido and coworkers have used this approach to design a material that undergoes oscillatory motion as a result of oxidation change at a Ru(bpy)\textsubscript{3} site (by the Belousov-Zhabotinsky reaction) adhered to a complex polymer gel.\textsuperscript{21} Using a crosslinked polymer with redox-active transition elements in the backbone would give an even distribution of metal sites throughout the gel. Unfortunately, no examples of well-defined crosslinked polymers with transition metals in the backbone have been reported.
1.4 Ferrocene and Ferrocenophanes

1.4.1 Ferrocene

Ferrocene (3) was discovered in 1952 and has been the hallmark of a class of organometallic compounds known as the sandwich complexes. Since that time, the chemistry and properties of ferrocene have been slowly elucidated. As a consequence of its low cost and air/thermal stability, interesting electronic properties, and characteristic optical properties, ferrocene is an attractive precursor to new materials. This has been realized by many researchers. For example, Miller, Epstein, et al. have synthesized molecular magnets incorporating the ferrocene derivative, decamethylferrocenium. Rao et al. have recently described aligned carbon nanofibres prepared from the pyrolysis of ferrocene in the presence of acetylene.

1.4.2 Ferrocenophanes

[n]Ferrocenophanes (4) are an interesting class of materials containing a covalent link of n atoms between the cyclopentadienyl (Cp) ligands of ferrocene. [n]Ferrocenophanes with n ≥ 3 may show slight ring tilts, but are not highly strained as the Cp ligands remain essentially planar. [2]Ferrocenophanes, on the other hand, show a large ring strain due to tilting of the Cp rings. In 1975, Osborne et al. reported the first [1]silaferrocenophanes (5 and 6) from the reaction of dilithioferrocene·TMEDA with SiCl₄ or Cl₂SiPh₂. A single crystal X-ray structure of 6 revealed that the rings are tilted by ca. 19°.
Subsequently, a variety of [1]ferrocenophanes have been prepared by a similar route as that used to prepare 6. [1]Ferrocenophanes containing Ge, Sn, As, P, S, Se, and B as the bridging element are now known.\textsuperscript{29-35} The distortion from sp\textsuperscript{2} geometry at the ipso-C atom has been held responsible for a large upfield shift of the ipso-C atom in the \textsuperscript{13}C NMR spectrum of [1]ferrocenophanes.\textsuperscript{36} As well, Mössbauer studies of these materials show a reduced quadrupolar splitting relative to ferrocene.\textsuperscript{36} This has been attributed to a weak Fe to heteroatom bond, but is still not fully understood.\textsuperscript{37}
1.5 Poly(ferrocenes)

1.5.1 Background

With the hope of preparing stable, metal-containing polymers with interesting properties, ferrocene is an attractive structural unit to incorporate into these materials. A variety of polymers have been prepared with pendant ferrocene groups, such as poly(vinylferrocene).\(^7\) Until recently, there were few reports of well-defined polymeric materials prepared with ferrocenyl groups in the backbone. Early work on poly(ferrocenes) concentrated on the condensation polymerization of dilithioferrocene with appropriate precursors (e.g. \(\text{Cl}_2\text{SiR}_2\)). However, only low-molecular weight polymers were obtained due to the difficulty of preparing pure dilithioferrocene.\(^{14}\)

1.5.2 Ring-Opening Polymerization of [1]Ferrocenophanes

Ring-opening polymerization of strained rings is the most common route to high molecular weight polysiloxanes, polyphosphazenes, and polycarbosilanes \((8)\).\(^{14}\) Polysilanes \((9)\)\(^{39}\) and poly(thionylphosphazenes) \((10)\)\(^{40}\) are recent additions to this class of polymers. The polymerization is usually driven by the enthalpy change that occurs
when the strain is released, though in rare cases the ROP may also be driven by an entropy gain.\textsuperscript{41}

\begin{align*}
\text{8} & \quad \begin{array}{c}
\text{Si} \\
\text{CH}_2
\end{array} \\
\text{n} \\
\text{R} & \quad \begin{array}{c}
\text{R}
\end{array} \\
\text{9} & \quad \begin{array}{c}
\text{Si} \\
\text{O} \\
\text{N} \\
\text{P} \\
\text{N}
\end{array} \\
\text{n} & \quad \begin{array}{c}
\text{R} \\
\text{R} \\
\text{R} \\
\text{R} \\
\text{R}
\end{array}
\end{align*}

In 1992, Manners \textit{et al.} reported the first example of high molecular weight poly(ferrocenylsilanes) from the thermal ROP of strained ferrocenophane precursors (11).\textsuperscript{42} This high molecular weight ($M_w \sim 10^6$) orange polymer 12 ($R = \text{Me}$) forms free-standing films.\textsuperscript{14} Although the polymer is an intrinsic insulator, oxidation of poly(ferrocenylsilane) 12 ($R = \text{Me}$) with I\textsubscript{2} gives a semiconducting polymer.\textsuperscript{43} Garnier \textit{et al.} have reported that poly(dihexylferrocenylsilane) 12 ($R = \text{C}_6\text{H}_{13}$) doped with TCNE displays bulk ferromagnetism at 1.8 K, but this has not been investigated further.\textsuperscript{44} It is clear that transition metal-containing polymers may have interesting properties.
The poly(ferrocenylsilane) system is also highly tunable.\textsuperscript{46-48} By varying the substituents at Si, the physical properties (e.g. $T_g$'s of -51 to > 150 °C have been observed) can be modified. Poly(ferrocenylsilanes) with liquid crystalline sidechains have also been prepared.\textsuperscript{49} Recently, ROP of ferrocenophanes has been extended to include materials with Ge, Sn, P, B, and S in the backbone by employing [1]ferrocenophanes with the appropriate element in the bridge. Moreover the polymer synthesis has been extended to include transition-metal catalyzed and living anionic polymerization of [1]ferrocenophanes.\textsuperscript{50,51} Using these techniques, polymers with controlled architectures and block copolymers have been produced.\textsuperscript{51-53}

1.6 Ceramics From Polymer Precursors

1.6.1 Background

Ceramics, such as SiC and Si$_3$N$_4$, are important structural materials as a consequence of their strength and high temperature resistance.\textsuperscript{54} They find use in applications as diverse as automobile engines and bullet-proof glass. Traditional routes to ceramics often require grinding the correct stoichiometry of elements and heating them at extremely high temperatures.\textsuperscript{55} These syntheses are strongly dependent on the purity and particle size of the starting materials, and often have very toxic by-products. Moreover, ceramic materials are obtained with little control of the resulting morphology (usually as a powder) and are heterogeneous at the microscopic level.\textsuperscript{54,55}

Recently, there has been a transition in ceramic science, coincident with the "materials revolution", away from the traditional "mix and grind" methods toward softer,
precursor-based methods.\textsuperscript{55-57} For example, crystalline SiC can be made in 60% yield using a polycarbosilane (13) precursor and crystalline $\alpha$-Si$_3$N$_4$ can be prepared from a polysilazane with a 69% yield.\textsuperscript{58,59} Ceramics obtained from polymer precursors have several advantages: (i) the composition and, thus, properties can be controlled at every step in the synthesis; (ii) synthesis from a polymer network allows for atomic level mixing and, therefore, more homogeneous ceramics; (iii) better control of morphology may be achieved; (iv) the ceramics may be preformed so they do not need to be pressed; and (v) they may have improved mechanical strength and properties. As an example of this process, Sneddon and coworkers have prepared shaped SiNCB ceramic materials from the pyrolysis of processible borane-functionalized hydridopolysilazane.\textsuperscript{60}

\begin{align*}
\begin{array}{c}
\text{Me} \\
\text{Si} \\
\text{Me} \\
\end{array}
& \xrightarrow{450 ^\circ C} \\
\begin{array}{c}
\text{Me} \\
\text{Si} \\
\text{CH}_2 \\
\text{Me} \\
\end{array}
& \xrightarrow{\text{high T}} \\
\begin{array}{c}
\text{SiC} \\
\end{array}
\end{align*}

\textbf{1.6.2 Ceramics From Transition-Metal Containing Polymers}

Nearly all studies of ceramics formed from polymer precursors have examined the mechanical properties of the material. The incorporation of transition metals into ceramics is also desirable to introduce new magnetic, electronic, and optical properties. A few ceramics have been reported from polymers containing transition-metal pendant groups. For example, Yajima and Omori pyrolyzed a resin containing
poly(acetylferrrocene) to give a glassy matrix containing Fe particles. Ungurenasu made an Fe-SiC composite from a polysilane with pendant Fe(CO)₃ groups (14). Ungurenasu made an Fe-SiC composite from a polysilane with pendant Fe(CO)₃ groups (14). Ungurenasu made an Fe-SiC composite from a polysilane with pendant Fe(CO)₃ groups (14).

\[
\begin{align*}
\text{A} &= \text{CH}_2 \equiv \text{CH}_2 \\
\text{B} &= \text{CH}_2 \equiv \text{CH}_2 \text{Fe} \left(\text{CO}_3\right)_3
\end{align*}
\]

In 1993, Manners and coworkers reported the first examples of ceramics from polymers with transition metals in the backbone. Pyrolysis of poly(ferrocenylsilanes) (12, \(R = \text{Me}; \ R = \text{Ph}\)) at 600 °C and 1000 °C gave ceramic materials containing ferromagnetic \(\alpha\)-Fe crystallites embedded in a \(\text{SiC}_x\text{N}_y\) matrix. However, the ceramic yields (22% - 45%) were unfavorable for potential applications. Crosslinking of the poly(metalloccenes) may be a way to increase the ceramic yield, but has not been explored.

Since 1993, there have been a couple of other reports of Fe-containing ceramics obtained from organometallic polymer pyrolysis. Corriu and coworkers have pyrolyzed low molecular weight Fe / carbosilane oligomers and poly(1,1'-bis(diorganosilylethynyl)-ferrocenes) (15) to give Fe-containing ceramics. Houser and Keller heated ferrocenylene-siloxy-diacetylene oligomers containing carborane units to yield magnetic ceramics.
1.7 Solid-State Inorganic Materials

1.7.1 Traditional Solid-State Synthesis

Solid-state chemists have developed a reputation for using crude high-temperature, high-pressure techniques to make ceramics, glasses, and other solids. Often, materials with excellent mechanical and physical properties may be obtained, but there is an apparent lack of control at the atomic level. While many materials are still being prepared by these methods, there is a trend emerging to use “softer” syntheses. Techniques such as sol-gel chemistry and coordination chemistry offer milder routes to traditional materials and to exciting new materials that are unavailable by “shake and bake” methods.

To be competitive, materials for the next century will need to be more sophisticated than those that are currently available.\textsuperscript{10} Like nature’s creations, our materials will have to demonstrate hierarchical construction - complexity and design at multiple length scales.\textsuperscript{67} Self-assembly, which depends upon specific, non-covalent interactions (e.g. hydrogen bonding) to organize a material, appears to be a promising methodology for building machines and devices with chemistry.\textsuperscript{68}
By "turning down the heat", one can exert more control over the composition, structure, and bonding in the final product. Weak intermolecular forces may then play a role in defining, even dictating, the structure of the solid and allow the tendency to form dense, thermodynamic products to be overcome. Control over both the internal structure and the morphology of materials is a relatively new ability. Metal sulfides are a class of materials that exemplify this transition from crude, traditional synthesis to modern, controlled methods.69

1.7.2 Metal Sulfides

Metal sulfides occur naturally and constitute many important minerals such as "Fool’s Gold" (FeS2), molybdenite (MoS2), and sphalerite (ZnS)70. In the laboratory, metal sulfides may be prepared by several routes; among these are heating of the elements and precipitation of a metal salt with H2S.70 These methods yield dense crystalline or amorphous metal sulfides, which have very interesting properties themselves (e.g. many are semiconductors). However, by using innovative syntheses, chemists have developed novel architectures based on metal sulfides.

Kanatzidis and coworkers have delaminated Li4MoS2, a layered sulfide, in water and restacked the sheets in CH2Cl2 / Co6S8(PPh3)4.71-72 This afforded a lamellar sulfide with the cobalt sulfide clusters pillared between the sheets. Various polymers (e.g. PEO, PVP) have also been intercalated into layered metal sulfides by these researchers and others.73 Mallouk and coworkers assembled exfoliated SnS2 and MoS2 colloids into electrostatic superlattices composed of alternating layers of metal disulfide and
Layered inorganic-organic composites of this type may have applications as cathodes in lithium batteries.

1.7.3 Microporous Materials

Zeolites are crystalline, ion-exchangeable aluminosilicates that occur naturally or may be prepared in the laboratory. Structurally, they contain corner-sharing AlO₄ and SiO₄ tetrahedra and possess well-defined pores with uniform dimensions. Zeolites have found extensive use in applications ranging from laundry detergents to cleaning up radioactive waste.

Prior to 1989, all microporous materials were based on oxides - zeolites, silicalite, and aluminophosphates, for example. Although the chemistry of metal sulfides had been established for a long time, nobody had extended the compositions of molecular sieves to include chalcogens. Microporous materials made with sulfur or selenium were expected to possess interesting electronic, optical and catalytic properties.

In 1989, Bedard and coworkers at UOP patented the first crystalline 3-dimensional microporous frameworks based on metal sulfides. These materials were prepared hydrothermally from the elements or metal sulfides with templating species (e.g. tetraalkylammonium salts). The crystalline frameworks contained well-defined pores where the templating cation resided. Although these germanium and tin sulfide materials were intended for catalysts and catalyst supports, their utility has not been realized since they collapse when cation removal is attempted. In fact, the first example of an ion-exchangeable sulfide-based microporous material was reported just this spring.
In 1994, Yaghi et al. reported the discovery of a crystalline $\text{TMA}_2\text{MnGe}_4\text{S}_{10}$ framework ($\text{TMA} =$ tetramethylammonium) that possessed a zinc blende network with the TMA cations inside the pores. They prepared the framework by combining $\text{Mn(OAc)}_2$ with $\text{TMA}_4\text{Ge}_4\text{S}_{10}$ in water. After 24 h, crystals of the microporous crystalline framework were obtained.

\[
\left[ \text{NMe}_4^+ \right]_4 \left[ \begin{array}{c}
\text{S} \\
\text{Ge} \\
\text{S} \\
\text{S} \\
\end{array} \right]
\]

Yaghi had discovered a low-temperature route to the same materials that Bedard et al. had prepared hydrothermally. The $[\text{Ge}_4\text{S}_{10}]^{4+}$ anion, which has been known since 1971, behaves as a tetradeinate ligand, linking the tetrahedral metals into the framework as illustrated on the following page. This coordination approach has been extended to include several other transition metals (e.g. $\text{Co}^{2+}$, $\text{Fe}^{2+}$, $\text{Zn}^{2+}$), templates (e.g. $\text{Cs}^+$, $\text{NH}_4^+$), and even metal dimers ($\text{Cu}_2^{+2}$, $\text{Ag}_2^{+2}$).
1.7.4 Mesoporous Materials

In 1992, Kresge et al. at Mobil reported the synthesis and characterization of mesoporous silica with a narrow pore size distribution and angstrom tunability between 10-100 Å.\textsuperscript{85,86} This remarkable new class of materials showed lamellar, hexagonal, or cubic organization, depending on the synthetic conditions used. Although it was patented for anticipated applications in catalysis, large molecule separation, and chemical sensors, none of these have been commercially realized. However, the synthesis of this class of materials represented a breakthrough in materials science. To emphasize the importance of their discovery, the original paper on MCM-41 (Nature, 1992)\textsuperscript{85} has over 1000
To put this into perspective, the original paper on bucky balls (*Nature*, 1985) has just over 2200 citations, but is much more mature.

The key aspect to the synthesis of MCM-41 was the use of a surfactant as the structure-directing template. While small organic and inorganic cations had been employed for decades in the preparation of zeolites and other microporous media, the extension to surfactants was not made until 1992. In water, surfactants assemble into micelles and liquid crystalline phases where the aliphatic tails agglomerate, leaving the charged headgroups exposed to the water. It is believed that the surfactant headgroups charge-balance the silicates that form during the sol-gel condensation and thus play a templating role in forming the silica around the liquid crystal. This mechanism is illustrated below.

Neutral amines and block copolymers, which assemble into similar lyotropic phases as surfactants, have subsequently been used to template mesoporous oxides. Moreover, mesoporous materials incorporating a wide-variety of oxides (e.g. ZrO₂, TiO₂, SnO₂) have been reported.

Mesoporous silica has been used to encapsulate or graft a variety of guest species. Bucky balls, taxol, and poly(phenolformaldehyde) are examples of a few
guests that have been incorporated into the hexagonal channels of MCM-41. Metallocene catalysts for olefin polymerization have been tethered to the walls of MCM-41.98,99 Feng et al. and Mercier and Pinnavaia have demonstrated that treating MCM-41 with mercaptopropyltrimethoxysilane HS(CH₂)₃Si(OR)₃ yields materials with thiol groups in the channels and they may be used to adsorb heavy metals from polluted waters.100,101 Preparing MCM-41 with RSi(OR')₃ gives functionalized mesostructures with alkyl groups lining the inside of the channels. Stein and coworkers reported a vinyl functionalized channel and the subsequent bromination of the vinyl groups inside MCM-41.102 These examples demonstrated the ability of MCM-41 to adsorb and discriminate guests based on their size.

The synthesis of mesoporous metal sulfides is an attractive goal as it may introduce interesting electronic and optical properties to the materials. However, the sol-gel chemistry of sulfides is virtually unknown, in part due to the rapid condensation of sulfides with metals, their insolubility, and the toxicity and odour of sulfur precursors. It is therefore not surprising that there have been very few reports of hexagonally structured mesoporous metal sulfides. Of the few reports that have emerged, there is only one that is very convincing. Stupp et al. reported that mesostructured CdS could be formed by passing H₂S over a mesophase containing a Cd salt with an oligoethylene oxide oleyl ether.103,104 TEM indicated that the material that precipitated was hexagonally ordered. A few other reports of mesostructured metal sulfides have emerged, but they were generally prepared by trial-and-error from poorly defined precursors and were not well characterized.105
1.8 Nanostructured Materials

We are quickly approaching the scaling limit of microchips that can be prepared by lithographic techniques. The computer industry is turning to chemists to develop synthetic methods to build computer chips by a bottom-up approach rather than from bulk material. Nanochemistry is the area of solid-state chemistry concerned with the synthesis of materials with nanometer dimensions. Synthetic molecular devices and machinery may constitute the computers of the future.

It has been realized that reducing the size of a material to nanometer dimensions has a dramatic effect on the chemical and physical properties of the material. Although nanomaterials were first discussed in the 1970's, it was not until the 1990s that widespread interest in them began. The study of materials with nanometer dimensions is now an area of immense research. As an example, there has recently been enormous activity in the area of nanosized silicon. Silicon possesses an indirect band gap and is therefore not luminescent in the bulk form. When domain sizes are reduced to nanometre dimensions, however, silicon luminesces. Luminescent silicon may be the next generation of cost-efficient LED materials.

Magnetic nanostructures are another class of materials that exhibit properties which are distinct from the bulk phase. The magnetic properties of nanomaterials have been thoroughly investigated. When the dimensions of a ferromagnetic substance are reduced to a single domain, the particles behave like giant paramagnets, a phenomenon referred to as superparamagnetism. In this state, thermal agitation overcomes the tendency of the clusters to align ferromagnetically. These materials are of interest for magnetic recording media, magnetic fluids, and other electronic devices.
Many synthetic routes to nanomaterials, such as ball milling, rapid cooling of a molten metal, sputtering, rapid precipitation (e.g., “Rieke metals”), and templating have been demonstrated. Templating is a method that should offer the most control of particle sizes and morphology with the least amount of effort. By choosing templates that have well-defined, uniform pores or “reaction chambers”, one could build a material with dimensions that are limited by the dimensions of the host.

Amphiphiles are versatile hosts for templating nanomaterials. Self-assembly inside lyotropic liquid crystalline phases can yield materials with a variety of structures and morphologies dictated by the phase of the liquid crystal. Fabrication inside reverse micelles has been used to form spherical nanoparticles.

Rigid hosts have also been employed in the preparation of nanomaterials. They have advantages over flexible hosts: the channels may be organized and they may show a narrower distribution of sizes. Lieber has grown metal carbides and boron carbide inside of buckytubes. Martin has developed an area of research based on templating nanomaterials inside track-etch polymeric membranes. Other researchers have grown nanomaterials inside porous alumina.

MCM-41 is an attractive material to utilize as a host for nanomaterials. The channel structure with tunable diameters would be expected to give rod-like nanomaterials. Unfortunately, only a few examples of well-characterized nanomaterials templated inside MCM-41 have been reported. Bein and coworkers have grown conductive polyaniline and graphite fibers inside the channels of MCM-41. Mallouk, Ozin, et al. reported the synthesis of poly(phenolformaldehyde) polymers inside the channels of MCM-41. TEM images of the extracted nanofibres revealed that they
were replicas of the oriented silica channels. Ozin and coworkers have prepared luminescent silicon clusters inside MCM-41 from the chemical vapour deposition of disilane.\textsuperscript{119} Iwasawa \textit{et al.} have very recently formed rhodium oxide nanoparticles inside MCM-41.\textsuperscript{120}

Clearly, investigations into the synthesis and characterization of new inorganic polymers and materials could be fruitful for the development of redox-active gels, novel ceramics, nanomaterials, and self-assembled materials. This thesis will report on our own investigations into the rational design of new materials.

1.9 Research Objectives

In 1995, I joined the research groups of Professors Manners and Ozin with the goal of creating a common project that combined the research directives of the two groups. With the Manners group establishing the field of poly(ferrocenes) from ring-opening polymerization of [1]ferrocenophanes and the Ozin group concentrating in the area of mesochemistry, I began with the aim to create composite materials with poly(ferrocenylsilanes) inside the channels of mesoporous silica. These might serve as precursors to well-defined Fe nanoparticles within the channels of the MCM-41. In addition to this project, I worked on other projects, the ideas coming from both my supervisors and myself. As I worked on projects shared between the groups and within each lab, the goals of my projects were:

(i) To understand the linking chemistry of \([\text{Ge}_4\text{S}_{10}]^{4+}\) clusters;
(ii) To synthesize and characterize mesoporous metal germanium sulfides;

(iii) To explore the chemistry and polymerization behaviour of spirocyclic [1]ferrocenophanes to generate new materials (e.g. redox active gels, ceramic precursors, thermosetting glasses); and

(iv) To prepare and characterize poly(ferrocenyilsilane) – mesoporous silica composites and to investigate their pyrolysis to give mesoporous silica containing Fe nanoparticles.

Many of these projects were carried out in collaboration with other students and researchers. All contributions will be outlined here. First, all TEM and SEM images were collected by Dr. Neil Coombs (Imagetek). In Chapter 2, all synthesis and characterization was carried out by me, except for the Rietveld refinement, which was carried out by Dr. Srebri Petrov. In Chapter 3, all synthesis and characterization was carried out by me except for EXAFS and elemental analyses, which were obtained by Dr. Robert L. Bedard at UOP. Figure 13 was drawn with the assistance of Emmanuel Chomski. In Chapter 4, all of the chemistry was performed by me or by students working under my guidance. In particular, Juan Zheng and Karena Thieme participated in the fcSiFc\textsubscript{2} and siloxanes / heterosiloxanes work. Madlen Ginzburg and Kevin Kulbaba have extended the ceramic work and gel work, respectively, beyond that described in this thesis. In Chapter 5, all syntheses and characterization were performed by myself except for the SCXRD structure of 6, which was solved by Dr. Alan Lough (he collected the data for the other structures as well). The electrochemistry of 6 was investigated by Prof. Bill Geiger (Vermont) and co-workers. In Chapter 6, the synthesis and characterization
of 4 was initially carried out by myself and optimized by Juan Zheng. Compound 5 was isolated and characterized by Juan Zheng. SCXRD experiments were performed by Dr. Alan Lough or Prof. Arnold Rheingold. Moreover, electrochemistry of 4 was investigated by Prof. Bill Geiger and students at Vermont. The work in Chapter 7 involving fcSiMe₂ was carried out by myself. Madlen Ginzburg synthesized and characterized the samples containing fcSi(CH₂)₃. Magnetization measurements were performed by Prof. John Greedan and Dr. N. P. Raju at McMaster University. I performed the analyses of the magnetization data, powder diffraction data, and TEM images.

Each chapter of this thesis is self-contained in the form of a scientific paper that has already been published or is intended to be published. The first drafts of each chapter were written by me.

Portions of this thesis have been published previously:

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**Chapter 6:** All text and figures were reproduced with permission from *Organometallics* **1999**, *18*, 1337. Copyright 1999 American Chemical Society.
1.10 References


(48) For the work of other groups on poly(ferrocenylsilanes) and related materials, see:


(87) Science Citation Index, ISI: Internet, 1999.


(89) Tanev, P. T.; Pinnavaia, T. J. Science 1995, 267, 865.


CHAPTER 2

Synthesis and Crystal Structure of $\delta$-GeS$_2$, the First Germanium Sulfide With an Expanded Framework Structure

2.1 Introduction

Germanium sulfides are attractive materials because of their interesting electronic and optical properties.\textsuperscript{[1]} They have potential applications in hologram recording media, optical coatings, fibre-optics, solid-electrolyte lithium batteries, and semiconductors.\textsuperscript{[1-4]} Although one might expect germanium sulfides to adopt the myriad of topologies found in silicates and aluminosilicates (for example, zeolites), only dense phases of GeS$_2$ are known to date, and they are generally prepared under extreme conditions. Here we report the low-temperature, self-assembly of adamantanoid $[\text{Ge}_4\text{S}_{10}]^{4-}$ clusters to yield a crystalline expanded framework modification of GeS$_2$.

The two common dense phases of GeS$_2$ are the $\alpha$ modification, a layered semiconductor that crystallizes in the monoclinic space group $Pc$, and the $\beta$ modification, which crystallizes in the monoclinic space group $P2_1/c$.\textsuperscript{[5]} Prewitt and Young reported a dense high-temperature and high-pressure $\gamma$-GeS$_2$ structure in which GeS$_4$ units are connected in a three-dimensional tetragonal cristobalite-related network (space group $I\bar{4}2d$).\textsuperscript{[6]} Moreover, Viaene and Moh reported a high-pressure/high-temperature ($\gamma$) form of GeS$_2$ that is stable above 3000 bar at 600 °C and can be quenched to give a metastable phase at room temperature.\textsuperscript{[7]} This phase was subsequently obtained by Wang and Horn.
from α-GeS₂ by hydrothermal synthesis at 1000 bar and 840 °C for 2 d, then 5000 bar at 575 °C for 7 d.[8] From powder diffraction data (ICCD PDF-2 Database file no. 27-0239), they identified the crystalline phase as a tetragonal compound in the space group \( I4_1/acd \) with \( Z = 32 \), but were unable to deduce its structure. Since 1973, this phase of GeS₂ has been absent from the literature. Although structures of other modifications were reported, no further studies of \( \gamma \)-GeS₂ were undertaken. In discussions of GeS₂, this form was frequently omitted or assumed to be identical to the phase described by Young et al. To avoid confusion with the \( \gamma \)-GeS₂ of Young et al., we renamed the phase described by Wang et al. as \( \delta \)-GeS₂.

\[
\begin{array}{c}
\text{[} + \text{NMe}_4 \text{]}_4 \\
\end{array}
\]

\[
\begin{array}{c}
\text{S}^- \\
\text{S}^- \\
\text{Ge} \\
\text{S}^- \\
\text{S}^- \\
\end{array}
\]
2.2 Results and Discussion

We have now discovered a low-temperature route to δ-GeS₂ that involves the condensation polymerization of [(CH₃)₄N]₄Ge₄S₁₀ (1) under acidic conditions. A representative scanning electron microscope image of crystals synthesized at 50 °C is shown in Figure 1. The material consists of fairly monodisperse rounded prisms. Energy dispersive X-ray analysis of the material established the composition to be GeS₂. Comparison of the Raman spectrum with that of the precursor 1 confirmed the presence of the adamantanoïd cluster in the product (Figure 2). Notably, the spectra are similar in the skeletal region (470-140 cm⁻¹), and the most intense totally symmetrical νGe-S₁ and νGe-S₂ stretching frequencies (S₁ and S₂ = terminal and bridging S atoms) of the product are blue-shifted with respect to the precursor by about 20 cm⁻¹. This implies that the clusters are intact and interlinked in the product. Exceptionally weak Raman bands in the C-H and S-H stretching regions indicate the presence of traces of surface-bound organic groups and thiol groups.

A detailed analysis of 47 unique reflections of the powder X-ray diffraction (PXRD) data confirmed the tetragonal space group I₄₁/acd (142). Moreover, besides the necessary extinction conditions for this space group, additional special conditions were revealed: hkl: l, h+k = 2n+1 and hkl: l = 2n; 2k+l = 4n. These suggest the presence of atoms in special positions with Wyckoff notations e (x, 0, 1/4) and d (0, 1/4, z). On the assumption that tetrahedral GeS₄ units would be the primary building blocks, as in all other GeS₂ structures, we concluded that the Ge atom and one S atom occupy general positions, and two S atoms occupy special positions.
Figure 1. A scanning electron micrograph of crystalline $\delta$-GeS$_2$ shows its fairly monodisperse rounded prism morphology. The average particle size is approximately 200 nm.
Figure 2. The Raman spectra of TMA$_4$Ge$_4$S$_{10}$ (1) and crystalline δ-GeS$_2$ are remarkably similar in the vGe-S stretching region. This confirms the presence of [Ge$_4$S$_{10}$] clusters in the structure.

A suitable starting model for Rietveld refinement of δ-GeS$_2$ was an extremely hygroscopic polymorph of ZnI$_2$, which has a similar space group to δ-GeS$_2$.[9,10] The result of the high-quality Rietveld refinement ($R_p = 8.4\%$) of δ-GeS$_2$ is shown in Figure 3. Atomic coordinates and isotropic displacement factors are presented in Table 1. Views of the adamantanoid [Ge$_4$S$_{10}$] cluster in the structure, the 24-atom ring composed of six Ge(μ-S)Ge-linked Ge$_4$S$_6$S$_{4/2}$ clusters in the network are shown in Figures 4a and 4b, respectively. The Ge-S bond lengths in the structure (2.194(4) – 2.225(4) Å) are nearly
identical and, like the bond angles, are consistent with those observed in the other Ge$_4$S$_{10}$-based structures.$^{[11-15]}$

**Figure 3.** Observed (+), calculated (solid line), and difference (lower solid line) profiles from Rietveld refinement of the PXRD data of δ-GeS$_2$. The solid vertical bars indicate calculated peak positions.

**Table 1.** Atomic Coordinates and Isotropic Displacement Factors $U_{iso}$ [Å$^2$] for δ-GeS$_2$

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>$U_{iso}$ x 10$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>0.3745(1)</td>
<td>0.3439(2)</td>
<td>0.0604(1)</td>
<td>2.77</td>
</tr>
<tr>
<td>S(1)</td>
<td>0.0</td>
<td>0.25</td>
<td>0.0124(2)</td>
<td>1.23</td>
</tr>
<tr>
<td>S(2)</td>
<td>0.2876(5)</td>
<td>0.0</td>
<td>0.25</td>
<td>2.18</td>
</tr>
<tr>
<td>S(3)</td>
<td>0.0345(3)</td>
<td>1.0166(3)</td>
<td>0.3760(2)</td>
<td>1.84</td>
</tr>
</tbody>
</table>
Figure 4. a) The adamantanoid [Ge₄S₁₀] cluster secondary building block of δ-GeS₂. b) The largest ring in each interpenetrating network of the δ-GeS₂ structure is a 24-atom [Ge₁₂S₁₂] ring that consists of six Ge(μ-S)Ge-linked [Ge₄S₆S₄/₂] clusters. c) Projection of the structure of γ-GeS₂ reported by Young and Prewitt on the ab plane. d) Projection of the structure of one of the interpenetrating cristobalite-like networks in δ-GeS₂ on the ab plane. e) Projection of the two interpenetrating cristobalite-like networks in δ-GeS₂ on the ab plane. They are related by a center of symmetry to give interpenetrating enantiomeric frameworks. f) As in e), but with projection on the ac plane. (The S atoms are omitted from c) - f) for clarity.)
There is an intriguing topological relationship between the $\gamma$-GeS$_2$ structure of Young et al. and that of the new $\delta$-GeS$_2$ structure. Both are based on tetrahedral building blocks: GeS$_4$ in the former and Ge$_4$S$_{10}$ in the latter. This can best be visualized by focusing on the Ge atoms and omitting the S atoms for the sake of clarity. Replacing the Ge atoms in $\gamma$-GeS$_2$ by an adamantanoid Ge$_4$ cluster and applying the acentric space group of $\gamma$-GeS$_2$ ($I\bar{4}2d$) produces one of the interpenetrating frameworks of $\delta$-GeS$_2$ (Figure 4c, d). The second interpenetrating framework of the $\delta$ form is the enantiomer of the first, to which it is related by a center of symmetry (Figure 4e,f), as indicated by the centric space group of the $\delta$-form, ($I4_1/acd$). In essence, the new structure is an expanded version of the earlier cristobalite-like structure of $\gamma$-GeS$_2$. An interesting analogy exists between the pairs $\gamma$-GeS$_2$ / $\delta$-GeS$_2$ and cristobalite / silica faujasite, in which tetrahedral SiO$_4$ units are replaced by Si$_{24}$O$_{48}$ sodalite cages to give the zeolite structure.$^{116}$ The expansion from Ge to Ge$_4$ structural units generates sufficient empty space for the co-crystallization of a second framework, which is the mirror image of the first.

We propose that the formation of $\delta$-GeS$_2$ in the aqueous acidic medium occurs by a bimolecular nucleophilic substitution ("SN$_2$") reaction in which protonated [Ge$_4$S$_{10}$]$^{4+}$ clusters undergo condensation-polymerization (Eq. 1).

$$\equiv\text{Ge-SH} + \equiv\text{Ge-SH} \rightarrow \equiv\text{Ge-S-Ge} \equiv + \text{H}_2\text{S} \quad (1)$$

This leads to formation of the unexpected crystalline product $\delta$-GeS$_2$ from the organized assembly of [Ge$_4$S$_{10}$]$^{4+}$ clusters (Eq. 2) rather than an amorphous cross-linked...
network that would be expected from random polymerization of the clusters. Figure 5 shows the proposed mechanism for the formation of $\delta$-GeS$_2$.

$$[(\text{CH}_3)_4\text{N}]_4\text{Ge}_4\text{S}_{10} + 4 \text{HCl} \rightarrow 4 \text{GeS}_2 + 4 [(\text{CH}_3)_4\text{N}]\text{Cl} + 2 \text{H}_2\text{S} \quad (2)$$

**Figure 5.** The proposed mechanism for the formation of $\delta$-GeS$_2$ from the addition of HCl to TMA$_4$Ge$_4$S$_{10}$. 
In situ high-temperature PXRD indicated that the $\delta$-GeS$_2$ phase is still stable above 620 °C. The volume of the unit cell increases steadily up to this temperature, while the $c$ axis of the unit cell contracts slightly. Differential expansion-contraction effects of the type are well-documented in uniaxial crystal systems whose lattices are composed of four-connected three-dimensional networks. The phenomenon originates from thermally induced changes in bond angles between tetrahedral building blocks, which result in an untwisting of the entire network.

2.3 Summary

We have demonstrated, for the first time, the preparation of the high-pressure/high-temperature phase $\delta$-GeS$_2$ under mild conditions in aqueous solution. This "very soft" sol-gel process provides a novel route to a new type of IV/VI binary metal dichalcogenide whose structure is based upon two interpenetrating expanded cristobalite frameworks. The structure may serve as a model for other expanded XY$_2$ phases. With a suitable template or solvent, we believe the interpenetration of the networks can be eliminated to generate a new family of crystalline open-framework germanium sulfides with a wide range of potential applications.
[(CH₃)₄N]₄Ge₄S₁₀ (I) was prepared by a literature procedure.\(^{[12]}\) \(\delta\)-GeS₂ was prepared by two methods: (a) Hydrochloric acid (9.6 mL, 0.22 M, 2.1 mmol) was added dropwise to a stirred solution of I (343 mg; 0.38 mmol) in 8.0 mL of water. The solution became viscous and cloudy, and H₂S was evolved. After 24 h at 50 °C, the off-white precipitate was isolated by centrifugation and washed with water, THF, and acetone to obtain 44 mg (22%) of product. (b) In a Teflon-lined vessel, I (579 mg, 0.638 mmol) in H₂O (1 mL) and hydrochloric acid (10 mL, 0.25 M, 2.5 mmol) were combined. A cloudy white mixture resulted. The vessel was sealed in a stainless-steel hydrothermal autoclave and heated to 150 °C for 24 h. Once cooled to room temperature, the off-white precipitate was isolated on a Buchner funnel and washed with water, THF, and acetone to give 157 mg (44%) of \(\delta\)-GeS₂. PXRD confirmed the crystallinity of both \(\delta\)-GeS₂ products.

The PXRD analysis of \(\delta\)-GeS₂ was carried out on a Siemens D5000 diffractometer with Bragg-Brentano 0/20 geometry. The source radiation (CuK\(_{\alpha}\), \(\lambda = 1.54059 \text{ Å}\)) was obtained from a high-power line-focus Cu target, and the secondary beam was monochromatized by a Kevex solid-state detector. The diffraction pattern was initially indexed with the program ITO,\(^{[18]}\) which provided a tetragonal, I-type unit cell. Further lattice refinement was performed with the Appleman and Evans program\(^{[19]}\) by using the first 51 measured reflections (34 unique) within the range 14° ≤ 20 ≤ 70°. The refinement gave the space group \(I4_1/acd\) (no. 142) based on both general and special conditions for systematic absences / extinctions, as discussed in the text. Several other
related space groups were also tested as possible sub- or superlattices, but were not fitted successfully. The final structure was obtained by refinement of atomic parameters with the program GSAS 6.0 (PC-version).\cite{gsas60} Crystallographic data for δ-GeS$_2$: $I4_1/acd$, $a = 11.0650(1)$, $c = 18.7178(2)$ Å, $V = 2291.71$ Å$^3$, $D_{\text{calc}} = 3.17$ g cm$^{-3}$, $Z = 32$, $R_{wp} = 0.1159$, $R_p = 0.0842$, $R_{\text{Bragg}} = 0.0927$, $\chi^2 = 4.351$, measured range $12^\circ \leq 2\theta \leq 80^\circ$, 3400 data points, 372 observed reflections, 34 parameters refined. The peak profiles were fitted by a pseudo-Voigt function,\cite{pseudoVoigt} and a Finger-Cox-Jephcoat asymmetry correction was applied.\cite{fingerCox}

Raman spectra were obtained on a Bomems MB-157 FT spectrometer with an InGaAs NIR laser (100 mW). The instrument was configured in 180° back-scattering mode, and samples were sealed in glass capillary tubes. Spectra were recorded with a resolution of 4 cm$^{-1}$, and about 100 scans were made to achieve an excellent signal-to-noise ratio.
2.5 References


[10] Other structures with similar networks are known. For example, a Na$_2$SnAs$_2$ Zintl phase which is isostructural and isoelectronic to δ-GeS$_2$ has been formed from the elements (see M. A. Asbrand, B. Eisenmann. *Z. Naturforsch. B* **1993**, *48*, 452).


CHAPTER 3

Mesostructured Metal Germanium Sulfides

3.1 Abstract

A new class of mesostructured materials has been prepared and characterized. The synthesis, via supramolecular assembly of well-defined cluster precursors in formamide, represents a new paradigm for the formation of this class of solids. Characterization by transmission electron microscopy (TEM) and powder X-ray diffraction (PXRD) revealed that the coordination framework is an ordered hexagonal mesostructure akin to hexagonal mesoporous silica, MCM-41. Raman spectroscopy and elemental analysis confirmed that the \([\text{Ge}_2\text{S}_{10}]^4^-\) clusters were intact in the resulting material. Additional characterization by IR, solid-state NMR, and reflectance UV-vis / near-IR spectroscopies and thermogravimetric analysis is described. Compelling evidence for a metal-metal bond in mesostructured Cu/Ge\(_2\)S\(_{10}\) is also provided.

3.2 Introduction

Microporous (pore diameters < 20 Å) and mesoporous (pore diameters 20-500 Å) materials (IUPAC convention\(^1\)) are used extensively as heterogeneous catalysts, adsorption media, and ion-exchange materials.\(^2\) For example, zeolites possess a
crystalline microporosity, a very narrow pore size distribution, and a large surface area. These properties make them ideal for such diverse applications as water-softening, radioisotope removal from sites of nuclear contamination, and xylenes isomerization catalysis. The discovery of aluminophosphates by Flanigen initiated the exploration of the periodic table for novel microporous materials. Since then, microporous materials have incorporated a variety of transition and main group elements.

In 1989, Bedard et al. patented a new class of microporous metal germanium sulfides (denoted GS-3 for its structure type) prepared hydrothermally from the elements. Yaghi et al. subsequently showed that these materials could be prepared at room-temperature. When adamantanoid \([\text{Ge}_4\text{S}_{10}]^{1+}\) clusters were combined with manganese acetate in water, crystals of the microporous manganese germanium sulfide formed. The framework contains tetradeutate \([\text{Ge}_4\text{S}_{10}]^{1+}\) clusters linked with transition metals to form a zinc blende framework of \(\text{Mn}^{2+}/[\text{Ge}_4\text{S}_{10}]^{1+}\) with the charge balancing TMA (TMA = tetramethylammonium) cations included in the pores. Others and we have extended this class of materials to incorporate a variety of templates and metals, including \([\text{Ag}_2]^{2+}\) and \([\text{Cu}_2]^{2+}\) dimers when silver or copper salts are introduced into the preparation.

\[
\left[ \overset{+}\text{NMe}_4 \right]_4
\]

\[
\begin{array}{c}
\text{S}^- \\
\text{Ge} \\
\text{S} \\
\text{Ge} \\
\text{S} \\
\text{Ge} \\
\text{S} \\
\text{S} \\
\end{array}
\]
The discovery of liquid-crystal templating of silica in 1992 represented a breakthrough in inorganic materials chemistry. A hexagonal honeycomb of silica was prepared by sol-gel condensation of silicates templated by the lyotropic liquid crystalline phase of a surfactant. Although the material is amorphous at the microscale, it has crystalline mesoporosity with well-ordered and aligned surfactant-filled silica channels. The surfactant can be removed from the material by calcination, solvent extraction, or even super-critical CO₂ extraction. By varying the length of the surfactant, pore size can be controlled to angstrom precision. Hydrophobic molecules serve to swell the liquid crystalline phase and have been used to prepare materials with 20-100 Å pore diameters.

Mesostructured materials are generally prepared by trial-and-error using poorly defined precursors that assemble via condensation. Although the materials possess long-range order at the mesoscale, short range order is not generally observed. There have been a few attempts to link cluster building blocks (e.g. Keggin ions) into a mesoporous material, but they have been unsuccessful.

To date, nearly all well-characterized, hexagonally mesostructured materials have been based on oxides. Mesostructured sulfides have been sought after because of their anticipated electronic and optical properties, and their affinity for heavy metals. There have been some reports of mesostructured sulfides, but most of these materials were poorly characterized. The synthesis of mesostructured sulfide-based materials has been hindered by the absence of suitable precursors and the poorly understood condensation behaviour of metal sulfides. Stupp et al. reported that hexagonally organized CdS and CdSe could be formed by flowing H₂S or H₂Se over a hexagonal mesophase containing
oligoethyleneoxide oleyl ether (C\textsubscript{18}H\textsubscript{35}(OCH\textsubscript{2}CH\textsubscript{2})\textsubscript{10}OH), water, and a Cd(II) salt.\textsuperscript{16} Ozin and coworkers have reported a liquid crystalline, mesostructured tin sulfide.\textsuperscript{17}

Kanatzidis et al. reported the synthesis and structural characterization of lamellar assemblies of [Ge\textsubscript{4}S\textsubscript{10}]\textsuperscript{4+} clusters charge balanced by surfactants.\textsuperscript{18} In these structures, the clusters formed hexagonal close-packed lamellae with interdigitated surfactant molecules between the layers. The clusters in this material were not connected. We recently reported that a mesostructured metal germanium sulfide framework could be assembled from TMA\textsubscript{4}Ge\textsubscript{4}S\textsubscript{10}, transition metals, and surfactants in formamide.\textsuperscript{19} Here we report further information on the synthesis and characterization of mesostructured metal germanium sulfides.
3.3 Experimental

3.3.1 Materials.

TMA₄Ge₄S₁₀ was prepared hydrothermally by the literature method.⁹a Ni(NO₃)₂·6H₂O and tetradecyltrimethylammonium bromide (TDTBr) were obtained from BDH and Fluka, respectively. CoSO₄·7H₂O and CuCl were obtained from Fisher Scientific. Cetyltrimethylammonium bromide (CTABr), cetylpyridinium chloride monohydrate (CPMCl), octadecyltrimethylammonium bromide (ODTBr), ZnCl₂, dodecyltrimethylammonium bromide, and formamide (98%) were purchased from Aldrich. All reagents were used without further purification.

3.3.2 Equipment.

All reactions were carried out in 20 mL capped vials under air. Solid-state 400 MHz ¹H MAS and 100.5 MHz ¹³C CP-MAS NMR spectra were obtained on a Bruker DSX 400 spectrometer. Powder X-ray diffraction patterns were obtained on a Siemens D5000 X-ray diffractometer using Ni-filtered Cu Kα radiation (λ = 1.54178 Å). In diffraction patterns where the 110 and 200 reflections could not be resolved, peaks were fit using a Voigt function. Fits were generally in excellent agreement with the values predicted from the d₁₀₀ peak. Variable-temperature PXRD patterns were obtained on the same instrument. The sample was layered onto a thin platinum strip in a hexanes suspension. Under vacuum, the sample was heated at ca. 5 °C min⁻¹ between data collection temperatures (100 °C, 150 °C, 200 °C, and every 20 °C after that) where it was held for ca. 10 min for data collection. Reflectance UV-vis / near-IR spectra were obtained on a Perkin-Elmer Lambda 900 UV-vis / near-IR spectrometer. Data were fit to
Gaussian lineshapes to estimate the number of contributing peaks. IR spectra were obtained using KBr pellets on a Perkin Elmer Paragon 500 FT-IR spectrometer. FT-Raman spectra were collected on a Bomems MB-157 FT-spectrometer with a Spectra Physics diode pumped Nd:YLF laser (1064 nm; 350 kHz repetition rate). The instrument was configured in 180° back-scattering mode using sealed glass capillary tubes to hold the neat, crystalline samples. Pyrolysis mass spectra were obtained using a VG 70-250S mass spectrometer. Samples were heated at 32.4 °C min⁻¹ and the volatile products were ionized by EI. Thermogravimetric analyses were obtained on a Perkin-Elmer TGA-7 analyzer equipped with a TAC-7 instrument controller. Samples were heated at a rate of 5 °C min⁻¹ under a flow of N₂. Transmission electron micrographs were obtained with a Phillips 430 microscope operating at 100 kV. Whole mounted samples were placed directly on a carbon grid as the embedding media used for sectioning the samples reacted with the materials. Elemental analyses were performed at UOP. For sulfur analyses, samples were combusted in a tube furnace and the SO₂ was analyzed by IR (relative error 5%). C, N, and H analyses were done by the standard combustion method (relative error 3-4%). Ge, Co, Cu, and Zn analyses were performed by ICP (inductively coupled plasma) after dissolution or fusion with a flux (variable sample pretreatment, depending on solubility) (relative error 2%). To determine water content, samples were heated in a tube furnace and the steam was dissolved in a solvent. The moisture content was then determined by a Karl-Fischer titration.
3.3.3 Synthesis.

Many samples of the mesostructured metal germanium sulfides were prepared with different metals (Co, Cu, Zn, Ni), surfactants \( (C_nH_{2n-1}NMe_3^-)X^- \) \( [n = 18, 16, 14, 12; \ X = Br^-, Cl^-] \), \( C_{16}H_{33}(NC_5H_5)^{-}Cl^- \), concentrations, and aging times (0-7 d). Examples of typical preparations are listed below along with the particular data measured for that sample. The materials are designated SURF-M/Ge_4S_10, where SURF = surfactant (CTA for cetyltrimethylammonium or CPM for cetylpyridinium) and M indicates the metal used. For each synthesis, it was first necessary to heat the surfactant-cluster solution to 100-120 °C to solubilize the precursors, then the solutions were cooled to 80 °C.

**Synthesis of CTA-Ni/Ge_4S_10.** A solution of 642 mg Ni(NO_3)_2·6H_2O (2.21 mmol) in 2 mL of formamide at 80 °C was added with a pipette to a solution of 1.00 g (1.10 mmol) TMA_4Ge_4S_10, 1.50 g (4.12 mmol) CTABr, and 14 mL of formamide at 80 °C. An immediate brown precipitate formed from the clear, colourless solution. The contents were shaken for ca. 5 s then aged at 80 °C for 16 h. The product was isolated on a Buchner funnel, washed with formamide at 80 °C (ca. 50 mL) then water at 80 °C (ca. 50 mL). The brown solid was dried under ambient conditions for 24 h prior to characterization. Yield: 1.37 g.

**Data for CTA-Ni/Ge_4S_10.** PXRD: 34.2 \( (d_{100}) \), 19.7 \( (d_{110}) \), 17.2 \( (d_{200}) \), 13.0 \( (d_{210}) \) Å. UV-vis / near-IR: \( \lambda_{\text{max}} = 2458\text{w.} \ 2417\text{w.} \ 2365\text{w.} \ 2327\text{w.} \ 2270\text{w.} \ 1956\text{m.} \ 1778\text{w.} \ 1747\text{w.} \ 1681\text{w.} \ 379\text{s.} \). Ash (500 °C): 52 %.
Synthesis of CTA-Cu/Ge$_4$S$_{10}$. A mixture of 437 mg CuCl in 4 mL of formamide at 80 °C was filtered, leaving ca. 300 mg (3 mmol) of CuCl in solution. This was added quickly with a pipette to a solution of 1.00 g (1.10 mmol) TMA$_2$Ge$_4$S$_{10}$, 1.50 g (4.12 mmol) CTABr, and 14 mL of formamide at 80 °C. An immediate brown-yellow precipitate formed. The mixture was shaken for ca. 5 s then placed in an oven at 80 °C for 18 h. The product was isolated on a Buchner funnel, washed with formamide at 80 °C (ca. 50 mL) and water at 80 °C (ca. 50 mL). The powder was dried under ambient conditions for 24 h prior to characterization. Yield: 1.43 g of yellow-green powder.

Data for CTA-Cu/Ge$_4$S$_{10}$. PXRD: d = 34.2 (d$_{100}$), 19.8 (d$_{110}$), 17.4 (d$_{200}$). UV-vis / near-IR: $\lambda_{\text{max}}$ = 2369w, 1941w, 362s nm. Anal. Found (%): Cu, 14.9; Ge, 18.2; S, 20; C, 32.4; N, 1.8; H, 6.1. Ash (500 °C): 56%.

Synthesis of CTA-Co/Ge$_4$S$_{10}$. A solution of 87 mg (0.31 mmol) CoSO$_4$·7H$_2$O in 1 g of formamide at 80 °C was added quickly with a pipette to a solution of 0.189 g (0.208 mmol) of TMA$_2$Ge$_4$S$_{10}$, 0.205 g (0.562 mmol) CTABr, and 2.08 g of formamide at 80 °C. A blue precipitate formed immediately. The mixture was shaken for ca. 5 s then filtered onto a Buchner funnel. The product was washed with formamide at 80 °C (ca. 20 mL) then water at 80 °C (ca. 20 mL). The aqueous wash resulted in a colour change of the powder from blue to green. After drying under ambient conditions for 24 h, the product was characterized. Yield: 0.13 g of green powder.
**Data for CTA-Co/Ge₄S₁₀.**  PXRD: d = 36.0 (d₁₀₀), 20.4 (d₁₁₀), 18.0 (d₂₀₀) Å.  UV-vis / near-IR: λₘₐₓ = 2414 w. 2365 w. 2329 w. 2270 w. 1600 s (very broad). 720 s. 362 s. Anal. Found (%): Co. 4.49; Ge. 20.2; S. 23; C. 39.2; N. 2.2; H. 8.1.

**Synthesis of CTA-Zn/Ge₄S₁₀.**  A solution of 0.305 g ZnCl₂ (2.24 mmol) in 2 mL of formamide at 80 °C was added quickly with a pipette to a solution of 1.00 g (1.10 mmol) TMA₄Ge₄S₁₀, 1.50 g (4.12 mmol) CTABr, and 14 mL of formamide at 80 °C. A white precipitate formed immediately. The mixture was shaken for ca. 5 s then aged at 80 °C for 9 h. The white product was isolated on a Buchner funnel, washed with ca. 50 mL of formamide (80 °C) then ca. 50 mL of distilled water (80 °C). After drying overnight under ambient conditions, the product was characterized. Yield: 1.41 g of white powder.

**Data for CTA-Zn/Ge₄S₁₀.**  PXRD: 33.7 (d₁₀₀), 19.2 (d₁₁₀), 16.8 (d₂₀₀).  UV-vis / near-IR: λₘₐₓ = 2423 w. 2367 w. 2327 w. 2274 w. 1956 w. 1778 w. 1746 w. 1689 w. 1432 w. 1231 w. 301 s nm. Anal. Found (%): Zn. 8.87; Ge. 20.6; S. 19; C. 36.0; N. 2.1; H. 7.3; Cl. 0.023; Br. < 0.01; H₂O. 8.06. Ash (500 °C): 53%.

**Synthesis of CPM-Zn/Ge₄S₁₀.**  A solution containing 320 mg of ZnCl₂ (2.35 mmol) in 2 mL of formamide at 80 °C was added quickly with a pipette to a solution of 1.00 g (1.10 mmol) TMA₄Ge₄S₁₀, 1.00 g (2.79 mmol) CPMCl·H₂O, and 14 mL of formamide at 80 °C. A white precipitate formed immediately. The mixture was shaken briefly (ca. 5 s) then aged for 18 h at 80 °C. The product was isolated on a Buchner funnel and washed
with ca. 50 mL of formamide (80 °C) then ca. 50 mL of water (80 °C) and dried overnight under ambient conditions. Yield: 1.30 g of white powder.

**Data for CPM-Zn/Ge$_4$S$_{10}$.** PXRD: d = 34.5 (d$_{100}$), 19.5 (d$_{110}$), 17.2 (d$_{200}$) Å. UV-vis/near-IR: $\lambda_{\text{max}}$ = 2438w, 2367w, 2327w, 2155w, 1957w, 1779w, 1746w, 1677w, 1433w, 1409w, 1231w, 311s. Anal. Found (%): Zn, 7.8; Ge, 22.4; S, 22; C, 35.4; N, 1.9; H, 6.0; Cl, 0.21; Br, < 0.01; H$_2$O, 3.51. Ash (500 °C): 50%.

**Synthesis of TDT-Ni/Ge$_4$S$_{10}$.** A solution of 255 mg Ni(NO$_3$)$_2$·6H$_2$O in 2 mL of formamide at 80 °C was added quickly with a pipette to a solution of 643 mg (0.708 mmol) TMA$_4$Ge$_4$S$_{10}$, 1.00 g (2.97 mmol) tetradecyltrimethylammonium bromide (TDTBr), and 10 mL of formamide. An immediate brown precipitate formed. After shaking the mixture for ca. 5 s, it was aged at 80 °C for 20 h. The product was isolated on a Buchner funnel, washed with ca. 50 mL of formamide (80 °C) then ca. 50 mL of water (80 °C). A fine brown powder was obtained after drying overnight under ambient conditions. Yield: 596 mg.

**Data for TDT-Ni/Ge$_4$S$_{10}$.** PXRD: d = 31.6 (d$_{100}$), 18.0 (d$_{110}$), 15.8 (d$_{200}$) Å. UV-vis/near-IR: $\lambda_{\text{max}}$ = 2419w, 2367w, 2331w, 2269w, 1971m, 1781w, 1747w, 1687w, 366s nm. Ash (500 °C): 41%.
3.4 Results

3.4.1 Synthesis.

We identified the linking of \([\text{Ge}_2\text{S}_{10}]^+\) clusters with transition metals as a route to a new type of mesostructured material. Initially, a series of \([\text{Ge}_4\text{S}_{10}]^+\) clusters charge balanced with surfactants (\([\text{C}_n\text{H}_{2n+1}\text{NMe}_3]_4\text{Ge}_4\text{S}_{10}, n = 12, 14, 16, 18\)) was prepared to serve as precursors for the mesostructured materials. They were found to be insoluble in common solvents that form lyotropic liquid crystalline phases (e.g. water, ethanol, ethylene glycol), but were very soluble in warm (\(\text{ca. } 80^\circ\text{C}\)) formamide. A preliminary reaction of (\(\text{C}_{12}\text{H}_{25}\text{NMe}_3\))_4\text{Ge}_4\text{S}_{10} with \(\text{ZnCl}_2\) in formamide gave a material that showed a peak in the low-angle diffraction pattern (\(d_{100} = 37\ \text{Å}\)). We felt that a synthesis directly from \(\text{TMA}_4\text{Ge}_4\text{S}_{10}\) would be a more convenient route.

In a typical preparation, \(\text{TMA}_4\text{Ge}_4\text{S}_{10}\) and the surfactant were dissolved in formamide to form a clear, viscous liquid. Rapid addition of \(\text{CoSO}_4\), \(\text{Ni(NO}_3)_2\), \(\text{ZnCl}_2\), or \(\text{CuCl}\) in formamide at 80 °C gave an immediate precipitate. After aging at 80 °C, the products were isolated, washed with hot formamide then water, and dried under ambient conditions. The products were all light, free-flowing powders obtained in a reasonable yield. A variety of cationic surfactant templates were used. Powder X-ray diffraction patterns of the materials indicated that they were all hexagonally ordered; evidence for a lamellar phase was only observed in samples prepared with \(\text{C}_{18}\text{H}_{37}\text{NMe}_3^+\) as surfactant.

\(\text{Ge}, \text{S}, \text{Cl}, \text{Br}, \text{C}, \text{N}, \text{H}, \text{H}_2\text{O},\) and metal analyses were obtained for several samples of the mesostructured materials. A summary of the data is provided in Table 1, using the \(\text{Ge}_4\) analysis as a reference (\(\text{Ge}_4\) was chosen as the reference as it represents a single
[Ge₄S₁₀]⁺ cluster and because the Ge analyses are more reliable than the S analyses).
From an average of 4 samples prepared without sulfate, a Ge:S ratio of 4:9.4(8) was
determined. This agrees with the ratio of 4:10 expected if the [Ge₄S₁₀]⁺ clusters are
intact. The ratio of M:Ge₄ varied between 1.1 and 3.8. Interestingly, the samples
prepared with Zn and Co all had M:Ge₄ analyses that were very close to or less than the
value expected from the synthesis. Cu, however, was unique in that a much higher than
expected Cu:Ge₄ ratio was observed, which was nearly double all other M:Ge₄ values.
As the Cu:Ge₄ ratio was double other M:Ge₄ ratios, a [Cu₂]²⁺ dimer may link the
[Ge₄S₁₀]⁺ clusters in this material. This is reminiscent of the microporous
TMA₂Cu₂Ge₄S₁₀ materials which contain a [Cu₂]²⁺ dimer linking the adamantanoid
clusters.¹¹ C and N analyses of the materials indicated that they contained approximately
2.2-2.5 CTA cations per Ge₄. Analysis of a CPM-Zn/Ge₄S₁₀ sample indicated a
CPM:Ge₄ ratio of 1.83.

Table 1. Summary of Elemental Analysis Results for Mesostructured Metal Germanium
Sulfides.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S:Ge₄ found</th>
<th>N:Ge₄ Found</th>
<th>M:Ge₄ Found</th>
<th>M:Ge₄ Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>9.9(5)</td>
<td>2.26</td>
<td>2.12</td>
<td>2.0</td>
</tr>
<tr>
<td>Zn</td>
<td>8.4(4)</td>
<td>2.11</td>
<td>1.91</td>
<td>2.1</td>
</tr>
<tr>
<td>Zn</td>
<td>9.0(5)</td>
<td>1.76</td>
<td>1.55</td>
<td>2.1</td>
</tr>
<tr>
<td>Cu</td>
<td>9.9(5)</td>
<td>2.05</td>
<td>3.74</td>
<td>2.7</td>
</tr>
<tr>
<td>Co</td>
<td>10.3(5)b</td>
<td>2.26</td>
<td>1.10</td>
<td>1.5</td>
</tr>
<tr>
<td>Co</td>
<td>11.6(6)b</td>
<td>2.07</td>
<td>1.94</td>
<td>2.3</td>
</tr>
</tbody>
</table>

a The sample was prepared with CPMCl as the template; all others are CTABr.

b Cobalt sulfate was the metal source and may explain why the S analyses are high.
Three meso-Zn/Ge₄S₁₀ samples were analyzed for Cl⁻, Br⁻, and H₂O. There was essentially no halide present in the samples. This is surprising since a large amount of halide was used in the preparations. Water analyses of the samples indicated that they contained 3-8% moisture by mass.

3.4.2 Characterization.

The mesostructured products were characterized by several techniques to confirm the molecular and supramolecular structures of the materials. Visibly, the materials appeared distinctly coloured depending on the metal incorporated. The materials were light green, deep green, white, and brown when Cu(I), Co(II), Zn(II), and Ni(II) were used, respectively. Interestingly, the materials did not have a sulfide odour, characteristic of volatile sulfur compounds discharged from other metal sulfides we have investigated.

3.4.3 Powder X-ray Diffraction.

Powder X-ray diffraction (PXRD) of the mesostructured materials typically showed 2-4 peaks consistent with a hexagonal unit cell. Often the (110) and (200) reflections overlapped in the diffraction patterns, possibly due to broadening associated with small particle sizes. Figure 1a shows a PXRD pattern of CTA-Ni/Ge₄S₁₀, where 4 peaks assigned to reflections from a hexagonal lattice with \( a_0 = 39.5 \) Å were observed. The observation of 4 peaks is unusual for reported hexagonal mesostructured materials (besides silica) and attests to the high degree of order in the solid. Measured and calculated peaks are listed in Table 2. For comparison, the unit cell dimension, \( a_0 \), observed for MCM-41 with a C₁₆ chain is 40 Å. In Figure 1b, the powder X-ray
diffraction patterns of CTA-M/Ge₄S₁₀ (M = Cu⁺, Zn²⁻, Co²⁻, Ni²⁺) are characteristic of hexagonal symmetry. In addition to the diffraction peaks, several broad, amorphous halos were apparent in the materials as illustrated in Figure 1c. These correspond to the most probable interatomic distances in the material.

Table 2. Measured and Calculated Reflections for CTA-Ni/Ge₄S₁₀ Based on a Unit Cell With a₀ = 39.45 Å.

<table>
<thead>
<tr>
<th>refl</th>
<th>obs (Å)</th>
<th>calc (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d₁₀₀</td>
<td>34.18(1)</td>
<td>34.18</td>
</tr>
<tr>
<td>d₁₁₀</td>
<td>19.75(8)</td>
<td>19.73</td>
</tr>
<tr>
<td>d₂₀₀</td>
<td>17.19(8)</td>
<td>17.09</td>
</tr>
<tr>
<td>d₂₁₀</td>
<td>13.0(5)</td>
<td>12.92</td>
</tr>
</tbody>
</table>

The channel dimensions of MCM-41 can be tailored by choice of surfactant or by swelling an organic species (e.g. mesitylene) in the preformed liquid crystalline template. To determine the effect of modifying the length of the surfactant’s aliphatic hydrocarbon chain in the formation of the mesostructured metal germanium sulfides, meso-Ni/Ge₄S₁₀ materials were prepared with CₙH₂ₙ₋₁NMe₃⁺X⁻ (n = 12, 14, 16, 18) surfactants. PXRD patterns of the synthesized materials are displayed in Figure 2a. The degree of order in the samples prepared with n = 14, 16, and 18 were similar, showing an intense peak corresponding to the 100 reflection plus 2-3 additional reflections consistent with hexagonal symmetry. Samples prepared with dodecyltrimethylammonium (n = 12) as surfactant were less well-ordered, showing only a single peak that was less intense. Samples prepared with C₁₈H₃₇NMe₃⁺ also contained a small fraction of a lamellar phase, d₁₀₀ = 27.7 Å (est. < 2% from integration of the 100(lam):100(hex) reflections).
Figure 1. (a) PXRD pattern of CTA-Ni/Ge$_4$S$_{10}$ (with expanded region in the inset) in the low 2θ region shows 4 peaks diagnostic of hexagonal symmetry. (b) PXRD patterns of CTA-M/Ge$_4$S$_{10}$ (M = (i) Co, (ii) Cu, (iii) Zn, (iv) Ni) in the low 2θ region also show hexagonal symmetry. (c) In the high 2θ, PXRD patterns of CTA-M/Ge$_4$S$_{10}$ (M = (i) Cu, (ii) Co, (iii) Zn, (iv) Ni) show only broad, amorphous halos.
The materials display mesoscopic order with an increasing value of \( d_{100} \) as the hydrocarbon chain length increased. Measured d-spacings of the reflections, the calculated hexagonal unit cell dimension, and the corresponding unit cell dimension reported for mesoporous silica are listed in Table 3. The unit cell dimensions nearly correspond with the values observed in MCM-41 templated with the same surfactants. An average increase in the pore diameter of ca. 2.1 Å per additional carbon atom agrees well with the expected increase of ca. 2.5 Å. When mesitylene was introduced into preparations, mesostructured materials were obtained. However, these materials showed diminished order (by PXRD) compared to materials prepared without mesitylene and the \( d_{100} \) position did not change with the mole ratio of mesitylene:CTABr up to 1:1.

**Table 3.** Effect of Surfactant Chain Length on Observed Reflections for Mesostructured Ni/Ge\(_4\)S\(_{10}\) Materials and Comparison of the Calculated Unit Cell Parameters With the Unit Cell Determined for Mesoporous Silica, MCM-41.

<table>
<thead>
<tr>
<th>Surfactant Chain Length(^a)</th>
<th>Observed Reflections From PXRD</th>
<th>Hexagonal Unit Cell Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n = 12 )</td>
<td>( d_{100} ) (Å)</td>
<td>( d_{110} ) (Å)</td>
</tr>
<tr>
<td>12</td>
<td>28.1</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>31.6</td>
<td>18.0</td>
</tr>
<tr>
<td>16</td>
<td>34.2</td>
<td>19.7</td>
</tr>
<tr>
<td>18</td>
<td>38.9</td>
<td>22.8</td>
</tr>
</tbody>
</table>

\(^a\) Surfactant was \( C_nH_{2n-1}NMe_3^+X^- \) (\( X = \text{Cl or Br} \))

\(^b\) \( a_0 = 2d_{100}/\sqrt{3} \) for hexagonal unit cell

\(^c\) Surfactant removed; ref. 13.
Figure 2. (a) PXRD patterns of meso-Ni/Ge₄S₁₀ prepared with surfactants CₙH₂n₋₁NMe₅⁻ ((i) n = 18, (ii) n = 16, (iii) n = 14, (iv) n = 12) show that the unit cell dimensions of the mesostructured material can be controlled by changing the length of the aliphatic hydrocarbon chain on the surfactant. (Note: the peak indicated by * is a small (ca. < 2%) impurity of a lamellar phase.) (b) PXRD pattern of CPM-Zn/Ge₄S₁₀ shows reflections characteristic of hexagonal symmetry.

Other surfactants also gave well-ordered mesostructured materials with hexagonal order. Figure 2b shows the PXRD pattern of CPM-Zn/Ge₄S₁₀ between 1 and 10 degrees 2θ. Three peaks associated with the hexagonal order of the material are clearly apparent.
The lattice dimension of the mesostructure ($a_0 \sim 40 \, \text{Å}$) is similar to that obtained with the surfactant CTABr.

The mesostructured metal germanium sulfides are remarkably stable over time. X-ray diffraction was performed on several samples that had been stored for more than a year under ambient conditions in the laboratory. The PXRD patterns of the aged samples were virtually identical and indicated no decrease in mesoscopic order in the samples.

### 3.4.4 Transmission Electron Microscopy.

Samples of the mesostructured metal germanium sulfides were examined by transmission electron microscopy (TEM). As the materials were unstable in the epoxy used to support the sample for microtoming, whole-mounted samples were used instead. This made the observation of mesoporosity extremely difficult, as the order was required to extend throughout the length of the particle between the electron beam and the detector. Survey of the samples showed that most of the particles were well ordered (very little amorphous material was observed) and no dense phases were apparent by TEM. Energy-dispersive X-ray (EDX) analysis of single particles indicated that they contained Ge, S, and the expected metal. There is a large contrast between the metal germanium sulfide channel walls and the surfactant filling the pores. Figure 3a shows a view of CTA-Ni/Ge$_4$S$_{10}$ parallel to the channel axis. A TEM micrograph of the CTA-Ni/Ge$_4$S$_{10}$, observed perpendicular to the channel axis of the material, is illustrated in Figure 3b. The interpore spacing of approximately 40 Å is in agreement with the value calculated from the diffraction pattern, $a_0 \sim 39.5 \, \text{Å}$. The hexagonal order of CTA-Cu/Ge$_4$S$_{10}$ is illustrated in Figure 3c. From the TEM micrograph, the interpore spacing is
ca. 48 Å, close to the expected value of 40 Å from the PXRD pattern (d_{100} = 34.5 Å for this sample). The thick channel wall (15-20 Å) visualized in the TEM image is an artifact of using whole-mounted thick samples as any curvature of the channels is projected onto the image. Figures 3d and 3e show images of the mesostructured CTA-Co/Ge_{4}S_{10} material parallel and perpendicular to the channel axis, respectively. Again, the interpore spacing is consistent with the value measured by PXRD.

TEM images of single particles show worm-like morphologies that are similar to those observed in MCM-41 (Figure 4).^{20} The hexagonal mesostructure of the material is reflected in the morphology of the resultant material, where the particles have a large aspect ratio. Some of the particles even show facets characteristic of a hexagonal unit cell. TEM images of the worm-like particles at higher magnification confirmed that the channels ran parallel to the length of the worm.
Figure 3. (a) TEM image of CTA-Ni/Ge₄S₁₀ parallel to the channel axis. (b) TEM image of CTA-Ni/Ge₄S₁₀ perpendicular to the channel axis. (c) TEM image of CTA-Cu/Ge₄S₁₀ perpendicular to the channel axis.
Figure 3. (Continued) (d) TEM image of CTA-Co/Ge$_4$S$_{10}$ parallel to the channel axis.
(e) TEM image of CTA-Co/Ge$_4$S$_{10}$ perpendicular to the channel axis.
Figure 4. TEM images of worm-like particles of CTA-Ni/Ge₄S₁₀. A magnified view of the particle in image (b) confirmed that the channels of the material run parallel to the longitudinal axis of the faceted shape.
3.4.5 Infrared Spectroscopy.

IR spectra of the mesostructured metal germanium sulfides were obtained. Overall, samples prepared with the same surfactant and transition metal were very similar. The spectra showed many of the same modes as the crystalline surfactant (CTABr, CPMCl, etc.), but the peaks had significantly different intensities and were broader in the composite materials. Moreover, many of the peaks were substantially shifted from the surfactant. Figure 5 shows the IR spectra of CTA-Co/Ge$_4$S$_{10}$ and crystalline CTABr for comparison.

In addition to showing evidence for the surfactant, the IR spectra also showed the presence of water in all of the samples. An intense peak in the region of 3200-3500 cm$^{-1}$ was characteristic of O-H stretching. This peak often showed fine structure that could arise from the presence of coordinated and physisorbed water. In the region of 1600-1680 cm$^{-1}$, one or two modes were observed in the samples. These are probably bending modes associated with coordinated and physisorbed water. In most of the samples, broad low frequency modes (ca. 1110 and 800 cm$^{-1}$) were also observed and their intensity appeared to scale with the other peaks associated with water. The former may be assigned to a MOH bending mode of hydroxyl species and the latter to a deformation mode of coordinated water. No evidence for S-H stretching modes were observed in the IR spectra of the materials, though this mode is usually a weak band in the IR.

The IR spectra were also examined for the signature modes of formamide and anions that were present in the preparation. While the NH stretching mode of formamide might be at a similar frequency to the O-H stretch for water and the carbonyl stretching mode might overlap with the bending mode for water, no characteristic C-H stretching
mode for an aldehyde was observed. Samples prepared with Ni(NO₃)₂ showed no intense mode in the region 1380-1350 cm⁻¹ that would be characteristic of coordinated nitrates. However, the samples prepared with CoSO₄ did show the presence of the anion, as indicated by an S-O stretching mode near 1100 cm⁻¹. In one sample, three bands were clearly resolved, indicating low site symmetry for the sulfate.

![Figure 5. IR spectra of (i) CTA-Co/Ge₄S₁₀ and (ii) crystalline CTABr.](image)

### 3.4.6 Raman Spectroscopy.

Raman spectra of the mesostructured metal germanium sulfides (M = Co, Cu, Ni) could not be obtained as they decomposed under the laser radiation. However, Raman spectra of meso-Zn/Ge₄S₁₀ materials were obtained and proved essential to understanding the bonding in the materials. Figure 6a shows the Raman spectrum of CTA-Zn/Ge₄S₁₀ and CTABr for comparison. The Raman spectrum of CTA-Zn/Ge₄S₁₀ shows most of the
modes characteristic of CTABr, but the peaks are generally broader and the intensities differ from pure CTABr. These observations are consistent with the presence of CTA− cations in a distribution of environments inside the mesostructured material. It is worth noting that there is no evidence for thiol groups in the sample since S-H stretching modes were not observed.

Below 600 cm⁻¹, the Raman spectrum of CTA-Zn/Ge₄S₁₀ differs significantly from the spectrum of CTABr. This region, which is expanded in Figure 6b, bears the vGe-S and vZn-S modes that are not present in the pure surfactant. For comparison, the spectra of microporous, crystalline TMA₂ZnGe₄S₁₀ and lamellar CTA₄Ge₄S₁₀ are provided. The spectrum of CTA₄Ge₄S₁₀, in which the adamantanoid [Ge₄S₁₀]⁺ clusters are unconnected, displays two sets of peaks that are assigned to terminal vGe-S₁ modes (340-480 cm⁻¹) and bridging vGe-S₂ modes. The symmetric vGe-S₁ mode is observed at 342.0 (± 0.1) cm⁻¹ with a full width at half maximum (FWHM) of 7.6 (±0.6) cm⁻¹. In the Raman spectrum of TMA₂ZnGe₄S₁₀, where all of the [Ge₄S₁₀]⁺ clusters are intact and linked to the tetrahedral metal centers, the symmetric mode has shifted to 350.7 (± 0.2) cm⁻¹, but the linewidth is virtually unchanged (FWHM = 8.8 (± 0.5) cm⁻¹). Weak modes attributed to vZn-S stretching modes are present between 250 and 320 cm⁻¹. The Raman spectrum of CTA-Zn/Ge₄S₁₀ strongly resembles the spectrum of the microporous TMA₂ZnGe₄S₁₀ framework in the vGe-S region, but the peaks are much broader. The symmetric vGe-S₁ mode is observed at 350.7 (± 0.2) cm⁻¹ in CTA-Zn/Ge₄S₁₀, diagnostic of metal-linked clusters. This peak is substantially broader (FWHM = 19 (± 2) cm⁻¹) than the symmetric vGe-S₁ mode of the crystalline CTA₄Ge₄S₁₀ and TMA₂ZnGe₄S₁₀ materials.
The region between 240 and 320 cm\(^{-1}\) contains many \(\nu\text{Zn-S}\) stretching modes, as observed in the metal-linked, microporous TMA\(_2\)ZnGe\(_4\)S\(_{10}\) materials.

The Raman spectrum of CPM-Zn/Ge\(_4\)S\(_{10}\) is very similar to the spectrum for CTA-Zn/Ge\(_4\)S\(_{10}\) between 600 and 100 cm\(^{-1}\) (Figure 6c). As with the other metal-linked materials, the symmetric \(\nu\text{Ge-S}\) mode is shifted to \(ca. 350\) cm\(^{-1}\) and broadened relative to CTA\(_4\)Ge\(_4\)S\(_{10}\) and TMA\(_2\)ZnGe\(_4\)S\(_{10}\). Moreover, a congested region of \(\nu\text{Zn-S}\) modes are present between 240 and 320 cm\(^{-1}\) in the mesostructured CPM-Zn/Ge\(_4\)S\(_{10}\) material.

Raman spectra of the mesostructured solids are consistent with the presence of metal-linked \([\text{Ge}_{10}]^{\text{I}+}\) clusters present in a number of sites, where the variation in the coordination environment may lead to the increased Raman linewidth of the Ge-S modes. Notably, the adamantanoid \([\text{Ge}_{10}]^{\text{I}+}\) clusters are still intact in the materials, in agreement with the Ge:S ratio determined by elemental analysis.
Figure 6. (a) Raman spectra of (i) CTABr and (ii) CTA-Zn/Ge$_4$S$_{10}$. (b) Raman spectra of (i) CTA$_4$Ge$_2$S$_{10}$, (ii) TMA$_2$ZnGe$_2$S$_{10}$, and (iii) CTA-Zn/Ge$_4$S$_{10}$ in the region 600-100 cm$^{-1}$ where υGe-S and υZn-S modes are observed. (c) Raman spectrum of CPM-Zn/Ge$_4$S$_{10}$ between 600 cm$^{-1}$ and 100 cm$^{-1}$.
3.4.7 Reflectance UV-vis / Near-IR Spectroscopy.

The optical spectroscopy of microporous TMA$_2$MGe$_4$S$_{10}$ materials have been investigated previously.$^{11,22,23}$ The precursor, TMA$_4$Ge$_4$S$_{10}$, shows only an intense HOMO to LUMO transition in the UV that begins at *ca.* 375 nm with a maximum at 330 nm. As metals are introduced, d-d transitions are observed and the optical spectra are strongly dependent on the metal. The microporous frameworks TMA$_2$ZnGe$_4$S$_{10}$ and TMA$_2$Cu$_2$Ge$_4$S$_{10}$ showed no d-d absorptions as they are both d$^{10}$ systems.$^{22}$ In TMA$_2$CoGe$_4$S$_{10}$, however, the metal is in a distorted tetrahedral environment with partially occupied d orbitals, so d-d absorptions in the visible and near IR regions were observed.$^{22}$ Moreover, each of the materials showed an intense absorption near 350 cm$^{-1}$ that is assigned to a ligand-to-metal charge transfer band. The position of this band is also dependent on the identity of the transition metal.

Two samples of each CTA-M/Ge$_4$S$_{10}$ (M = Zn$^{2+}$, Cu$^+$, Co$^{2+}$, Ni$^{2+}$) were investigated by reflectance UV-vis/near-IR spectroscopy between 200 and 2500 nm. The spectra of different samples prepared with the same metal were remarkably similar. The spectra for each of the materials CTA-M/Ge$_4$S$_{10}$, shown in Figure 7, will be discussed in turn.

The near-IR region of the spectrum of CTA-Zn/Ge$_4$S$_{10}$ shows several weak peaks that may be assigned to overtones and combinations of the IR modes of the surfactant and water in the sample. As expected for a d$^{10}$ system, there are no absorptions in the visible portion of the spectrum. In the UV region, an absorption edge begins at *ca.* 450 nm and peaks at 300 nm. This is shifted slightly from the precursor, TMA$_4$Ge$_4$S$_{10}$, which shows an absorption edge beginning at *ca.* 375 nm with a maximum at 330 nm.
Figure 7. (a) Reflectance UV-vis/near-IR spectra of the mesostructured metal germanium sulfides CTA-M/Ge$_4$S$_{10}$. (b) The UV absorption spectra for the same materials between 200 and 600 nm.

The spectrum for Co showed peaks in the near-IR between 2260-2370 nm that can be assigned to combination modes of adsorbed water. Between ca. 1100 and 2200 nm, an intense near-IR absorption was observed that appears to consist of 2 or more transitions when fitted to Gaussian curves. An optical transition in the visible portion of the spectrum between ca. 600 and 900 nm (peak at 720 nm) shows fine structure
consistent with multiple overlapping peaks. A fit to Gaussian curves suggested that there are at least 5 overlapping peaks from 640-820 nm. An absorption edge beginning at ca. 600 nm shows a maximum at 367 nm. Deconvolution of this peak indicated the presence of at least 2 peaks: 362 nm and 269 nm. The former band might be assigned to ligand-to-metal charge transfer (LMCT).

Co(II) is a $d^7$ ion, giving rise to 8 terms in which $^4P$ and $^4F$ are the terms with highest spin multiplicity. In a tetrahedral environment, the $^4P$ term has $^4T_1$ symmetry and the free ion ground term ($^4F$) is split into $^4A_2$, $^4T_1$, and $^4T_2$ terms, with $^4A_2$ being the ground state. This gives rise to three expected transitions ($^4T_2 \leftrightarrow ^4A_2$, $^4T_1(F) \leftrightarrow ^4A_2$, and $^4T_1(P) \leftrightarrow ^4A_2$), which generally occur in the visible and near-IR regions. In the microporous $\text{TMA}_2\text{CoGe}_4\text{S}_{10}$ frameworks, where the Co is coordinated by 4 sulfide ligands, these transitions were observed in the regions of 2000, 1400, and 700 nm. Kirkby et al. deduced that splitting of the absorption near 700 nm was characteristic of a distorted tetrahedral environment. In the mesostructured CTA-Co/Ge$_4$S$_{10}$ materials, broad regions of overlapping bands centered near 700 and 1600 nm suggest that the Co has a similar microenvironment to Co in the microporous framework. The presence of defect sites (where Co is coordinated by water or sulfate instead of sulfide at one coordination site, for example), which would result in a change in the orbital splitting, could be responsible for the breadth of these transitions.

It is interesting that Ni forms a very well-ordered mesostructured framework but not the analogous microporous framework. In the reflectance spectrum, several modes were observed between 1690 and 2500 nm. They are nearly the same as those observed in the CTA-Zn/Ge$_4$S$_{10}$ material and can be assigned to combination and overtone modes.
of the surfactant and water. A very broad absorption edge began at \textit{ca.} 1200 nm, spanned the entire visible spectrum (hence the brown colour of the material), and peaked at 380 nm. The absorption fit quite well to 5 Gaussian peaks centered at \textit{ca.} 750, 670, 460, 357, and 246 nm. The first 3 transitions are assigned to d-d transitions of the Ni (note that they are very broad and there may be many more contributing peaks) and the peak at 357 nm may be a LMCT band.

Ni(II) is a \(d^8\) metal. In a tetrahedral field, three fairly intense bands would be expected, with a \(^3A_2 \leftarrow ^3T_1(F)\) transition typically detected in the near-IR (\textit{ca.} 1400 nm).\textsuperscript{25} The absence of a peak in this region strongly suggests that the Ni(II) in the mesostructured material is not in a tetrahedral geometry. All of the absorption bands in octahedral and square planar Ni(II) are typically observed at high energy. Thus, these two geometries are the most likely candidates.

It seems highly unlikely that Ni(II) would coordinate to 6 [Ge\(_4\)S\(_{10}\)]\(^{2+}\) clusters due to steric interactions. Many nickel tetrathiolate complexes are found in a square planar geometry.\textsuperscript{26} The possibility of octahedral or 5-coordinate Ni centers where some of the coordination sites are occupied by solvent or anions cannot be excluded.

Reflectance UV-vis / near-IR spectroscopy of the microstructured TMA\(_2\)Cu\(_2\)Ge\(_4\)S\(_{10}\) framework showed no transitions in the near-IR or visible, but an absorption edge rising from \textit{ca.} 550 nm and peaking near 360 nm. This optical transition was observed in the mesostructured CTA-Cu/Ge\(_4\)S\(_{10}\) materials, rising from 550 nm and peaking at 365 nm. A weak band was also observed at 238 nm.

In the near-IR, however, the spectrum of the mesostructured framework is distinct from the microstructured material. Weak overtone / combination modes were observed
at 2280-2370 nm. A very broad, intense transition extending from about 600 nm to over 2500 nm, its center near 2000 nm, dominated the near-IR portion of the spectrum. Broad, intense near-IR absorptions similar to this have been observed in mixed valence Cu(I)/Cu(II) dimers.\(^{27}\)

3.4.8 NMR Studies.

Solid-state \(^1\)H magic-angle spinning (MAS) and \(^{13}\)C cross-polarization (CP) MAS NMR of CTA-Cu/Ge\(_4\)S\(_{10}\), CTA-Zn/Ge\(_4\)S\(_{10}\), and CPM-Cu/Ge\(_4\)S\(_{10}\) confirmed the identity of the surfactant in the mesostructured materials. The spectra look virtually the same, showing two broad resonances for the hydrophobic carbon chain near 1 ppm and a broad resonance for the protons on the methyl and methylene groups adjacent to N. In CPM-Zn/Ge\(_4\)S\(_{10}\), this latter resonance is much smaller as there are only 2 protons adjacent to N, and a broad resonance has emerged near 8 ppm. \(^{13}\)C CP-MAS NMR spectra of these materials are illustrated in Figure 8. A peak observed at \(\delta = 68\) ppm in the samples containing CTA and \(\delta = 62\) ppm in the sample prepared with CPM surfactant is assigned to the CH\(_2\) adjacent to the nitrogen atom. A resonance observed at \(\delta = 54\) ppm in CTA-Zn/Ge\(_4\)S\(_{10}\) and CTA-Cu/Ge\(_4\)S\(_{10}\) is assigned to methyl groups attached to N. Resonances between 10-40 ppm can be assigned to the remainder of the C\(_{16}\)H\(_{33}\) aliphatic hydrophobic chain of the surfactants. Two peaks observed at 128 and 144 ppm are consistent with resonances of the pyridinium head group in CPMCl.

Perhaps the most interesting aspect of the NMR spectra is the absence of resonances attributed to formamide (\(^{13}\)C NMR, \(\delta = 167\) ppm). As the samples were washed with formamide then water, the former solvent may have been removed from the
samples. The $^1$H MAS NMR resonance for water in the samples would likely overlap with the broad NCH$_2$/NCH$_3$ resonances observed at 3-4 ppm.

Figure 8. $^{13}$C CP-MAS NMR spectra of (i) CTA-Cu/Ge$_4$S$_{10}$, (ii) CTA-Zn/Ge$_4$S$_{10}$, and (iii) CPM-Zn/Ge$_4$S$_{10}$. (Spinning side-bands are marked with *.)
3.4.9 Thermal Stability.

We investigated the thermal stability of the mesostructured metal germanium sulfides by thermogravimetric analysis (TGA), pyrolysis mass spectrometry, and high-temperature powder X-ray diffraction (for CTA-Cu/Ge$_4$S$_{10}$). All of the materials prepared with CTABr as the surfactant showed similar thermal properties. Figure 9a shows the TGA traces for samples of CTA-M/Ge$_4$S$_{10}$ (M = Cu$^+$, Zn$^{2+}$, Ni$^{2+}$, Co$^{2+}$) heated under N$_2$. Each of the samples showed a small weight loss (ca. 1-5 wt%) between room temperature and 150 °C, probably due to loss of physisorbed water from the material. Then, beginning at ca. 200 °C, each of the materials underwent a weight loss of ca. 50 wt% up to 500 °C. This weight loss occurs at nearly the same temperature as surfactant decomposition in the channels of MCM-41. Figure 9b shows the TGA trace for CTA-Ni/Ge$_4$S$_{10}$ along with the differential TGA trace. There appear to be two components to the weight loss, centered at ca. 250 °C and 320 °C, respectively. Pyrolysis mass spectrometry indicated that all weight loss corresponded to the decomposition of the surfactant. Me$_2$NCH$_2^+$ and C$_{16}$H$_{33}$NMe$_2^+$ were the major decomposition products. Water and fragments of the surfactant, distinguished by a progression of CH$_2$ losses, were observed. Notably, there was no evidence for S-containing compounds such as H$_2$S, HSMe, and Me$_2$S. This is in stark contrast to TMA$_2$MGe$_4$S$_{10}$ frameworks that undergo decomposition via methyl transfer to S followed by elimination of Me$_2$S and NMe$_3$. Thus, the decomposition of the mesostructured frameworks occurs through a different mechanism than in the microstructured GS-3 materials.

The distinction may be traced to the existence of coordinatively unsaturated sites around the transition metal that connect [Ge$_4$S$_{10}$]$^{1+}$ building blocks in the mesostructure.
These metal sites may facilitate fragmentation reactions of the surfactant that are not possible in the microstructured framework, where the tetrahedrally coordinated metal sites are spatially more congested.

Figure 9. (a) TGA traces of the mesostructured metal germanium sulfides. (b) TGA (solid) and DTGA (dash-dot) traces for CTA-Ni/Ge₄S₁₀.
Mesostructured CTA-Cu/Ge$_4$S$_{10}$ was examined by high-temperature PXRD under vacuum. Diffraction of the region 1-10 ° 2θ was monitored at 100, 150, and 200 °C, then every 20 °C from 200-400 °C. The PXRD patterns obtained are illustrated in Figure 10. Initially, three peaks were observed, with the most intense d$_{100}$ peak observed at d = 33.2 Å. As the sample was heated, the material expanded slightly to d$_{100}$ = 33.6 Å at 200 °C. The order of the mesostructure was maintained as the full width at half-maximum (FWHM) of the d$_{100}$ reflection (0.41° 2θ) was constant up to this temperature. Then, the material underwent a dramatic structural change between 200 °C and 400 °C. The 100, 110, and 200 reflections decreased in intensity, with the latter two completely absent after ca. 240 °C. The FWHM of the d$_{100}$ peak tended to increase from 200 - 400 °C, ending with a value of 1.1° 2θ.

![Figure 10](image_url)

**Figure 10.** High-temperature PXRD patterns of CTA-Cu/Ge$_4$S$_{10}$ under vacuum. The temperatures at which the spectra were obtained are indicated.
As the mesostructural organization of the CTA-Cu/Ge$_4$S$_{10}$ was lost, the material underwent a large contraction and the $d_{100}$ decreased by a third between 200 °C and 400 °C. Figure 11 shows a graph of $d_{100}$ versus temperature and FWHM of the 100 reflection versus temperature. The contraction correlates well with the loss of surfactant observed by TGA. Also, as indicated in Figure 11, there is a one-to-one correspondence between the decrease in the pore size (proportional to $d_{100}$) and the increase in FWHM. Clearly, loss of surfactant from the material results in contraction, and ultimately collapse, of the mesostructured metal germanium sulfides.

**Figure 11.** Graph of (i) $d_{100}$ versus temperature and (ii) FWHM of the 100 reflection versus temperature for CTA-Cu/Ge$_4$S$_{10}$. The material shows a concomitant contraction and loss of order above 200 °C.
3.5 Discussion

The absence of well-characterized non-oxide mesostructures in the literature inspired us to create a sulfide material like mesostructured silica, MCM-41. During our initial attempts to prepare mesostructured metal germanium sulfides, we encountered a solubility difficulty that prevented the synthesis of the materials in water, the conventional route to MCM-41 materials. We chose formamide as a solvent because it readily dissolved all of the starting materials and phase diagrams of surfactants in formamide resemble those in water.38

The data presented indicates a strong resemblance between the mesostructure observed in the meso-M/Ge₄S₁₀ materials and in MCM-41. The mesostructured inorganic-organic composites obtained show a high degree of order as manifested in the hexagonal symmetry of the PXRD patterns and TEM images of the materials. All of the samples visualized displayed hexagonal order extending over whole particles. Worm-like morphologies analogous to those observed in mesoporous silica were imaged in the metal germanium sulfides. Moreover, the channels were shown to run parallel to the longitudinal axis of the worm. This implies that a similar micelle templated growth process determines the form of these mesostructures.

Thermogravimetric analysis, IR, and Raman spectroscopy of the materials indicated that they contained a similar amount of surfactant to MCM-41. From the contrast in the TEM images, the surfactants are surrounded by the inorganic matrix.

The solid-state ¹³C CP-MAS NMR of the samples prepared with CTA and CPM showed very sharp peaks. All of the peaks associated with the surfactant headgroup were
observed as well as the aliphatic hydrocarbon chain. The absence of a peak associated with a carbonyl group indicated that virtually no formamide was present in the mesostructured metal germanium sulfides. This was also consistent with IR and Raman studies.

While the mesostructure of the metal germanium sulfides resembles MCM-41, the microstructure of the materials are very similar to those present in the microcrystalline GS-3 frameworks. Elemental analysis confirmed that the materials possessed a Ge:S ratio that is consistent with intact [Ge₄S₁₀]⁺ clusters. From the analyses, the materials appeared to possess a formula that was close to (CTA)₂M₂Ge₄S₁₀ (M = Zn²⁺, Co⁺², Ni⁺², Cu₂⁺). We speculate that this stoichiometry could arise from the structure of the liquid crystalline assembly. For example, there may be two CTA molecules interacting closely with a single adamantanoid cluster, although we have no direct evidence for this. The remainder of the charge on the materials may be accounted for from the presence of anions such as hydroxyl groups or sulfate coordinated to the metals.

Raman spectra for the meso-Zn/Ge₄S₁₀ frameworks indicated that the [Ge₄S₁₀]⁺ clusters are present in similar environments to those in the microcrystalline GS-3 frameworks. Thus, the framework contains metal to sulfur bonds linking the clusters together. The breadth of the vGe-S and vZn-S modes indicate that there is a distribution of environments present. IR spectroscopy confirmed that anions and water were present which, if coordinated to the metal sites as defects in the place of sulfide ligands, would be expected to generate a distribution of metal sites. Anions such as sulfate and hydroxyl groups could balance the charge on the framework.
From the reflectance optical spectroscopy of the materials, it is clear that Zn$^{2+}$ and Co$^{2+}$ are in similar microenvironments to those observed in the GS-3 frameworks (distorted tetrahedral, $S_4$ site symmetry). The breadth of the absorption peaks in the CTA-Co/Ge$_4$S$_{10}$ spectrum is consistent with a distribution of microenvironments that might arise if solvent or anions were coordinated to the metals. The fact that the CTA-Co/Ge$_4$S$_{10}$ material changes colour from blue to green upon washing with water is consistent with the presence of coordinated solvent.

It is very interesting that Ni(II) forms a mesostructured metal germanium sulfide, and that it appears to be the best ordered. To date, Ni$^{2+}$ has been noticeably absent from the list of GS-3 compositions. In spite of several efforts in our group to form the microstructured Ni/[Ge$_4$S$_{10}$]$^+$ material, we have been unsuccessful. The reflectance spectrum of meso-Ni/Ge$_4$S$_{10}$ samples indicated that the Ni was not present in a tetrahedral environment. The data suggest that the metal is more likely present with a square planar geometry, possibly with water coordinated as well. The resistance of Ni(II) to exhibit tetrahedral coordination in the presence of [Ge$_4$S$_{10}$]$^+$ clusters may be the reason it will not form the microstructured GS-3 framework.

None of the powder X-ray diffraction patterns of the mesostructured materials showed any other crystalline products (e.g. surfactant, GeS$_2$, GS-3 frameworks). When the syntheses were done in the absence of surfactant, crystalline microstructured GS-3 materials were obtained for Fe$^{2+}$, but no product formed for Zn$^{2+}$. This is in contrast to the same reaction in water, where TMA$_2$ZnGe$_4$S$_{10}$ frameworks precipitate instantly from solution.
The presence of the transition metal is essential for formation of the products. If no transition metal was added, the solution remained clear and colourless at 80 °C for months. It is interesting that no product was obtained when manganese (II) acetate was added to the liquid crystalline assembly, although this was the first transition metal complex used in the preparation of the microstructured metal germanium sulfides. Kinetics of ligand displacement may be unfavourable in formamide, but this is only speculation. Attempts to form the mesostructured metal germanium sulfide framework with titanium, iron, and silver have also been unsuccessful thus far.

When TMA₄Ge₄S₁₀ is combined with CuCl in water, a microstructured metal germanium sulfide is obtained that contains [Ge₄S₁₀]⁺⁺ clusters linked by [Cu₂]²⁻ dimers as determined by a Rietveld structure solution. It is therefore reasonable that mesostructured CTA-Cu/Ge₄S₁₀ could also possess a Cu-Cu bond. The elemental analysis of a CTA-Cu/Ge₄S₁₀ sample indicated that it contained approximately twice as much metal per [Ge₄S₁₀]⁺⁺ cluster as the Zn and Co analogues although substantially less Cu was used in the preparation. The mesostructured material is similar in colour to the microstructured material, yellow-green. Mesostructured CTA-Cu/Ge₄S₁₀ showed no absorptions in the visible region, but an intense absorption in the UV at 361 nm. This corresponds well with the absorption edge observed in the microstructured TMA₂Cu₂Ge₄S₁₀ framework, ca. 360 cm⁻¹. This transition has been previously assigned to a ligand-to-metal charge transfer band.

In the near-IR spectrum of CTA-Cu/Ge₄S₁₀, an intense band was observed that may be due to an intervalence charge transfer band for Cu(I)-Cu(II) dimers. Bands in this region have been observed for other systems.
A Cu-edge EXAFS experiment was performed on each of meso-Cu/Ge₄S₁₀ and microstructured TMA₂Cu₂Ge₄S₁₀. Preliminary results suggest that both of the materials have very similar Cu environments. However, it has not yet been possible to fit the data to a suitable model. We have provided compelling, though indirect, evidence that CTA-Cu/Ge₄S₁₀ contains a metal-metal bond in the mesostructured framework.

Like MCM-41, the mesostructured M/Ge₄S₁₀ materials may be prepared with a variety of surfactants. It should prove possible to modify the optical, electronic, and adsorptive properties of the materials by varying the surfactant (e.g. using metal-containing surfactants). Variation of surfactants can also be used to control the size of the pores in the resulting material. Preliminary experiments with mesitylene showed no pore expansion.

Our data suggests that the mesostructure of the meso-M/Ge₄S₁₀ materials is very similar to that of MCM-41 while the microstructure is similar to that of microcrystalline TMA₂MGGe₄S₁₀ frameworks. We feel justified to explain the formation of the mesostructured metal germanium sulfides by a liquid crystal templating mechanism that is analogous to the mechanism proposed for the formation of MCM-41.¹³ First, TMA₄Ge₄S₁₀ and CTABr in formamide at 80 °C form a lyotropic inorganic liquid crystalline phase. In this liquid crystal, the hydrophobic chains of the surfactant are aggregated into cylindrical or micellar species with the TMA⁺, [Ge₄S₁₀]²⁺, and Br⁻ in the solvent around the headgroups. As transition metals (Co⁺², Cu⁺, Zn⁺², Ni⁺²) are added, they are rapidly coordinated by the tetradentate [Ge₄S₁₀]⁺⁺ clusters. “freezing” the M/Ge₄S₁₀ framework around the surfactant and immediately precipitating from solution. Figure 12 is a model of the proposed framework in which transition metals are linked to
the adamantanoid $[\text{Ge}_4\text{S}_{10}]^{1-}$ clusters around a lyotropic liquid crystalline phase in formamide.

Figure 12. Idealized 2-D model of a mesostructured metal germanium sulfide showing the cluster-linked framework templated around the surfactant.

The thermal properties of the materials are worthy of further discussion. Pyrolysis mass spectrometry of the materials indicated that only surfactant fragments and water were present in the decomposition. In contrast to the microstructured analogues, we think that the collapse of the mesostructure occurs by a physical transformation rather than a chemical one. Initially, the material exists as a sheet of metal germanium sulfide
"wrapped around" the surfactant. During thermal treatment, the surfactant undergoes fragmentation beginning at \textit{ca.} 200 °C. The loss of surfactant from the pores makes room for the inorganic sheets to buckle and occupy the space that is created. Whereas the silica walls of MCM-41 are able to undergo condensation-polymerization of residual hydroxyls, heal, and reconstruct to thicken and maintain the integrity of the material, the metal germanium sulfide sheets can only fold. This is illustrated in Scheme 1. There are two consequences of this "crumpling" mechanism that are expected from powder X-ray diffraction: the $d_{100}$ peak will shift to lower values; and the $d_{100}$ peak will broaden (the crystallinity of the material will seem to be lost). These were both observed during the high temperature PXRD experiment. Yet, the overall order of the material could be maintained and it is conceivable that the mesostructure could be re-inflated in an appropriate medium with added surfactant.

![Scheme 1](image-url)
3.6 Conclusions

We have discovered a new class of non-oxide mesostructured materials with hexagonal symmetry. The supramolecular assembly of adamantanoid \([\text{Ge}_4\text{S}_{10}]^+\) clusters in the presence of transition metals is a new approach to developing materials with mesostructural and hierarchical order. It should be possible to extend this paradigm to other transition metals and clusters to form an assortment of interesting materials.

The supramolecular organization of the materials is very similar to that of MCM-41. PXRD and TEM confirmed that the materials possess hexagonal symmetry. By varying the length of the aliphatic hydrocarbon chain, the pore size of the materials can be controlled.

At the molecular level, the meso-M/\text{Ge}_4\text{S}_{10} materials strongly resemble the metal-linked germanium sulfide cluster environments present in the microstructured GS-3 materials. Characterization by IR, UV-vis/near-IR, TGA, Raman, and elemental analysis characterized the molecular composition and microstructure of the materials. Indeed, transition metals are linked to the \([\text{Ge}_4\text{S}_{10}]^+\) clusters in the final material. In the cases of \(M = \text{Zn}^{2+}\) and \(\text{Co}^{2+}\), the meso-M/\text{Ge}_4\text{S}_{10} materials contain tetrahedral metal sites coordinated to the \([\text{Ge}_4\text{S}_{10}]^+\) clusters. When \(M = \text{Ni}^{2+}\), however, evidence suggests that the metal is in either a distorted octahedral or square planar geometry, but not tetrahedral. In the case of \(M = \text{Cu}^+\), an intense near-IR absorption may indicate the presence of a mixed-valence Cu(I)-Cu(II) dimer in the material. EXAFS spectroscopy indicated that the Cu environment of the material is very similar to the microstructured TMA_2\text{Cu}_2\text{Ge}_4\text{S}_{10}, which contains a metal-metal bond.
The thermal stability of mesostructured CTA-Cu/Ge₃S₁₀ was investigated. It is thermally stable to 200 °C and retains a high degree of order to nearly 400 °C. A thermal transformation, where the framework undergoes a physical collapse rather than a chemical decomposition, is proposed.

There are a number of investigations of these materials that would be worthwhile. Conductivity measurements, investigation of adsorption properties, magnetic measurements, and chemistry in the channels would be fascinating. Materials of this genre may be useful for cleaning up heavy metal spills and for use in chemical sensors.

3.7 References


CHAPTER 4

Chemistry of the Spirocyclic [1]Ferrocenophanes

4.1 The Spirocyclic [1]Ferrocenophanes

In 1975, Osborne and Whiteley reported the first [1]ferrocenophanes, fcSiPh$_2$ and fc$_2$Si (fc = (η-C$_5$H$_4$)$_2$Fe), compounds that were previously predicted to be too strained to exist.$^{1,2}$ The spirocyclic ferrocenophane fc$_2$Si (3) was only isolated in 7% yield, though in a paper that followed in 1980, the same authors had increased the yield to 17% and characterized the ferrocenophane by several spectroscopic techniques.$^3$ However, they were unable to obtain a crystal structure of 3 due to disorder$^4$ and, unlike fcSiPh$_2$, which has appeared in the literature several times since 1980, the spirocyclic ferrocenophane lay to rest for 15 years...

Prior to 1992, the chemistry and polymerization behaviour of [1]silaferrocenophanes was virtually unexplored.$^5$ It was then that we reported the synthesis of high molecular weight poly(ferrocenyilsilanes) (e.g. 1 $\rightarrow$ 2, Scheme 1) from the ring-opening polymerization (ROP) of [1]silaferrocenophanes.$^6$ Others and we have been exploring this new class of polymers that gives materials with interesting physical and chemical properties.$^8$
In 1996, we reinvestigated the spirocyclic \([1]\text{ferrocenophane fc}_2\text{Si}(3)\) and found that it could be used to crosslink poly(ferrocenylsilanes), giving swellable organometallic gels.\(^\text{10}\) We also reported that the spirocyclic \([1]\text{silaferrocenophane fcSi(CH}_2)_3\) (16) can be used as a crosslinking agent (Scheme 2).\(^\text{10}\) Figure 1 shows a photograph of a crosslinked, swellable gel.

**Figure 1.** Crosslinked swollen poly(ferrocenylsilane) gel (in THF).
Since that time, we have developed an area of chemistry based on the spirocyclic [1]silaferrocenophanes 3 and 16, including new chloroferrocenylsilanes, silanols, siloxanes, shape retaining ceramics, transparent thermosetting organometallic glasses, and Si cations (Schemes 3 and 4). I would like to summarize the chemistry I have helped to develop, first discussing the areas that have been derived from 3, then from 16.
Scheme 3

1. \(2 \text{HCl}\)

2. \(\text{H}_2\text{O} \text{NOM}_{3}\)

3. \(\text{NaOH} \text{EtOH reflux, 2.5 h}\)

4. \(\text{Li}_2\text{TEMEDA}\)

5. \(60^\circ\text{C} / 10 \text{min}\)

6. \(\text{HOTf}\)

7. \(\text{Cp}_2\text{Zr(NOMe)_2}\)

8. \(200^\circ\text{C}\)

9. \(\text{C}_4\text{H}_3\text{N}\)
Scheme 4

Shaped Fe-Si-C Ceramic

17

600-1000 °C

HCl

18

H₂O / NEt₃

19

280 °C

20

300 °C

21

22
4.2 Silanols, Siloxanes, Cations, and Other Ferrocenophanes

For the spirocyclic [1]silaferrrocenophane 3 to be useful as a precursor, it was first necessary to improve the yield. By modifying the work-up procedure, 3 could be isolated in 80% yield, a significant improvement from the original report.\textsuperscript{11} Surprisingly, although the ferrocenophane possesses two highly strained rings, the red crystals are air and moisture stable for years. Compound 3 was fully characterized and, notably, is a textbook case for “accidental magnetic equivalence” in \(^1\)H NMR spectroscopy. Although the [1]ferrocenophane displays the expected two pseudo-triplet signals for the Cp ligands in CDCl\(_3\), only a singlet is observed by \(^1\)H NMR in C\(_6\)D\(_6\) (the \(^{13}\)C NMR spectrum shows 3 peaks in both solvents, indicating that the carbons were in different magnetic environments). A single-crystal structure of 3 (Figure 2) revealed that it has \(C_{2v}\) symmetry and contains two strained, ring-tilted ferrocenophane rings.\textsuperscript{11} Cyclic voltammetry of 3 indicated that the compound undergoes two irreversible oxidation steps (\(\Delta E_{ox} = 0.37\) V), indicating the presence of substantial Fe---Fe interaction.\textsuperscript{11}
Figure 2. Single crystal X-ray structure of spirocyclic [1]ferrocenophane 3 (thermal ellipsoids are drawn at the 50% probability level).

With the spirocyclic [1]ferrocenophanes, we developed a reaction that appears of general utility to many other [1]ferrocenophanes.\textsuperscript{12} When spirocyclic [1]ferrocenophane 3 was treated with 2 eq of HCl, ring-opening addition of HCl to both ferrocenophane rings occurred to yield large crystals of Fc\textsubscript{2}SiCl\textsubscript{2} (4, Fc = (\eta\textsubscript{5}-C\textsubscript{5}H\textsubscript{4})Fe(\eta\textsubscript{5}-C\textsubscript{5}H\textsubscript{5})) in 88% yield. This is an improved, selective route to 4 over the previous method, which yielded 8% after fractional sublimation.\textsuperscript{13} Acid addition to [1]ferrocenophanes also has the advantage of producing virtually no byproducts. In the past, the synthesis of chloroferrocenylsilanes has been plagued by the difficulty of preparing FcLi and by obtaining a mixture of moisture sensitive byproducts Fc\textsubscript{x}SiCl\textsubscript{4-x}. With the discovery of a convenient synthesis of 4, we explored some chemistry of this molecule.
Hydrolysis of 4 in the presence of base afforded the air-stable silanediol Fe₂Si(OH)₂ (5) in 90% yield.¹² Silanediol 5 crystallizes in a bead and chain motif, a new pattern for silanediols (Figure 3). As a consequence of the bulky Fc substituents, this silanediol is remarkably stable, melting at 160 °C. Base-catalyzed condensation of 5 yielded [Fe₂SiO]₃ (6) in 74% yield.¹⁴ Differential pulse voltammetry measurements of 6 revealed metal-metal interactions between ferrocenyl substituents on adjacent Si atoms, the first evidence of ferrocene coupling across a siloxane bridge. A single crystal study of 5 indicated that the Si₃O₃ ring is essentially planar (Figure 4).¹⁴

Figure 3. The hydrogen-bonding motif present in silanediol 5. Ferrocenyl substituents have been omitted for clarity.
Figure 4. Single crystal structure of [Fc$_2$SiO]$_3$ (6) with thermal ellipsoids drawn at the 30% probability level.

At lower temperatures, 5 undergoes incomplete condensation and an intermediate in the synthesis of 6. [Fc$_2$SiOH]$_2$O (7), could be isolated in 78% yield (Figure 5). Disiloxanediol 7 crystallizes in a unique hydrogen-bonded double-chain motif. When 7 was crystallized from CH$_2$Cl$_2$/hexanes in the presence of 6, a cocrystallization of 6, 7, and solvent was observed. Of particular interest, the disiloxanediol 7 assembles into a helix with CH$_2$Cl$_2$ bridges in the cocrystal as illustrated in Figure 6.
Figure 5. Single crystal structure of disiloxanediol 7 with thermal ellipsoids drawn at the 30% probability level.
Figure 6. The helical hydrogen-bonding assembly of disiloxanediol 7 in the crystal structure (Fc groups have been removed for clarity). Legend: black, Si and O; purple, Cl; green, C.
We have also used disiloxandiol 7 to develop a series of novel borato- and zirconacyclosiloxanes with Fc substituents, 8. Figure 7 shows the crystal structure of one of the boratocyclosiloxanes. Initial experiments show that the heterosiloxanes 8, like 6, are resistant to anionic or cationic initiators for ring-opening polymerization (ROP). Compounds of this type are fundamentally interesting, and with appropriate substituents may also be useful as olefin polymerization catalysts.

**Figure 7.** Single crystal structure of [(PhBO)(Fc₂SiO)]₂ with thermal ellipsoids drawn at the 50% probability level.
Figure 8. The Mössbauer spectrum of 9 shows quadrupolar doublets for each of the two Fe environments in fcSiFcz. The data points and fit are shown on the bottom, the deconvoluted spectrum on the top.

Treatment of 4 with fcLi2 gave a ferrocenophane with two ferrocenyl substituents, fcSiFcz (9). Mössbauer spectroscopy of 9 (Figure 8) distinguished the two Fe environments and indicated that they have very similar recoil free fractions. A single crystal X-ray diffraction study of 9 showed that it possesses a highly strained, ring-tilted ferrocenophane that crystallizes in planes (Figure 9). When heated in the solid state at 200 °C, 9 underwent ring-opening to form cyclic oligomers, 10. The formation of cyclic oligomers probably results from the bulkiness of the Fc substituents on Si. This is the first observation of cyclic oligomers from the thermal ROP of a [1]silaferrocenophane...
and is relevant to mechanistic studies. When 9 was heated with ferrocenophane 1, copolymers 11 formed (not shown in Scheme 3).\textsuperscript{16}

\textbf{Figure 9.} Projection of [001] plane of 9 showing the arrangement of 9 in its crystal structure.

With a new [1]ferrocenophane possessing bulky Fc groups, we explored the chemistry of this species. HCl addition to 9 gave the novel compound Fc\textsubscript{3}SiCl (12).\textsuperscript{16} Hydrolysis of 12 afforded Fc\textsubscript{3}SiOH (13), which crystallizes as hydrogen-bonded dimers as a result of the bulky substituents (Figure 10).\textsuperscript{16} Addition of HOTf (OTf = triflate) to 9 yielded Fc\textsubscript{3}SiOTf (14), which possesses a strong Si\textsuperscript{+}…OTf interaction in the solid state.\textsuperscript{17}
Reaction of 9 with HBF₄ gave ferrocenyfluorosilanes, indicating that a highly electrophilic intermediate formed that was able to extract F⁻ from BF₄⁻.¹⁷ When an acid with a non-coordinating anion (e.g. tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, TBTPB) was utilized, solvated silicon cations could be isolated.¹⁸ For example, Figure 11 shows a pyridine adduct of Fc₃Si⁺, 15.¹⁸ We hope that the electron-rich Fe atoms and bulky Fc substituents may stabilize a cationic Si.
Figure 10. Single crystal structure of Fe$_3$SiOH (13) shows that it crystallizes in hydrogen-bonded dimers (thermal ellipsoids are drawn at the 50% probability level).
Figure 11. Single crystal structure of $[\text{Fc}_3\text{Si}(\text{pyridine})]^+\text{[TBTPB]}^-$ (15) with thermal ellipsoids drawn at the 50% probability level.
4.3 Ferrocenyl Silacyclobutane Chemistry

Ferrocenophane 16 can be readily prepared from the reaction of $\text{FcLi}_2\cdot\text{TMEDA}$ with $\text{Cl}_2\text{Si(CH}_2\text{)}_3$.\textsuperscript{11} Differential scanning calorimetry indicated that 16 melts at 89 °C and then immediately polymerizes, forming the crosslinked network 17.\textsuperscript{19} This rigid polymer took the shape of the polymerization tube. Pyrolysis under $N_2$ affords lightweight superparamagnetic and ferromagnetic ceramics in 90% yield with shape retention (Figure 12).\textsuperscript{19} The composition of the final ceramic is controlled by the pyrolysis conditions.\textsuperscript{20} Figure 13 shows a TEM image of Fe nanoclusters in a ceramic film prepared from 17.\textsuperscript{19} We have observed the gradual growth of Fe, graphite, and $\text{Si}_3\text{N}_4$ when 16 is pyrolyzed under $N_2$ - the genesis of a ceramic.\textsuperscript{20} Magnetic measurements of the ceramics indicated that they contained superparamagnetic iron nanoclusters. Room-temperature hysteresis, characteristic of ferromagnetic iron particles, was only observed in ceramics prepared above 850 °C.

![Image]

Figure 12. Photograph of shaped ceramic obtained from polymer 12. The coin is included for size comparison.
Addition of HCl to the spirocyclic [1]ferrocenophane 16 yielded FeSi(CH$_2$)$_3$Cl (18) in 84% yield.$^{12}$ Surprisingly, the reaction is highly specific and opens only the ferrocenophane ring. Controlled hydrolysis of 18 afforded the disiloxane 19 with silacyclobutane groups (Figure 14).$^{21}$ Alternatively, reaction of 16 with fcLi$_2$-TMEDA yielded the trimer FeSi(CH$_2$)$_3$fcSi(CH$_2$)$_3$Fc (20).$^{21}$

Figure 13. TEM image of a ceramic film obtained from a film of network 12.
Figure 14. Single crystal structures of 19 (top) and 20 (bottom) reveal 2 strained silacyclobutane rings in each compound (thermal ellipsoids drawn at the 50% probability level).

Both 19 and 20 show distinct melting endotherms and ROP exotherms by DSC (Figure 15). When heated, 19 and 20 form hard, transparent, red solids (21, 22) in the shape of the container. The solids are very tough and do not readily break, even when
hit with a hammer. These organometallic thermosets represent a new class of glassy materials that may be useful as optical coatings or redox-active smart windows.

![Figure 15. Differential scanning calorimetry of [FeSi(CH2)3]2O shows a large difference between the melt endotherm and the polymerization exotherm.](image)

4.4 Future Directions and Summary

With the chloroferrocenylsilanes now readily available (we also reported a convenient synthesis of FeSiCl3), there is a variety of chemistry analogous to other chlorosilane chemistry that may be explored. For example, Wurtz coupling of compound 4 may yield redox-active polysilanes, cyclosilanes, or even a disilylene with bulky Fe substituents. Reduction of 12 may generate a disilane with a very long Si-Si bond due to
the bulky Fc substituents. There is also potential for forming interesting metal silylene complexes with Fc₂SiCl₂.

Further exploration of the magnetic ceramics obtained in 90% yield may be useful. Pyrolysis under different atmospheres (e.g. B₂H₆, Ar, NH₃) may give unique properties to the ceramics. We have observed formation of ceramic films in which monodisperse Fe nanoparticles were obtained upon pyrolysis, with retention of the film shape. A detailed investigation of the ceramic films would be exciting. As well, studies of the mechanical and physical properties of the ceramics would be useful.

Organometallic thermosets, such as 21 and 22, are new materials that are worthy of further study. Templating around a crystal colloid array of latex spheres could give glassy organometallic materials with order in the micrometre domain. Studies of the pyrolysis of the organometallic thermosets 21 and 22 may yield ceramics with shape retention and interesting magnetic properties. The ease of processing 21 and 22 into useful forms could permit the utility of these ceramics in applications such as magnetic shielding and magnetic recording media. Moreover, pyrolysis of thermosets templated by latex crystal colloid arrays could yield shaped ceramic materials with hierarchical structure – nanoparticles, macroporosity, and bulk shape.

Clearly, the spirocyclic [1]ferrocenophanes are useful precursors to a variety of chemistry and new materials. The ease of preparing these compounds on a large scale may make them of general practicality for the preparation of chloroferrocenylsilylanes. There appear to be a variety of exciting avenues to explore with these materials, the spirocyclic ferrocenophanes.
In this brief chapter, I have provided an overview of the component of my work involving the spirocyclic [1]ferrocenophanes. In the two chapters that follow, I will present two modules of this chemistry that I have selected to represent my work. The interested reader may consult the references listed in this chapter for more information on the other results.

4.5 References


(19) MacLachlan, M. J.; Ginzburg, M.; Coombs, N.; Raju, N. P.; Greedan, J. E.; Ozin, G. A.; Manners, I. Manuscript Submitted.


(21) MacLachlan, M. J.; Thieme, K.; Ozin, G. A.; Manners, I. Manuscript to be submitted.
CHAPTER 5


5.1 Abstract

The spirocyclic [1]ferrocenophanes \([\text{Fe(}\eta\text{-C}_5\text{H}_4\text{)}_2\text{E}]_2\text{E} (3, \text{E} = \text{Si}; 4, \text{E} = \text{Ge})\) and \(\text{Fe(}\eta\text{-C}_5\text{H}_4\text{)}_2\text{Si(CH}_2\text{)}_3\) (5) have been prepared by the reaction of \(\text{Fe(}\eta\text{-C}_5\text{H}_4\text{Li})_2\text{-TMEDA}\) (TMEDA = tetramethylmethylenediamine) with SiCl\(_4\), GeCl\(_4\), and Cl\(_2\)Si(CH\(_2\))\(_3\), respectively. Single crystal X-ray diffraction studies of 3 - 5 revealed that the molecules possess highly strained structures with tilt-angles between the planes of the cyclopentadienyl rings of 19.4(2)°, 19.1(5)°, and 20.61(8)°, respectively. The Fe---Fe distances in 3 and 4 are 5.314(1) Å and 5.518(4) Å and evidence for metal-metal interactions in the form of substantial redox coupling (\(\Delta E_{1/2} = 0.37 \text{ V for 3 and 0.25 V for 4}\) is present in the cyclic voltammograms of these species. For structural comparison, tetraferrocenylsilane \([(\eta\text{-C}_5\text{H}_5)\text{Fe(}\eta\text{-C}_5\text{H}_4)]_4\text{Si}\) (6) was prepared and was characterized by single crystal X-ray diffraction. Cyclic voltammetry of 6 showed four reversible oxidation waves with \(E_{1/2}\) values of -0.03 V to +0.39 V versus ferrocene; \(\Delta E_{1/2}\) values of 0.10 - 0.18 V were indicative of significant metal-metal interactions. The results of Mössbauer, IR, and Raman studies of compounds 3, 4, and 6 are also discussed.
5.2 Introduction

The incorporation of transition metals into polymer backbones has been shown to generate materials with unusual physical and chemical properties.\textsuperscript{1,2} In this regard, ferrocene represents an appealing structural unit to include in a polymer main chain, but until recently, reports of high molecular weight poly(metalloccenes) have been very rare.\textsuperscript{3-5} We have previously shown that strained silicon-bridged [1]ferrocenophanes such as 1a undergo thermal ring-opening polymerization (ROP) to afford high molecular weight poly(ferrocenylsilanes) (e.g. 2a).\textsuperscript{5} Recently, anionic and transition metal catalyzed ring-opening polymerization have also been established as facile routes to these materials.\textsuperscript{6} Ring-opened poly(metalloccenes) are now known with a variety of bridging elements (for example, Ge as in 2b), and studies have shown that these materials possess intriguing physical properties.\textsuperscript{2,7-9} As crosslinking of poly(ferrocenes) is essential for many applications (e.g. for the formation of redox-active gels\textsuperscript{10}), we targeted a convenient method of crosslinking materials such as 2a which would be expected to lead to enhanced mechanical properties, thermal stability, and ceramic yields.

![Diagram of polymerization process]

\begin{align*}
1a & (E = \text{Si}) \\
1b & (E = \text{Ge}) \\
2a & (E = \text{Si}) \\
2b & (E = \text{Ge})
\end{align*}
We identified the spirocyclic [1]ferrocenophanes 3 and 4 as possible crosslinking agents for poly(ferrocenes) 2a and 2b, respectively. In addition, as silacyclobutanes are also known to undergo thermal and transition metal catalyzed ROP, the novel spirocyclic [1]silaferrocenophane 5 incorporating a silacyclobutane group was also expected to function as a crosslinking agent. It is noteworthy that compounds such as 3 - 5 also function as volatile precursors to novel composite materials. In this paper, we report full details on the synthesis, characterization, and properties of all three potential crosslinking agents (3 - 5). We also describe the synthesis and properties of tetraferrocenylsilane 6 which provided useful comparative spectroscopic and structural data for 3. Details of the polymerization behaviour of 3 and 5 and the properties of the novel crosslinked poly(ferrocene) products, which were briefly described in a recent communication, will be discussed in detail elsewhere.
5.3 Results and Discussion


In 1975, Osborne and Whiteley reported the synthesis of 3, which was the first characterized spirocyclic [1]ferrocenophane. These researchers isolated 3 in very low yield (7%) from the reaction of two equivalents of dilithioferocene-TMEDA (FcLi₂·TMEDA) with tetrachlorosilane and the product was characterized by mass spectrometry, \(^1\)H NMR, and UV-vis spectroscopy. In 1980, the same group reported further spectroscopic studies (Mössbauer, \(^{13}\)C NMR) of the compound and a slight improvement in the yield (17%). Interestingly, they attempted to determine the X-ray crystal structure of 3, but reported that the crystals obtained were disordered and not suitable for X-ray diffraction studies. The synthesis of the spirocyclic [1]germaferrocenophane 4 was also reported by Osborne and coworkers via an analogous route from GeCl₄. This species was obtained in a low, unquantified yield and was characterized by mass spectrometry, NMR, and elemental analysis. The authors indicated that the isolation and purification of 4 were frustrated by decomposition in solution. Both compounds, 3 and 4, have subsequently been investigated for protective derivatization of photoelectrochemical n-doped Si substrates.

In our laboratory, 3 and 4 were synthesized using the same route as that described by Osborne and coworkers. However, the work-up procedure was modified to improve the product yields. Filtration through a short column of alumina allowed any chlorinated silane / germane species and salts to be removed. The products isolated after the filtration
were stable indefinitely in solution. The yield of 3 was improved significantly (70%), but the yield of 4 was still very low (<5%), probably due to a competition between Cp-Ge bond formation and anion-induced cleavage. Both 3 and 4 are air-stable, red, crystalline compounds. In order to allow additional comparison, we synthesized tetraferrocenylsilane 6 by the reaction of FcLi with SiCl₄ using a procedure analogous to that briefly described by Rosenberg in a patent.¹⁷

The spirocyclic species, 3 and 4, were characterized by ¹H, ¹³C, and ²⁹Si NMR, mass spectrometry, and IR, Raman, Mössbauer, and UV-vis spectroscopy. The ¹H NMR spectrum of 3 is interesting as it displays a pair of pseudo triplets in CDCl₃, as expected, but only a singlet in C₆D₆. When a sample of 3 in CDCl₃ was treated with a few drops of C₆D₆, the pseudo triplets remained, confirming, as expected, that an unusual exchange mechanism was not responsible for the magnetic equivalence of the protons. Since rotation of the Cp rings is impossible without ring-opening, there must be a fortuitous magnetic equivalence of the Cp protons in C₆D₆. This could be a consequence of unsymmetrical proton shielding from the solvent. Due to steric crowding of the molecule, the β protons are more accessible to solvent and may experience enhanced shielding from the aromatic ring of C₆D₆ relative to the α protons. Exact compensation for the greater shielding usually observed for the Cp α protons (closest to the Si atom) would therefore arise. In contrast to 3, the ¹H spectrum of the germanium analogue 4 is typical of a symmetric [1]ferrocenophane, with two pseudo triplets in both C₆D₆ and CDCl₃. Compounds 3 and 4 display ¹³C NMR spectra consistent with the assigned structures. The ¹³C NMR chemical shifts for the resonances assigned to the ipso carbon atoms for 3 and 4 were found at 31.1 ppm and 27.8 ppm, respectively. These resonances
show a dramatic high-field shift compared to those for unstrained species, which is characteristic of [1]ferrocenophanes.\(^1\) The \(^{29}\)Si NMR spectrum of 3 showed a single resonance at -16.6 ppm, upfield of diphenyl[1]silaferrrocenophane, Fe(η\(_1\)-C\(_5\)H\(_4\))\(_2\)SiPh\(_2\) (δ = -11.7 ppm). Interestingly, the \(^{29}\)Si resonance of tetraferrocenylsilane, 6, also lies downfield at -10.1 ppm (CD\(_2\)Cl\(_2\)). The additional shielding observed in 3 might be attributed to a weak dative Fe→Si interaction, and is consistent with the single crystal X-ray structure and Mössbauer data (vide supra). Both 3 and 4 have UV-vis absorptions between 480-490 nm typical of [1]ferrocenophanes. In contrast, 6 has \(\lambda_{\text{max}} = 452\) nm, similar to that for other unstrained ferrocene derivatives.

![Chemical Structures]

Spirocyclic metalloarenophanes bridged by silacyclobutane rings (7 and 8) were first synthesized by Elschenbroich in 1995.\(^1\) These mononuclear species were used as control compounds in the study of metal-metal interactions in dinuclear compounds bridged by disilacyclobutane moieties. Silacyclobutanes are known to undergo thermal or transition metal catalyzed ROP and their polymerization behaviour has recently been reviewed.\(^1\) We anticipated that incorporation of a ferrocenophane ring and a
silacyclobutane ring into the same molecule should afford a tetrafunctional monomer suitable as a crosslinking agent for poly(ferrocenes).

The reaction of Fe(η-C₅H₅Li)₂·TMEDA with an excess of Cl₂Si(CH₂)₃ afforded red, hygroscopic, air-sensitive needles of 5. Both the ¹H and ¹³C NMR chemical shifts were consistent with the assigned structure; the ¹³C resonance of the ipso carbon atoms was observed at 31.9 ppm. The ²⁹Si NMR spectrum showed one singlet, at 3.6 ppm; this is shifted upfield from the resonance at 18.3 ppm observed in dichlorosilacyclobutane and downfield from the resonance at -4.6 ppm for 1a. The UV-vis spectrum of 5 shows a peak at 482 nm with a weak shoulder at shorter wavelength. In addition, the mass spectra of 3 - 6 were all consistent with their structures, giving the molecular ion as the dominant peak.


As no previous crystallographic data for spirocyclic [1]ferrocenophanes had been reported, single crystal X-ray diffraction studies of 3 and 4 were undertaken. Orange-red prisms of 3 suitable for X-ray diffraction were grown at -55 °C from a solution of the compound in CH₂Cl₂ and hexanes (ca. 1:1). Red crystals of 4 were obtained by slow evaporation from a solution of 4 in C₆D₆ inside a glovebox. Figures 1 and 2 show views of the molecular structures of 3 and 4, respectively. A summary of cell contents and data collection parameters is included in Table 1, and selected bond lengths and bond angles are listed in Tables 2 and 3. A summary of important structural features for 3 and 4 is presented in Table 4.

<table>
<thead>
<tr>
<th></th>
<th>1a</th>
<th>3</th>
<th>5</th>
<th>1b</th>
<th>4</th>
</tr>
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<td>Fe-E dist, Å</td>
<td>2.690(3)</td>
<td>2.6572(5)</td>
<td>2.7113(5)</td>
<td>2.804(2)</td>
<td>2.759(2)</td>
</tr>
<tr>
<td>Σ(rFe + rE)Å</td>
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<td>2.41</td>
<td>2.41</td>
<td>2.47</td>
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</tr>
<tr>
<td>Fe displacement, Å</td>
<td>0.216(1)</td>
<td>0.210(3)</td>
<td>0.222(2)</td>
<td>0.221(9)</td>
<td>0.214(9)</td>
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<td>19.4(2)</td>
<td>20.61(8)</td>
<td>19.0(9)</td>
<td>19.1(5)</td>
</tr>
<tr>
<td>β, deg</td>
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<td>39.5(1)</td>
<td>37.4(1)</td>
<td>36.8(5)</td>
<td>37.5(5)</td>
</tr>
<tr>
<td>Cl-E-C6, θ, deg</td>
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<td>98.5(1)</td>
<td>95.83(6)</td>
<td>91.7(3)</td>
<td>94.7(4)</td>
</tr>
<tr>
<td>Cp-Fe-Cp, δ, deg</td>
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<td>165.3(2)</td>
<td>164.4(1)</td>
<td>165.3(5)</td>
<td>165.1(4)</td>
</tr>
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<td>20</td>
<td>this work</td>
<td>this work</td>
<td>21</td>
<td>this work</td>
</tr>
</tbody>
</table>

a Is the sum of the covalent radii of Fe and the bridging atom E.

b The displacement of the iron atom from the line joining the two centroids of the cyclopentadienyl rings.

c The average of the angle(s) between the planes of the cyclopentadienyl ligands and the C(Cp)-E bonds (where E = bridging atom).

Figure 1. Molecular structure of the spirocyclic [1]ferrocenophane 3 (thermal ellipsoids drawn at the 50% probability level).
Both 3 and 4 crystallize in the same space group (C2/c) and are isostructural. The Si and Ge atoms lie on special positions (on a 2-fold axis) in the unit cell, reflecting the C$_{2v}$ symmetry of the molecule. To accommodate the larger atomic size of Ge (covalent radius of 122 pm for Ge vs. 117 pm for Si), the unit cell of 4 is ca. 2% larger (by volume) than 3. Similarly, the Fe---Fe distance in 4 (5.518(4) Å) is greater than in 3 (5.314(1) Å). The Cp rings of both 3 and 4 are eclipsed (torsion angles of 1.1° and 0.8°, respectively) and are essentially planar; mean deviations of 0.002 and 0.005 Å from the plane containing C(1)-C(5) and 0.003 and 0.003 Å for the C(6)-C(10) plane are present in 3 and 4, respectively. The tilting of the planes of the cyclopentadienyl ligands with respect to one another in 3 ($\alpha = 19.4(2)^{\circ}$) is less than in 1a ($\alpha = 20.8(5)^{\circ}$) indicating that

Figure 2. Molecular structure of the spirocyclic [1]ferrocenophane 4 (thermal ellipsoids drawn at the 50% probability level).
introduction of a second ferrocenophane ring at silicon slightly reduces the ring-tilt observed. On the other hand, the ring-tilt of 4 (α = 19.1(5)°) is similar to the ring-tilts of 3 and 1b (α = 19.0(9)°), although the large estimated standard deviations of the angles for 1b and 4 make meaningful comparisons difficult. The Si-C_ipso bond lengths in 3 (1.871(3) Å and 1.874(3) Å) are similar to the bond lengths in 1a (1.858(9) Å) and tetraferrocenylsilane 6 (1.851(7) Å to 1.870(6) Å) (see below). Likewise, the Ge-C_ipso bond lengths in 4 (1.952(9) Å) are only slightly shorter than the same bond lengths in 1b (1.978(6) Å). The values of the angle β between the planes of the Cp ligands and the C_ipso-bridging atom bonds for 3 and 1a indicate that 3 possesses a larger distortion from planarity at the ipso carbon atom than does 1a (β = 39.5(1)° for 3, β = 37.0(6)° for 1a). For ferrocenophane 4, the β angle is 37.5(4)°, consistent with the value for 1b (β = 37.0(6)°). While the C-C-C angles in the Cp ring of ferrocene are 108°, there is a small distortion from a perfect pentagon in the Cp ring of 3 and 4. The C_ipso-E-C_ipso bond angles in 3 (98.5(1)°) and 4 (94.7(4)°) are significantly smaller than the ideal tetrahedral value (109.5°) consistent with the analogous angles in other [1]silaferrocenophanes and [1]germaferrocenophanes. However, these angles are larger than in 1a (95.7(4)°) and 1b (91.7(3)°), suggesting that the Si and Ge tetrahedral environments are less distorted in 3 and 4. It is probably the combination of near-tetrahedral geometry at the bridging atom and the steric hindrance imparted by four Cp rings that is responsible for the unusual air and moisture stability in these [1]ferrocenophanes.
5.3.3 X-Ray Structure of Tetraferrocenylsilane 6.

A search of the Cambridge Structural Database revealed that no other compounds containing a silicon atom attached to four Cp ligands have been characterized by X-ray crystallography. A structural investigation of tetraferrocenylsilane was undertaken to permit a comparison with the spirocyclic [1]silaferrocenophane 3. Crystals of 6 were obtained by slow evaporation of a solution of 6 in C₆D₆ under a nitrogen atmosphere. Figure 3 gives a view of the molecular structure of 6. The cell contents and data collection parameters are summarized in Table 1, and selected bond lengths and bond angles are listed in Table 5.

![Molecular structure of 6](image)

**Figure 3.** Molecular structure of 6 (thermal ellipsoids drawn at the 25% probability level).
Despite the apparent symmetry of 6, it crystallizes in the chiral, orthorhombic space group Pca2₁ where the molecule possesses no symmetry elements. The chirality of the structure was determined unambiguously by X-ray diffraction, as indicated by the small absolute structure factor. This rigid, chiral conformation is probably induced by the steric demands of the ferrocenyl substituents at Si. One can view the structure as a pinwheel of three ferrocenes with the fourth ferrocene attached above the plane. The Fe-Fe separation varies from 5.27 Å to 6.14 Å between the ferrocenes. Each of the Cp ligands is essentially planar, with very slight ring tilts of 0.7(5)°, 1.3(5)°, 2.4(5)°, and 3.6(6)° observed for the ferrocenyl substituents. Notably, values of the angle β between the planes of the Cp ligands and the C₉°-bridging atom bonds in 6 are 3.0(6)°, 4.3(6)°, 4.9(6)°, and 6.6(6)°. This small distortion from sp² hybridization of the ipso carbon atoms is likely also the result of steric crowding around Si.

5.3.4 The $^{57}$Fe Mössbauer Spectra of 3, 4, and 6.

Mössbauer spectra of ferrocene derivatives can provide valuable insight into the Fe environment. Studies of [1]ferrocenophanes have indicated a reduction in quadrupolar splitting relative to ferrocene (2.31 mm s⁻¹) while the isomer shift is similar (0.43 mm s⁻¹) (data relative to Fe powder). Silver has attributed the quadrupolar splitting shift to a weak iron-to-heteroatom interaction.²² Osborne et al. reported the Mössbauer spectroscopic data for 3 at 77 K; these workers measured an isomer shift δ of 0.51 mm s⁻¹ and a quadrupolar splitting value $\Delta E_q$ of 2.01 mm s⁻¹.¹⁴ At room temperature, we found the isomer shift value δ (relative to Fe powder) for 3 was 0.442(5) mm s⁻¹, while the quadrupolar splitting value $\Delta E_q$ was 2.013(5) mm s⁻¹. The corresponding values for 4
were $\delta = 0.454(5) \text{ mm s}^{-1}$ and $\Delta E_q = 2.090(5) \text{ mm s}^{-1}$. This postulate for a weak dative interaction between the Fe and the bridging atom$^{22}$ is consistent with the $^{29}$Si NMR data, where the $^{29}$Si resonance of 3 (-16.6 ppm) is upfield from that of 6 (-10.1 ppm). However, it was predicted that the quadrupolar splitting values for 3 and 4 might be significantly higher than other $^{[1]}$sila- and $^{[1]}$germaferrocenophanes, respectively, because the atom bridging the two ferrocenophanes would be unable to accommodate the same degree of electron density from the two Fe centers as in other $^{[1]}$ferrocenophanes. The observation that 3 and 4 have similar quadrupolar splitting values to other $^{[1]}$ferrocenophanes suggests that other factors, such as changes in bonding in the ferrocenophane due to ring-tilting and C(1) distortion, may be required to explain the quadrupolar splitting. As expected, the Mössbauer spectroscopic data for 6 are very similar to ferrocene, where the measured isomer shift value $\delta$ (relative to Fe powder) was 0.429(5) mm s$^{-1}$ and the quadrupolar splitting value, $\Delta E_q$, was 2.262(5) mm s$^{-1}$.

**5.3.5 X-Ray Structure of 5.**

Single crystals of 5 suitable for X-ray diffraction were obtained by solvent evaporation from the filtered reaction mixture. Figure 4 shows the molecular structure of 5. A summary of cell constants and data collection parameters is included in Table 1 and important bond lengths and angles are listed in Table 6. A summary of important structural features is presented in Table 4.
As in 3 and 4, the two cyclopentadienyl rings of 5 are virtually eclipsed and each is essentially planar with an observed mean deviation from the plane of 0.004 Å calculated by a weighted least-squares plane through the cyclopentadienyl ligand containing C(1)-C(5), with the same value for the cyclopentadienyl ligand containing C(6)-C(10). The Cp rings are tilted with respect to one another in 5 (α = 20.61(8)°) to a similar degree as in 1a (α = 20.8(5)°). The Si-C_{ipso} bond lengths in 5 (1.883(2) Å and 1.884(2) Å) are in accord with other [1]silaferrrocenophanes such as 1a. The value of the angle β between the planes of the Cp ligands and the C_{ipso}-Si bond for 5 (β = 37.4(1)°) indicates a large distortion from the linear sp^{2} hybridization at the C_{ipso} atom. The C_{ipso}-Si-C_{ipso} bond angle in 5 (95.83(6)°) is also significantly less than the tetrahedral value.
(109.5°) and agrees with the value for 1a (95.7(4)°). In 1a, a scissoring effect is observed, giving rise to a wider CMe-Si-CMe angle (114.8(6)°) than expected for a tetrahedral geometry. In 5, however, the C(11)-Si-C(13) angle (81.10(8)°) is constrained by the silacyclobutane ring. This leaves a large part of the Si atom exposed and may explain why 5 is very moisture sensitive. The Fe---Si distance in 5 (2.7113(5) Å) is only slightly longer than in 1a (2.690(3) Å), but is significantly longer than in 3 (2.6572(5) Å). There is possibly a weak interaction between the Fe and Si atoms in 5, just as has been proposed for other [1]silaferrocenophanes. The carbosilane ring in 5 is also clearly strained with skeletal C-Si-C and C-C-C bond angles significantly less than 109.5°. Interestingly, the silacyclobutane ring in 5 is puckered23 by only 20.6(2)° from planarity, significantly less than in bis(η⁶-benzene)vanadiumsilacyclobutane 7 (23°)18 and 4-sila-3,3-spiroheptane, (CH₂)₃Si(CH₂)₃ (30(2)° by electron diffraction²⁴).

5.3.6 Cyclic Voltammetry of 3 - 6.

Cyclic voltammetry (CV) of 5 showed a single, reversible oxidation with E₁/₂ = 0.11 V vs. ferrocene in CH₂Cl₂. This is typical of [1]silaferrocenophanes; for example, 1a exhibits a single reversible oxidation with E₁/₂ = 0.00 V with respect to the ferrocene/ferrocenium couple.25 CV of 3 showed two oxidations. The first, with E₁/₂ = 0.14 V, corresponds to the formation of the mixed valence Fe^{II}/Fe^{III} compound; this wave was reversible at all of the scan rates studied. Surprisingly, the second oxidation, corresponding to the formation of an Fe^{III}/Fe^{III} species, was irreversible. A large separation between the two oxidation waves, ΔEox = 0.37 V (scan rate 0.25 V s⁻¹), indicates a significant Fe---Fe interaction between the two ferrocenophane units.
\[
\text{CV of 4 also showed two oxidation waves (Figure 5). In this case, the first oxidation, at } E_{1/2} = 0.11 \text{ V, was reversible at all scan rates. The second oxidation at } E_{1/2} = 0.36 \text{ V was reversible for all scan rates faster than } ca. 0.25 \text{ V s}^{-1}. \text{ As expected, the } E_{1/2} \text{ separation, } \Delta E_{1/2}, \text{ was less for 4 (} \Delta E_{1/2} = 0.25 \text{ V) than 3 (} \Delta E_{\text{ox}} = 0.37 \text{ V), implying a larger Fe---Fe interaction for the Si bridged compared to Ge. Clearly, the large } \Delta E_{1/2}\]
values for 3 and 4 indicate a significant Fe---Fe interaction in these molecules (cf. $\Delta E_{1/2} = 0.34$ V in biferrocene$^{26}$ (CH$_2$Cl$_2$)).

Cyclic voltammetry of 6 in CH$_2$Cl$_2$ and THF provided poor resolution of the four oxidation waves. In benzonitrile, however, the four reversible oxidations were readily resolved. Figure 6 shows the cyclic voltammogram and differential pulse voltammogram of 6. The redox potentials (versus ferrocene) for each oxidation are listed in Table 7.

**Table 7.** Redox Potentials of 6 From Cyclic Voltammetry.

<table>
<thead>
<tr>
<th>Oxidation Wave</th>
<th>$E_{1/2}$ (V Versus Ferrocene)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 / [6]$^+$</td>
<td>-0.03</td>
</tr>
<tr>
<td>[6]$^{2+}$ / [6]$^{3+}$</td>
<td>+0.29</td>
</tr>
</tbody>
</table>

$^a$ In benzonitrile.

Recently, a number of papers have appeared reporting the preparation and electrochemical characterization of multiply-ferrocenyl-substituted complexes.$^{27}$ These studies are relevant in general to the question of how biological systems deliver several electron equivalents to redox sites.$^{27,28}$ It has been demonstrated, for example, that the four Fe centers in cytochrome C$_3$ undergo electron transfer at very similar potentials, the spread of the four Fe$^{II}$ / Fe$^{III}$ $E_{1/2}$ values being only 0.11 V.$^{29}$

In the present work on compound 6, the spread of the four potentials is 0.42 V, implying appreciable interactions between the ferrocenyl moieties as they are
successively oxidized. This fact stands in contrast to MeSi[(aryl)Cr(CO)₃]₃, in which the oxidations of the three Cr(CO)₃ groups occur at virtually the same potential, implying electronic isolation of the redox centers. The results for 6 are more in line with those of a multiferrocenyl analogue having boron as the bridging atom, namely Fc₄B, which was formulated as the zwitterion (ferrocenium)tris(ferrocenyl)borate. This complex showed four reversible one-electron oxidations with $E_{1/2}$ values (versus Ag/AgCl) of -0.18 V, -0.09 V, 0.29 V, and 0.41 V. The overall spread of 0.59 V is even larger than that measured for complex 6. It may be concluded that single bridging atoms of group 13 or group 14 both allow significant interactions between ferrocenyl substituents in their multiply-ferrocenyl-substituted complexes.

5.3.7 Vibrational Spectroscopy.

The vibrational spectroscopy of [1]ferrocenophanes has not been explored. A systematic vibrational analysis of [1]ferrocenophanes may reveal trends in vibrational frequencies as a function of ring-tilt, distortion from sp² hybridization at the Cᵦ atom, or other geometric properties. Furthermore, these techniques offer the possibility of examining structural dynamics in solution and gas phase. To corroborate the structures of the spirocyclic molecules 3 and 4, both IR and Raman spectra were obtained. Table 8 lists the IR absorption frequencies for compounds 3 and 4, along with tentative peak assignments. Table 9 presents the Raman peaks for compounds 3, 4, and 6 with their tentative assignments.
Figure 6. (a) Cyclic voltammogram of 0.31 mM 6 in benzonitrile at Pt disk electrode, scan rate 0.05 V s⁻¹; (b) Differential pulse voltammogram of 0.31 mM 6 in benzonitrile at Pt disk electrode, scan rate 2 mV s⁻¹, drop time 1 s.
Molecules of 3 and 4 both possess C$_2v$ symmetry and are identical except for the bridging atom. As expected, the Raman and IR spectra of both compounds are thus very similar. Though a normal coordinate analysis of the vibrational modes of these compounds, as well as in 6, is beyond the scope of this paper, many of the vibrations can be identified by comparison with other ferrocene derivatives in the literature.$^{32-34}$

The Raman spectra of 3 and 4 are very similar between 800 cm$^{-1}$ and 4000 cm$^{-1}$ (Figure 7, top). By comparison with the assignments of Raman active modes of ferrocene and some ferrocene derivatives, tentative peak assignments have been made. Surprisingly, all of the vibrations observed in ferrocene that are attributed to Cp vibrations could be readily assigned to peaks in the Raman spectra of 3 and 4. Three peaks near 3100 cm$^{-1}$ are due to C-H stretching modes of the Cp rings. Though there are only two C-C stretching modes observed near 1400 cm$^{-1}$ in ferrocene, we have assigned three peaks to C-C stretching in accord with Butler's assignments for ferrocene derivatives.$^{33}$ The C-C stretches in 3 (1349 cm$^{-1}$ and 1400 cm$^{-1}$) and 4 (1347 cm$^{-1}$ and 1401 cm$^{-1}$) are observed at lower frequency than in ferrocene (1356 cm$^{-1}$ and 1412 cm$^{-1}$).$^{32}$ Raman modes due to C-H deformations (in-plane and out-of-plane of the Cp rings) and ring distortions are consistent with the spectrum of ferrocene. All of the peaks between 800 cm$^{-1}$ and 4000 cm$^{-1}$ appear to be independent of the bridging element, indicating that they are due only to cyclopentadienyl modes.

Between 100 cm$^{-1}$ and 800 cm$^{-1}$, however, many of the Raman frequencies of 3 and 4 are significantly different suggesting that these peaks are coupled to the pseudo-tetrahedral bridging element (Figure 7, bottom). Indeed, Si-C and Ge-C stretching modes are expected in this spectral region. The mode near 390 cm$^{-1}$ has been assigned to the symmetric ring-tilt of the Cp rings. It is interesting that this mode is nearly unperturbed
from the same mode in ferrocene. This may reflect some torsional freedom along the Cp-E bond.

**Figure 7.** Raman spectra of (i) 3 and (ii) 4. For clarity, the spectra have been divided into two regions: 4000 - 800 cm\(^{-1}\) (top) and 800 - 100 cm\(^{-1}\) (bottom).
The most characteristic peak in the spectra of 3 and 4 is the symmetric ring-metal stretching mode near 300 cm\(^{-1}\). This frequency is strongly affected by the bridging element as the peak is observed about 40 cm\(^{-1}\) higher in 3 than in 4. The frequency of this mode has a strong dependence on the substituents of the Cp rings as exemplified by the difference between ferrocene (301 cm\(^{-1}\)), decamethylferrocene (169 cm\(^{-1}\)), and 1,1'-dichloroferrocene (344 cm\(^{-1}\)).

The Raman spectrum of 6 shows stretching vibrations due to the cyclopentadienyl rings that are consistent with other ferrocene derivatives. Moreover, the positions of the ring stretching and deformation modes are not significantly different from those observed for 3 and 4. The intense resonance at 316 cm\(^{-1}\) has been tentatively assigned to the Fe-Cp symmetric stretch after comparison with ferrocene and the spirocyclic [1]ferrocenophanes.
5.4 Summary

The strained, spirocyclic [1]ferrocenophanes 3 - 5 were synthesized and characterized by a variety of techniques. Single crystal X-ray diffraction studies revealed the presence of highly strained, ring-tilted structures. As the Fe centers in compounds 3 and 4 are in close proximity, significant metal-metal interactions were observed by cyclic voltammetry. Furthermore, Mössbauer studies of the spirocyclic [1]ferrocenophanes showed smaller quadrupolar splitting than for ferrocene. A possible interpretation of this is the presence of a metal - bridging atom interaction. Tetraferrocenylsilane 6 was prepared and structurally characterized for comparison with 3 and 4. This compound showed four reversible one electron oxidations by cyclic voltammetry which were also consistent with metal-metal interactions. The first vibrational analysis of [1]ferrocenophanes was reported and many vibrations of the ferrocenyl moiety could be assigned by analogy with the spectra of ferrocene. Detailed studies of the controlled crosslinking of poly(ferrocenes) by spirocyclic [1]ferrocenophanes will be reported elsewhere.\textsuperscript{12}
5.5 Experimental Section

5.5.1 Materials and Equipment.

Ferrocene. 1.6 M butyllithium in hexanes, silicon tetrachloride (semiconductor grade; 99.999%) and tetramethylethlenediamine (TMEDA) were purchased from Aldrich. Germanium tetrachloride (Strem) and cyclotrimethylenedichlorosilane (Gelest) were used as received. Dilithioferrocene-TMEDA and tributylferrocenylstannane (FcSn"Bu3) were synthesized as reported previously.35-37

All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Innovative Technologies) unless otherwise noted. Solvents were dried by standard methods, distilled, and stored under nitrogen. 400 MHz 1H NMR spectra and 100.5 MHz 13C NMR spectra were recorded on a Varian Unity 400 spectrometer. 79.5 MHz 29Si NMR spectra were recorded on a Varian Unity 400 spectrometer using either a normal (for 3 and 6) or a DEPT (for 5) pulse sequence and were referenced externally to TMS. Room temperature 57Fe Mössbauer spectra were obtained using a Ranger Scientific Inc. VT-1200 instrument with a MS-1200 digital channel analyzer. The gamma ray source was a 6 milliCurie 57Co sample supplied by Amersham. The data were collected in a -15.8 mm s⁻¹ to +15.8 mm s⁻¹ range and referenced to Fe powder. Data were acquired as long as necessary to obtain a suitable fit to standard independent Lorentzian line shapes for sinusoidal baselines. Cyclic voltammograms of 3 - 5 were obtained under N₂ by analysis of ca. 5 mM dichloromethane solutions (0.1 M [Bu₄N][PF₆] electrolyte) using an EG&G Princeton Applied Research Model 273 potentiostat with a Pt working electrode,
a W secondary electrode, and a Ag wire pseudo-reference electrode in a Luggin capillary. Cyclic voltammetry of 6 was performed at ambient conditions under N₂ by analysis of a 0.31 mM solution in benzonitrile using a PAR Model 173 potentiostat with a 250 µm diameter Pt disk (polished with diamond paste before use) as the working electrode and an aqueous S. C. E. as the reference electrode, separated from the analyte solution by a fine frit. Potentials in this paper are given versus the ferrocene / ferrocenium couple. This was not used as the internal standard, however, because its wave overlapped those of the analytes. Rather, decamethylferrocene was employed as an internal standard (E₁/₂ = -0.07 V versus S. C. E. in the present experiments) and potentials were converted to the ferrocene scale by subtraction of 0.51 V for benzonitrile and 0.55 V for dichloromethane solutions. A PAR 174 potentiostat was employed for differential pulse voltammetry measurements, using 1 s drop time and 25 mV modulation amplitude settings. UV-vis spectra were obtained in CH₂Cl₂ (ca. 5 x 10⁻⁴ M) on a Perkin-Elmer Lambda 900 UV-vis - near IR spectrometer using a 1 cm quartz cuvette. IR spectra were obtained as Nujol mulls with a Nicolet Magna-IR 550 spectrometer. FT-Raman spectra were collected on a Bomems MB-157 FT-spectrometer with a Spectra Physics diode pumped Nd:YLF laser (1064 nm; 350 kHz repetition rate). The instrument was configured in 180° back-scattering mode using sealed glass capillary tubes to hold the neat, crystalline samples. Electron impact (EI) mass spectra were obtained with a VG 70-250S mass spectrometer. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, N.J.
5.5.2 Synthesis of Spirocyclic [1]Silaferrocenophane 3.

This compound was synthesized in the same manner as Osborne, but with modifications to the work-up we found to improve the yield substantially.

Tetrachlorosilane (0.65 mL, 5.7 mmol) was added slowly via syringe to a suspension of dilithioferrocene-TMEDA (4.47 g, 14.2 mmol) in 100 mL of hexanes cooled to -78 °C. The solution was then warmed slowly to room temperature over a period of 3 h, giving a deep red solution with an orange precipitate. The reaction mixture was then heated to reflux for 3 h. After cooling the solution to room temperature with a water bath, 0.5 mL of n-butanol was added to quench the excess dilithioferrocene and the mixture was stirred for 10 min. The solution was cooled to -10 °C and filtered on a Buchner funnel. The orange residue was dissolved in dichloromethane to give a cloudy, red solution. Following filtration through a Buchner funnel and a 10 cm column (5 cm diameter) of alumina (BDH, Brockman, activity II; 100-200 mesh) under air, the solution was rotary evaporated to dryness. The solid was redissolved in a minimum of dichloromethane and was chromatographed on a 30 cm x 5 cm column of alumina (hexanes) and the initial yellow band (ferrocene) was discarded. Compound 3 eluted with dichloromethane and was rotary evaporated to dryness, affording 1.57 g (4.0 mmol, 70%) of 3. Compound 3 is obtained as red, air-stable crystals moderately soluble in toluene, benzene, THF, dichloromethane, and chloroform and nearly insoluble in hexanes and DMSO.
Data for 3: $^{13}$C NMR (100.5 MHz, C$_6$D$_6$) $\delta = 78.3$ (Cp), 75.5 (Cp). 31.1 (ipso-Cp) ppm. $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta = 4.47$ (s, 16H, Cp) ppm. $^{29}$Si NMR (79.5 MHz, C$_6$D$_6$) $\delta = -16.6$ ppm. MS (El, 70eV): m/z (%) = 396 (M$^+$, 100). Mössbauer spectrum: doublet IS = 0.44, QS = 2.01 mm s$^{-1}$. UV-vis (CH$_2$Cl$_2$): $\lambda_{max} (\varepsilon) = 483$ (590) nm (L mol$^{-1}$ cm$^{-1}$). IR (Nujol mull): 1178, 1122, 1032, 1019, 1013, 890, 881, 852, 803 (d), 696, 567, 536, 509 cm$^{-1}$.


This compound was synthesized in the same manner as Osborne and coworkers, but a modified work-up procedure afforded a measurable yield. Germanium tetrachloride (0.75 mL, 6.6 mmol) was added dropwise via syringe to a stirring suspension of dilithioferrocene-TMEDA (4.92 g, 15.7 mmol) in 100 mL of hexanes at -78 °C. The solution was allowed to warm up to room temperature over 3 h. After the reaction mixture was refluxed for 10 min, the hot mixture was gravity filtered under air. The filtrate was rotary evaporated to dryness, giving an orange-red crystalline solid. Once redissolved in dichloromethane, the clear, red solution of 4 was flash chromatographed through a 10 cm x 5 cm column of alumina (BDH, Brockman, Activity II, 100-200 mesh). The red solution was rotary evaporated to dryness to give red crystals which were ca. 95% pure by NMR, with ferrocene as the major impurity. Recrystallization from dichloromethane afforded ca. 100-150 mg (0.23 - 0.34 mmol, 3 - 5%) of red, air-stable crystals. Variation of reaction conditions including longer reflux times, lower reaction temperature, different solvents (THF, ether) and alternative work-up procedures (e.g. omission of the flash chromatography) gave no improvement in the yield.
Data for 4: $^{13}$C NMR (100.5 MHz, C₆D₆) $\delta$ = 77.7 (Cp), 76.0 (Cp), 27.8 (ipso-Cp) ppm. $^1$H NMR (400 MHz, C₆D₆) $\delta$ = 4.46 (t, 8H, Cp), 4.40 (t, 8H, Cp) ppm. MS (EI, 70eV): m/z (%) = 442 (M⁺, 100), 368 (M⁺ - Ge, 92). Mössbauer spectrum: doublet IS = 0.45, QS = 2.09 mm s⁻¹. UV-vis (CH₂Cl₂): $\lambda_{max}$ (e) 489 (560) nm (L mol⁻¹ cm⁻¹). IR (Nujol mull): 1294, 1183, 1117, 1024, 876, 848, 804, 662, 532, 514 cm⁻¹.

5.5.4 Synthesis of Spirocyclic [1]Silaferrrocenophane 5.

Cyclotrimethylenedichlorosilane (3.0 mL, 26 mmol) was added dropwise to a stirring suspension of 5.31 g (16.9 mmol) of dilithioferrocene-TMEDA in 100 mL of diethylether cooled to -78 ºC. The solution was allowed to warm up slowly to 0 ºC over a period of 2 h. At -60 ºC the solution started to turn red and was deep red in colour at -40 ºC. The reaction mixture was filtered through a frit at 0 ºC to give a deep red, clear solution. The ether was removed under vacuum to leave dark red crystals. After drying under dynamic vacuum at room temperature for 24 h, the product was dissolved in a minimum volume of hexanes and filtered again. Recrystallization at low temperature gave large red needles. Subsequent sublimation at 40 ºC afforded 3.39 g (13.3 mmol, 79%) of pure 5. These deep red crystals possessed a pungent odour and are very air- and moisture-sensitive. Compound 5 is very soluble in toluene, hexanes, THF, benzene, and dichloromethane.

Data for 5: $^{13}$C NMR (100.5 MHz, C₆D₆) $\delta$ = 78.0 (Cp), 74.7 (Cp), 31.9 (ipso-Cp), 18.3 (CH₂CH₂CH₂), 16.0 (SiCH₂) ppm. $^1$H NMR (400 MHz, C₆D₆) $\delta$ = 4.39 (s, 4H, Cp), 4.04 (s, 4H, Cp), 2.38 (qt, $^3$J_HH = 8.2 Hz, 2H, CH₂CH₂CH₂), 1.44 (t, $^3$J_HH = 8.2 Hz, 4H, SiCH₂)
ppm. $^{29}$Si NMR (79.5 MHz, C$_6$D$_6$) $\delta = 3.6$ ppm. MS (EI, 70eV): m/z (%) = 254 (M$^+$, 100), 226 (M$^+$ - C$_2$H$_4$, 62), 213 (M$^+$ - C$_3$H$_5$, 20), 148 ((C$_5$H$_4$)FeSi$^+$, 38). UV-vis (CH$_2$Cl$_2$): $\lambda_{max}$ ($\varepsilon$) 482 (420) nm (L mol$^{-1}$ cm$^{-1}$). Mp 92 ºC. Anal. Calc'd for C$_{13}$H$_{14}$FeSi: C, 61.43; H, 5.55. Found: C, 61.29; H, 5.40.

5.5.5 Synthesis of Tetraferrocenylsilane 6.

This compound was prepared by the patented procedure of Rosenberg. A solution of 20.25 g of FeSn$^+$Bu$_3$ (42.6 mmol) dissolved in 125 mL of THF was cooled to -78 ºC in a dry-ice/acetone bath. With stirring, 26 mL of 1.56 M $^+$BuLi (in pentanes) (40.6 mmol) were added via syringe to give an orange-red solution. After 2 h of stirring at -78 ºC, 1.0 mL of SiCl$_4$ (1.5 g, 8.7 mmol) was added and the solution was slowly warmed to room temperature. The reaction mixture was then refluxed 16 h at 70 ºC. The solvent was reduced to ca. 40 mL under vacuum, giving an orange precipitate and a red liquid. Ethanol (95%, 125 mL) was added to the flask and the solution was warmed to 50 ºC with constant stirring. After cooling to -55 ºC in a freezer, the crude product was isolated on a Buchner funnel and washed with 3x20 mL of cold ethanol, discarding the filtered solution. The solid was dissolved in a minimum of CH$_2$Cl$_2$ and filtered twice through a short (ca. 15 cm) column of alumina. Rotary evaporation afforded 4.15 g of an orange-yellow solid. Recrystallization from CH$_2$Cl$_2$ / hexanes (ca. 2:1) afforded 2.34 g (3.05 mmol, 35%) of orange-red needles.

Data for 6: $^{13}$C NMR (100.5 MHz, C$_6$D$_6$) $\delta = 74.3$ (Cp), 71.5 (ipso-Cp), 70.7 (Cp), 69.2 (Cp) ppm. $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta = 4.46$ (t, $^3$$J_{HH} = 1.76$ Hz, 8H, Cp), 4.30 (t, $^3$$J_{HH} =$
1.71 Hz, 8H, Cp), 4.02 (s, 20H, Cp) ppm. $^{29}$Si NMR (79.5 MHz, CD$_2$Cl$_2$) $\delta = -10.1$ ppm. MS (EI, 70eV): m/z (%) = 768 (M$^+$, 100), 517 (M$^+$ - Fc - C$_5$H$_5$. 49). Mössbauer spectrum: doublet $\vartheta_s = 0.43, \vartheta_q = 2.26$ mm s$^{-1}$. UV-vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\varepsilon$) 452 (490) nm (L mol$^{-1}$ cm$^{-1}$).

5.5.6 X-ray Structure Determination Technique.

Crystals of 3 - 6 were each mounted on a glass fibre and coated with epoxy glue. The orange-red prisms of 3 and 4 had dimensions of approx. 0.3x0.3x0.1 mm and 0.2x0.2x0.05 mm, respectively. Due to surface decomposition (hydrolysis), the dimensions of the crystal of 5 could not be measured (all were less than 0.5 mm). The crystal of 6 was an orange needle with approximate dimensions of 0.31x0.15x0.15 mm. Intensity data for the compounds 3 - 6 were collected at 168(2) K on a Siemens P4 diffractometer using graphite-monochromated Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Intensities of three standard reflections were measured every 100 reflections; all three crystals showed negligible decay (< 1%) during the data collection. A semi-empirical absorption correction was applied using the SHELXA-90 routine in SHELXL.$^{38}$

The positions of all atoms for 3, 5, and 6 were determined by direct methods using Siemens SHELXTL PC.$^{39}$ For each structure, all non-hydrogen atoms were refined anisotropically by full-matrix least squares to minimize $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/[\sigma^2(F_o)^2 + (a*P)^2 + 0.000*P]$, $P = (\text{Max}(F_o^2, 0) + 2*F_c^2)/3$, and $a$ is the weighting factor listed in Table 1. The structure of 4 was solved using the solution of 3 and refined in a similar manner. For compounds 3 - 6 the hydrogen atoms were refined isotropically. Crystal data, details of data collection, and least-squares parameters are listed in Table 1.
Selected bond lengths and bond angles are provided in Tables 2, 3, 5, and 6. All calculations were performed and all diagrams (Figures 1 - 4) were created using SHELXTL-PC and SHELXL-93 on a 486 personal computer.

5.6 References and Footnotes


(12)  MacLachlan, M. J.; Manners, I. Manuscript in Preparation.


(23) We define the ring pucker as the angle between the plane defined by Si, C(11), and C(13) and the plane defined by C(11), C(12), and C(13). Thus, it quantifies the fold in the silacyclobutane ring.


CHAPTER 6

Ferrocenylsiloxane Chemistry: Synthesis and Characterization of Hexaferrocenylecyclotrisiloxane and Tetraferrocenyldisiloxanediol

6.1 Abstract

Base-catalyzed condensation of diferrocenylsilanediol, \( \text{Fc}_2\text{Si} \text{(OH)}_2 \) (3) \((\text{Fc} = (\eta\text{-C}_5\text{H}_4)\text{Fe}(\eta\text{-C}_5\text{H}_5))\), in refluxing 95% ethanol (ca. 90 °C) affords the novel cyclotrisiloxane with six ferrocenyl substituents, \([\text{Fc}_2\text{SiO}]_3 \) (4), in 74% yield. At 60°C, the intermediate tetraferrocenyldisiloxanediol, \([\text{HOSiFc}_2]_2\text{O} \) (5), could be isolated in 78% yield. NMR, IR, Raman, and UV-vis data for 4 and 5 were consistent with the proposed structures. Electrochemical studies of 4 showed that there are substantial interactions between the ferrocenyl groups attached to the same Si atom, and weaker interactions between the ferrocenyl groups attached to adjacent Si atoms. Furthermore, single crystal X-ray diffraction studies of these compounds revealed an essentially planar \( \text{Si}_3\text{O}_3 \) ring in 4 and a novel hydrogen-bonded chain motif for disiloxanediol 5. Surprisingly, 4 and 5 cocrystallize in a 1:3 ratio from a \( \text{CH}_2\text{Cl}_2/\text{hexanes} \) mixture to afford an interesting helical hydrogen-bonding structure for the siloxanediol 5.

6.2 Introduction

The incorporation of transition elements into polymeric structures is attractive, as it may allow the combination of the interesting physical properties of metals with the solubility and processibility of polymers.\(^1\)-\(^2\) Recent advances in the field suggest that materials with unique mechanical and physical properties may be obtained in this way.
Unfortunately, synthetic routes to high molecular weight transition metal-containing polymers are still generally underdeveloped. Our group has been exploring ring-opening polymerization (ROP) of cyclic inorganic rings as a route to well characterized, high molecular weight polymers.³

Poly(siloxanes) (silicones), \([\text{R}_2\text{SiO}]_n\), are appealing polymers for many applications as a consequence of their chemical stability, low toxicity, high gas permeability, and insulating characteristics.⁴ ⁵ For example, this class of inorganic polymers can be found in sealants, contact lenses, coatings, and a variety of biomedical applications.⁶ The most practical route to high molecular weight poly(siloxanes) (e.g. polydimethylsiloxane, PDMS) is through the ROP of cyclic siloxane trimers and tetramers rather than the hydrolytic condensation of dichlorosilanes, which generally yields only oligomers and low molecular weight polymers.⁴b

The thermal stability and interesting electrochemistry of ferrocene makes it an attractive moiety to incorporate into polysiloxanes.⁷ ⁸ Attachment of ferrocenyl substituents to a polysiloxane chain may allow electrochemical control of the polymer properties such as gas permeability as well as modification of other chemical and mechanical characteristics. Indeed, several groups have recently reported poly(siloxanes) with ferrocene-containing moieties on the side chains.⁸ As these materials have all been prepared by grafting ferrocene-containing precursors onto a polysiloxane backbone, they suffer from the inherent difficulties of incomplete substitution. This may create an inhomogeneous distribution of ferrocene-containing substituents in the polymer. Furthermore, the ferrocenyl substituents, which are separated from the siloxane backbone by an organic spacer, are unable to interact electrochemically. Thus, we targeted cyclic siloxanes with ferrocenyl side-groups or siloxane-bridged ferrocenophanes as suitable precursors for ROP.⁹

To date, however, very few cyclic siloxanes with redox-active substituents have been prepared. Star polymers with a cyclotetrasiloxane core and oligo(ferrocenylsilane)
arms have been recently prepared by a transition metal-catalyzed, grafting, ROP reaction.\textsuperscript{10} Prior to this, Cuadrado and coworkers reported the synthesis of silsesquioxanes functionalized with ferrocenylethylidimethylsiloxyl groups and cyclotetrasiloxanes substituted with ethylferrocenyl groups.\textsuperscript{11} We identified siloxanediol 3 as a convenient precursor to cyclosiloxanes with ferrocenyl substituents. In this paper, we report the synthesis and characterization of a novel cyclotrisiloxane with six ferrocenyl substituents, [Fc\textsubscript{2}SiO\textsubscript{3} (4; Fc = (η\textsubscript{C}-C\textsubscript{5}H\textsubscript{4})Fe(η\textsubscript{C}-C\textsubscript{3}H\textsubscript{5})). An intermediate in the condensation, [HOSiFc\textsubscript{2}]\textsubscript{2}O (5), has been isolated and characterized. Moreover, an interesting co-crystallization of 4 and 5 has been discovered and examined by single crystal X-ray diffraction.

6.3 Results and Discussion

6.3.1 Synthesis and Characterization of Hexaferrocenyleclotrisiloxane (4).

We have recently reported a convenient, high yield (> 88%) synthesis of diferrocenyldichlorosilane, Fc\textsubscript{2}SiCl\textsubscript{2} (2) via treatment of the spirocyclic [1]silaferrocenophane 1, fc\textsubscript{2}Si (fc = (η\textsubscript{C}-C\textsubscript{5}H\textsubscript{4})\textsubscript{2}Fe), with HCl.\textsuperscript{12} The subsequent hydrolysis of 2 gave diferrocenylsilanediol, Fc\textsubscript{2}Si(OH)\textsubscript{2} (3) in 90\% yield.\textsuperscript{12} After 3 was refluxed in 95\% ethanol for 2.5 h, the reaction mixture contained only a single new product 4 by \textsuperscript{1}H NMR spectroscopy. After isolation, this air-stable, orange crystalline compound was identified as the cyclotrisiloxane 4.\textsuperscript{13} The \textsuperscript{1}H NMR spectrum of the product showed two pseudo-triplets and a singlet for the Cp ligands. In the \textsuperscript{13}C NMR spectrum, four resonances were observed, with the ipso resonance at 67.4 ppm. The \textsuperscript{29}Si NMR spectrum of 4 showed only a single resonance at -26.2 ppm (C\textsubscript{6}D\textsubscript{6}), slightly upfield from the resonance observed in silanediol 3 (-25.1 ppm in DMSO-d\textsubscript{6}). Mass spectrometry gave the molecular ion (m/z = 1242) as the major peak. In addition, UV-vis spectroscopy and elemental analysis were consistent with the proposed structure.
Figure 1. (a) $^1$H NMR (400 MHz) and (b) $^{13}$C NMR (100.5 MHz) of tetraferrocenylsiloxanediol 5 in CDCl$_3$ shows splitting of the resonances attributed to the Cp rings as a result of the asymmetry in the molecule.
To investigate the thermal stability of 4, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed. DSC showed no transitions below 250 °C (under N₂). By TGA, compound 4 is stable to over 300 °C under nitrogen, showing a ca. 50% weight loss between 300 and 500 °C. The ceramic product obtained at 900 °C was attracted to a bar magnet.

6.3.2 Synthesis and Characterization of Tetraferrocenyldisiloxanediol (5).

Silanols, which are more acidic and reactive than alcohols, are key intermediates in the hydrolytic condensation of chlorosilanes to form low molecular weight poly(siloxanes). These species are generally unstable but can be isolated as solids under very stringent conditions or where the substituents at Si are bulky. Furthermore, silanols are known to assemble into fascinating hydrogen-bonded structures in the solid state.¹⁴

When silanediol 3 was heated to 60 °C in ethanol for 10 min, a new product was isolated. The mass spectrum of the yellow-orange crystals showed a peak at m/z = 846, suggesting that the compound was the disiloxanediol [HOSiFc₂]₂O (5). However, the ¹H and ¹³C NMR spectra showed doubling of the cyclopentadienyl CH resonances that is consistent with two different ferrocenyl groups in the structure (Figure 1). These initially unanticipated spectra can be rationalized by the unsymmetrical environment of the silicon atoms. Specifically, the absence of a mirror plane bisecting the cyclopentadienyl ligands and the Si atom to which they are attached renders the protons of the Cp ligand unequivalent. The ¹H NMR resonance for the OH protons of the siloxanediol was observed at 2.66 ppm in CDCl₃ and appears to be independent of concentration. The ²⁹Si NMR spectrum of 5 shows a resonance at -25.6 ppm (CDCl₃), which is almost the same as in compound 4. UV-vis spectroscopy and elemental analysis were also consistent with the proposed structure of disiloxanediol 5.
Scheme 1 shows the synthetic pathway to compounds 4 and 5 from the spirocyclic \([1]\)silaferrrocenophane 1. To prove that disiloxanediol 5 was indeed an intermediate in the synthesis of cyclotrisiloxane 4, a sample of pure 5 was heated in 95% ethanol in the presence of NaOH. The primary product formed in the reaction was 4, confirming that 5 is an intermediate in the condensation of silanediol 3 to give 4. This reaction must proceed by a base-catalyzed rearrangement of the siloxane, possibly involving a cyclotetrasiloxane intermediate that we have been unable to isolate. Rearrangements of this type are well known in siloxane chemistry.\(^{15}\)

Scheme 1
6.3.3 Vibrational Spectra of Cyclotrisiloxane 4 and Disiloxanediol 5.

To corroborate the structures of 4 and 5, IR and Raman spectra were obtained. Both Raman and IR spectra of the compounds confirmed the presence of ferrocenyl moieties in the structure; the major peaks are identified in Table 1. Peaks attributed to cyclopentadienyl modes and ring deformation were assigned by comparison with ferrocene and the spirocyclic [1]ferro~eno~hanes.\textsuperscript{16,17} The asymmetric vSi-O stretch in cyclotrisiloxane 4 was observed at 1015 cm\textsuperscript{-1} (Nujol and CCl\textsubscript{4}) in the IR, but not observed in the Raman spectrum. For comparison, hexaphenylcyclotrisiloxane shows two resonances due to Si-O stretching at 1015 and 1032 cm\textsuperscript{-1}.\textsuperscript{18} There may be a second Si-O stretch present near 1032 cm\textsuperscript{-1}, but it would overlap with the intense out-of-plane C-H bending mode of the cyclopentadienyl ligands. In the disiloxanediol 5, the Si-O asymmetric stretches are observed at 1099 and 1051 cm\textsuperscript{-1}. This is similar to other siloxanediols; for example, the Si-O stretching vibration of tetraphenyldisiloxanediol is observed at 1078 cm\textsuperscript{-1}.\textsuperscript{19a} The Si-OH stretch of the disiloxanediol was observed as a medium intensity peak at 864 cm\textsuperscript{-1}, in agreement with other silanols.\textsuperscript{19b} It was not possible to identify the symmetric vSi-O mode expected in the region 450-630 cm\textsuperscript{-1} for 4 and 5. Figure 2 shows the IR spectrum of the O-H stretching region disiloxanediol 5 in the solid-state. Notably, in the solid-state there is a sharp absorption due to free O-H observed at 3605 cm\textsuperscript{-1} together with a very broad peak between 3300-3600 cm\textsuperscript{-1} (center at ca. 3470 cm\textsuperscript{-1}), consistent with hydrogen-bonded OH groups. In solution (CCl\textsubscript{4}), however, there is only a single resonance due to free O-H stretching and it is observed at 3676 cm\textsuperscript{-1}, typical of disiloxanediols.\textsuperscript{13}
Figure 2. IR spectrum of the O-H stretching region for disiloxanediol 5 in a Nujol mull.

6.3.4 Electrochemical Studies of Hexaferrocenylcyclotrisiloxane (4).

To the best of our knowledge, studies revealing the electrochemical interaction of ferrocenyl substituents separated by a siloxane unit have not been reported. The differential pulse voltammetry of 4 in benzonitrile shows several oxidation waves as illustrated in Figure 3. We believe that the first wave between 0 and 250 mV (referenced to ferrocene) is attributed to the oxidation of three Fc substituents, i.e. one Fc substituent attached to each Si atom. We assign the peak near 300 mV to the oxidation of the
remaining three ferrocenyl substituents. These are expected to occur at higher potential, as oxidation of the second Fc attached to a single Si atom must result in significant Coulombic repulsion between the cations. Interestingly, the first oxidation wave shows fine structure attributed to overlapping oxidation waves of the first three Fc centers on adjacent Si atoms. This electronic interaction ($\Delta E < ca. 0.1 \text{ V}$) is comparable to the coupling observed between two ferrocenyl groups joined by a trisilane bridge ($\Delta E = 0.08 \text{ V}$).^{20}

Figure 3. Differential pulse voltammogram of hexaferrocenylcyclotrisiloxane 4 (benzonitrile).
6.3.5 Single Crystal X-ray Diffraction (SCXRD) Studies of 4-6.

As relatively few single crystal structures of cyclotrisiloxanes have been reported (none possessing ferrocenyl substituents), we undertook an investigation of the structure of the hexaferrocenycyclotrisiloxane 4. Single crystals suitable for SCXRD were obtained from warm dichloromethane. Data collection and refinement parameters for 4 are summarized in Table 2. Selected bond lengths and angles from the siloxane ring of 4 are provided in Table 3.

Compound 4 crystallizes in the triclinic P-1 space group with Z=4. The two independent molecules of the asymmetric unit (A and B) are shown in Figure 4. In both molecules, the siloxane rings are essentially planar with mean deviations of 0.015 and 0.022 Å in molecules A and B, respectively. The sum of the interior angles of the two rings are 719.7(12)° and 719.5(12)°, in good agreement with the expected sum of 720° for a planar 6-atom ring. In both molecules, the Fc substituents are arranged in two opposing pinwheels that rotate counter-clockwise when viewed on top of the siloxane ring. The Fe atoms of the ferrocenyl substituents attached to the same Si center are separated by 5.44 - 5.64 Å. For ferrocenyl substituents on adjacent Si atoms, however, the Fe centers are separated by 6.88 - 7.29 Å for the cis-adjacent ferrocenyl groups and 6.71 - 9.40 Å for the trans-adjacent ferrocenyl groups. From these values, it is expected that metal-metal interactions would be most significant for ferrocenyl moieties attached to the same Si atom.
Figure 4. The molecular structure of hexaferrocenylcyclotrisiloxane 4. Both molecules (A and B) are shown with thermal ellipsoids drawn at the 30% probability level.
The ferrocenyl substituents in the molecule are all slightly tilted, with ring tilts of 0.6° - 3.8° between the planes of the cyclopentadienyl ligands. This may be a result of steric interactions. In other respects, the ferrocenyl substituents are similar to ferrocene, with normal C-C bond lengths and Fe-Cp distances (1.637(3) - 1.651(3) Å).

Hydrogen-bonding in disiloxanediols can lead to intriguing double chain structures. Several simple disiloxanes of the general formula (HOR₂Si)₂O (R = Me, Et, ℛPr, ℛPr, c-C₅H₁₀, or Ph) have been structurally characterized and assemble into 3 simple motifs. As no diffraction studies of disiloxanediols with bulky ferrocenyl substituents have been undertaken, we investigated compound 5 by single crystal X-ray diffraction. Data collection and refinement parameters for 5 are given in Table 2. Selected bond lengths, intermolecular distances, and angles for 5 are provided in Table 4.

Compound 5 crystallizes in the monoclinic space group Cc. The molecular structure of 5 is illustrated in Figure 5. Notably, the Si-O-Si angle is 157.1(3)°, similar to that observed in other siloxanediols. When the molecule is viewed along the Si---Si axis, the substituents are approximately halfway between staggered and eclipsed; the torsion angle, ω, between O1..Si1..Si2..O2 is 31.5°. Small ring tilts (1.8° - 3.0°) are present between the Cp ligands of the ferrocenyl substituents and may be the result of steric interactions in the solid state. The Fe--Fe separations vary between 6.09 and 6.10 Å for ferrocenyl groups on the same Si atom to 7.54 and 7.84 Å for ferrocenyl groups attached to different Si atoms.
Figure 5. The molecular structure of tetraferrocenyldisiloxanediol 5. The molecule is shown with thermal ellipsoids drawn at the 30% probability level.

The disiloxanediol packs into a hydrogen-bonded double chain structure parallel to the c-axis. The arrangement is unique and has not been observed in other disiloxanediols with very bulky groups, \((\text{HOR}_2\text{Si})_2\text{O} (\text{R} = '\text{Pr}, \text{c-C}_8\text{H}_{18})\).\(^{12}\) This novel hydrogen-bonding network is depicted in Scheme 2. In this motif, only 3/4 of the protons participate in hydrogen-bonding. Indeed, this is consistent with the IR spectrum of 5, in which a sharp O-H stretching mode attributed to free O-H is observed at 3605 cm\(^{-1}\) and a
broad absorption at 3470 cm$^{-1}$ is attributed to hydrogen-bonded O-H groups. Figure 6 shows the arrangement of the two hydrogen-bonded chains and intermolecular O--O distances. Figure 7 shows three projections of the unit cell, illustrating the orientation of the disiloxanediol chains.

**Scheme 2**

![Scheme 2](image)

**Figure 6.** A segment of the hydrogen-bonded double chain present in compound 5 showing the intermolecular O--O distances. The ferrocenyl substituents have been omitted for clarity.
Figure 7. Projections of (a) the $ab$ plane, (b) the $bc$ plane, and (c) the $ca$ plane in the structure of $5$ illustrate the hydrogen-bonded pairs of chains running parallel to the $c$ axis. Ferrocenyl substituents have been omitted for clarity.

The use of synthetic strategies to design and control the solid-state structure of materials, crystal engineering, is a current area of research in materials chemistry.$^{22}$ Cocrystallization is a fascinating method of controlling the solid-state conformation of molecules. From studies of cocrystals, one may also obtain information about the energy difference between conformations and the forces that direct the crystal packing. As an example, Pannell and coworkers have recently obtained structures of 1,1,3,3-tetramethyl-1,3-diferrocenyldisiloxane in the neat crystalline form and as a cocrystal with ferrocene and calculated the energy difference between the conformations observed.$^{23}$ During our attempts to grow single crystals from CH$_2$Cl$_2$ / hexanes, we obtained a remarkable cocrystallization of cyclotrisiloxane $4$ and disiloxanediol $5$. The cocrystal incorporates $4$ and $5$ into a trigonal lattice (space group $R3$) in a 1:3 ratio along with a molecule each of 3-methylpentane (from the hexanes) and CH$_2$Cl$_2$ in the asymmetric unit. The $^1$H NMR spectrum of the single crystals confirmed the presence of $4$, $5$, CH$_2$Cl$_2$, and hexanes, but
resonances for 3-methylpentane could not be specifically resolved. The structure of the cyclotrisiloxane and the disiloxanediol in the cocrystal will be discussed in turn.

Figure 8 shows the structure of cyclotrisiloxane 4 in the cocrystal. Selected bond lengths and angles for 4 as observed in the cocrystal are summarized in Table 5. The cyclotrisiloxane ring lies on a 3-fold rotational axis. As in the neat crystal, the Si₃O₃ ring is essentially planar with a mean deviation of only 0.005 Å from planarity and an interior angle sum of 720(2)°, as predicted for a planar 6-sided polygon. Although the ferrocenyl substituents are also arranged in two opposing pinwheels around the siloxane ring, they appear to be oriented differently from the structure of pure 4 with respect to the plane of the siloxane ring. In fact, the ferrocenes are oriented so that they rotate clockwise when viewed from the top of the siloxane ring; thus, the structure is nearly a mirror image of that observed in the neat crystal of 4. The Fe atoms of the ferrocenyl substituents attached to one Si atom are 5.404 Å apart, slightly closer than observed in crystals of pure 4. The Fe atoms of cis-adjacent ferrocenyl substituents are 7.414 and 7.449 Å apart, whereas trans-adjacent ferrocenyl substituents show Fe---Fe separations of 6.790 and 9.534 Å.
Figure 8. The molecular structure of hexaferrocenyleclyotrisiloxane 4 in the cocrystal. The molecule is shown with thermal ellipsoids at the 50% probability level.

The structure of tetraferrocenyldisiloxanediol 5 as it appears in the cocrystal structure is illustrated in Figure 9. Selected bond lengths, intermolecular distances, and bond angles for 5 in the cocrystal are given in Table 6. As in the structure of pure 5, the Si-O-Si angle is 157.1(3). However, the similarity between the two structures ends there.
When viewed along the Si---Si axis, the substituents on the Si atoms appear more staggered in the cocrystal with respect to pure 5. Indeed, the O71..Si2..Si3..O73 torsion angle (\( \omega \)) is 48.2° in the cocrystal, but only 31.5° in the crystal of 5. As in the other structures, the ferrocenyl substituents exhibit small ring tilts (0.4° - 3.4°). Metal-metal separations vary between 5.91 Å and 5.94 Å for ferrocenyl groups on the same Si atom to 7.60 Å and 7.92 Å for ferrocenyl groups on adjacent Si atoms.

Figure 9. The molecular structure of tetraferrocenyldisiloxanediol 5 in the cocrystal. The molecule is shown with thermal ellipsoids at the 50% probability level.
The disiloxanediol assembles into a fascinating 3-fold counter-clockwise helical structure along the c-axis. One helical chain is illustrated in Figure 10. Interestingly, there are no hydrogen bonds between the disiloxanediol molecules (closest Si-O contacts are 6.760 Å), but dichloromethane molecules link the disiloxanediol molecules in the helix. Closest contacts between the O atom of the siloxanediol and the Cl atoms of dichloromethane are 2.727 and 3.279 Å, values that would be typical for hydrogen bonding. In addition, the close O(71)...C(91) contact (C(91) from CH₂Cl₂) of 2.748 Å suggests that there is hydrogen bonding between the O atom of the siloxanediol and the H atom of the dichloromethane.
Figure 10. The structure of a helix formed by 5 with dichloromethane inside the cocrystal.
6.4 Summary

Hexaferrocenylcyclotrisiloxane (4) and tetraferrocenyldisiloxanediol (5) were synthesized and characterized. Electrochemistry of 4 revealed metal-metal interactions between ferrocenyl groups on the same and adjacent Si atoms. Single crystal X-ray diffraction of 5 revealed a new double-chain hydrogen bonding motif for disiloxanediols. A cocrystal of 4, 5, CH₂Cl₂, and 3-methylpentane was obtained from CH₂Cl₂ / hexanes. The structures of 4 and 5 in the cocrystal were found to be similar to the structures of the pure compounds, but not identical. Disiloxanediol 5 assembles into a 3-fold hydrogen-bonded helical structure linked with dichloromethane solvent molecules. Future work will involve studies of the ROP of 4 and related cyclic species.

6.5 Experimental Section

6.5.1 Materials and Equipment.

Triethylamine was purchased from Aldrich and distilled from Na prior to use. Anhydrous 1 M HCl in diethylether and sodium hydroxide were purchased from Aldrich and used as received. The spirocyclic ferrocenophane 1, dichlorodiferrocenylsilane (2), and diferrocenylsilanediol (3) were prepared by literature methods.¹²,¹⁷

All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Innovative Technologies) unless otherwise noted. Solvents were dried by standard methods, distilled, and stored under nitrogen. 400 MHz ¹H NMR spectra, 100.5 MHz ¹³C NMR spectra, and 79.5 MHz ²⁹Si NMR spectra were recorded on a Varian Unity 400 spectrometer and were referenced externally to TMS. UV-vis spectra were obtained in CH₂Cl₂ (ca. 5 x 10⁻⁴ M) on a Perkin-Elmer Lambda 900 UV-vis / near IR spectrometer using a 1 cm quartz cuvette. IR spectra were obtained as Nujol mulls or CCl₄ solutions.
with a Nicolet Magna-IR 550 spectrometer. FT-Raman spectra were collected on a Bomem MB-157 FT-spectrometer with a Spectra Physics diode pumped Nd:YLF laser (1064 nm; 350 kHz repetition rate). The instrument was configured in 180° back-scattering mode using sealed glass capillary tubes to hold the neat, crystalline samples. Electron impact (EI) mass spectra were obtained with a VG 70-250S mass spectrometer. Thermogravimetric analyses were obtained on a Perkin-Elmer TGA-7 analyzer equipped with a TAC-7 instrument controller. Samples were heated at a rate of 10 °C min⁻¹ under a flow of N₂. Differential pulse voltammetry of 4 was performed at room temperature under N₂ on a 0.31 mM benzonitrile solution using a PAR Model 174 potentiostat using 1 s drop time and 25 mV modulation amplitude settings. Potentials in this paper are given versus the ferrocene/ferrocenium couple. Melting points were determined on a Fisher-Johns hot-stage melting point apparatus and are uncorrected.

6.5.2 Synthesis of Hexaferrocenylcyclotrisiloxane (4).

A mixture of difeferrocenyilsilanediol 3 (0.200 g, 0.463 mmol) and ca. 5 mL of 95% ethanol was refluxed at 95 °C, giving a yellow-orange solution. Three drops of 4M NaOH (aqueous) were added, giving an immediate orange precipitate. The mixture was refluxed for an additional 2.5 h, giving a pale yellow solution and orange powder. After cooling at -55 °C, the product was isolated on a Buchner funnel (under air) and washed with cold ethanol. The yellow powder was dried under vacuum to afford 0.142 g (0.114 mmol; 74%) of cyclotrisiloxane 4.

Data for 4: ¹³C NMR (100.5 MHz, C₆D₆) δ = 74.3 (Si-Cp), 71.9 (Si-Cp), 69.5 (Cp), 67.4 (ipso-Cp) ppm. ¹H NMR (400 MHz, C₆D₆) δ = 4.85 (t, ³JHH = 1.65 Hz, 12H, Cp), 4.35 (t, ³JHH = 1.65 Hz, 12H, Cp). 4.18 (s, 30H, Cp) ppm. ²⁹Si NMR (79.5 MHz, C₆D₆): δ = -26.2 ppm. UV-vis (CH₂Cl₂): λmax = 452 nm (ε = 665 L mol⁻¹ cm⁻¹). MS (EI, 70eV): m/z
6.5.3 Synthesis of Tetraferrocenyldisiloxanediol (5).

A 50 mL round bottom flask was charged with 2.125 g (4.92 mmol) of 3 and 30 mL of 95% ethanol. The flask was then heated to ca. 80 °C to dissolve all of the silanediol. The solution was maintained at 60 °C in a water bath. While stirring, 7 drops of 4 M NaOH(aq) were added and an immediate orange precipitate formed. The mixture was heated at 60 °C for an additional 10 mins. After cooling to -55 °C, the product (5) was collected on a Buchner funnel and washed with ca. 10 mL of cold ethanol. Yield: 1.630 g (1.93 mmol, 78%) of orange crystals.

Data for 5: $^{13}$C NMR (100.5 MHz, CDCl$_3$) $\delta = 73.55$ (Si-Cp), 73.34 (Si-Cp), 71.24 (Si-Cp), 71.20 (Si-Cp), 68.6 (Cp), 67.5 (ipso-Cp) ppm. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 4.38$ (m, 12H, Cp), 4.30 (m, 4H, Cp), 4.15 (s, 20H, Cp), 2.66 (s, 2H, OH) ppm. $^{29}$Si NMR (79.5 MHz, CDCl$_3$): $\delta = -25.6$ ppm. UV-vis (CH$_2$Cl$_2$): $\lambda_{max} = 449$ nm ($\varepsilon = 481$ L mol$^{-1}$ cm$^{-1}$). MS (EI, 70eV): m/z (%) = 846 (100, M$^+$). Mp 197-8 °C. Anal. Calc’d: C, 56.77; H, 4.53; N, 0.00. Found: C, 56.81; H, 4.46; N, <0.05.

6.5.4 Conversion of Disiloxanediol 5 to Cyclotrisiloxane 4.

A suspension of disiloxanediol 5 (100 mg, 0.118 mmol) in 20 mL of 95% ethanol was heated to reflux at ca. 90 °C. Three drops of 4M NaOH (aq.) solution were added and the solution was refluxed for 2 h. After cooling to room temperature, the yellow powder was isolated on a Buchner funnel and, after drying under vacuum, gave 0.042 g (0.034 mmol, 43%) of pure cyclotrisiloxane 4 by $^1$H NMR. The yellow filtrate was evaporated to dryness and $^1$H NMR of the residue showed that it contained primarily the product 4 and unreacted 5, with a small quantity of unidentified species.
6.5.5 Crystallographic Structural Determination

Selected crystal, data collection, and refinement parameters for 4, 5, and the cocrystal are given in Table 2. Selected inter- and intramolecular distances and bond angles for 4 and 5 are provided in Tables 3 and 4, respectively. Data for 4 and 5 were collected on a Nonius Kappa-CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The data from 180° φ scans were integrated and scaled using the Denzo-SMN package. The structure was solved and refined using the SHELXTL/PC package. Refinements were by full-matrix least-squares on F² using all data (negative intensities included). All hydrogen atoms were included in calculated positions and treated as riding atoms except for the silanol hydrogens, which could not be located and, thus, were omitted for refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Suitable crystals of the cocrystal were grown from a mixture of CH₂Cl₂/hexanes (ca. 1:1), were sectioned, and were mounted on thin glass fibres with epoxy cement. The data were collected on a Siemens P4 diffractometer equipped with a SMART/CCD detector. Selected inter- and intramolecular bond angles for 4 and 5 in the cocrystal are given in Tables 5 and 6, respectively.

The unit cell parameters, systematic absences, and occurrences of equivalent reflections in the cocrystal are consistent with the rhombohedral space groups R-3, R3, R3m, R32, and R-3m. The absence of a molecular mirror plane and a two-fold rotation axis excluded space groups R3m, R32, and R-3m. Chemical composition suggested the space group R3, which yielded chemically reasonable and computationally stable results of refinement.

The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Further refinement of the crystal structure showed signs of merohedral twinning; a [b, a, -c] transformation matrix was applied to resolve the twinning, decreasing the R factor from
14% to 5%. Hexaferrocenylcyclotrisiloxane is located on a three-fold axis and tetraferrocenyldisiloxanediol is in a general position. The asymmetric unit also contains a molecule of 3-methylpentane and dichloromethane. All non-hydrogen atoms of the solvent molecules were refined isotropically. The hydrogen atoms on the silanol oxygen atoms could not be located from the difference map and were ignored, and the hydrogen atoms on the dichloromethane carbon atom were ignored. The remaining hydrogen atoms were treated as idealized contributions. All other non-hydrogen atoms were refined with anisotropic displacement parameters.

All software and sources of the scattering factors are contained in the SHELXTL (5.1) program libraries (G. Sheldrick. Siemens XRD, Madison, WI).

6.6 References

(1) For recent examples of transition metal-based polymeric materials, see, for example:


(21) The torsion angle (\(\omega\)) of A..B..C..D is defined as the angle between vector BA and vector CD when viewed down BC. \(\omega\) is positive if BA must be rotated clockwise into CD, and is negative if the rotation is counterclockwise.


CHAPTER 7


7.1 Abstract

[1]Silaf errocenophanes fcSiMe_2 (1) and fcSi(CH_2)_3 (3) (fc = (η-C_5H_4)2Fe) have been incorporated into the well-ordered, hexagonal channels of mesoporous silica (i.e., MCM-41). Characterization of the composite materials indicates the presence of ring-opened species, oligomers, polymer, and, in the case of 1, free monomer. Differential scanning calorimetry of a sample containing excess monomer 1 showed an exothermic transition at 75-200 °C corresponding to ring-opening polymerization (ROP) of the strained monomer within the channels of MCM-41. The ferrocenophane 3 inside MCM-41, however, was completely opened, but the silacyclobutane ring was still mostly intact. When pyrolyzed in a nitrogen atmosphere, the mesoporous silica / ferrocenophane composites formed Fe nanoparticles in the ca. 20-30 Å channels of MCM-41. Characterization of the magnetic properties of the product formed when 1 is pyrolyzed in the channels of mesoporous silica indicated that the clusters were superparamagnetic. Magnetization versus field data at 300 K were fit to a sum of two Langevin functions, implying that two distinct magnetic phases were present. From the magnetization data,
the two phases are best described as Fe nanoparticles with diameters of 50-64 Å coated with a thin (ca. 4-6 Å) Fe₃O₄ layer.

7.2 Introduction

Materials with sub-micron dimensions (e.g. nanofibers, nanotubes, nanoparticles) represent an exciting new class of materials.¹-² As a consequence of their tiny size, nanomaterials often display unique physical and chemical properties that are atypical of the bulk material.² They are of interest for applications including solid-state lubricants, electronic interconnects in microchip technology, and ceramics reinforcement.³ Magnetic nanomaterials, in particular, are attractive as components in magnetic recording media and magnetic fluids.⁴ Moreover, studies of the physical properties of magnetic nanoparticles are relevant to understanding the ecological significance of magnetosomes in magnetic bacteria (e.g. Magnetospirillum magnetotacticum).⁵

When nanoclusters of a magnetic substance are formed with dimensions smaller than that of a single Weiss domain, the material displays superparamagnetism.⁶⁷ Specifically, the particles behave as ferromagnets below the blocking temperature (Tₘ) and as giant paramagnets above Tₘ. Hence, above Tₘ, thermally-induced fluctuations result in a random orientation of the magnetic dipoles of the clusters. Superparamagnetic nanoparticles are of interest for use as contrast agents for magnetic resonance imaging (MRI) of biological tissues.⁸
Although nanomaterials are still predominantly prepared by physical methods (e.g. sputtering and molecular beam epitaxy), there is a desire to prepare the materials by chemical techniques, a route that is generally simpler and less expensive.\textsuperscript{1} This approach also has the advantages of improved stoichiometric control and intimate mixing. Numerous methods for the preparation of metal nanoparticles have been reported, including reduction of metal salts and thermolysis or sonication of organometallic complexes.\textsuperscript{2,6,7} Ideally, the fabrication technique should have control over the particle size, distribution, and morphology. By forming the nanoparticles inside templates such as zeolites, micelles, block copolymers, porous alumina, and polycarbonate membranes, greater control over the particle-size distribution can be exerted.\textsuperscript{6,9}

In 1992, Kresge \textit{et al.} reported the synthesis of mesoporous silica, MCM-41, possessing ordered channels arranged in a hexagonal lattice (space group \textit{P6mm}).\textsuperscript{10} With uniform channel sizes readily varied between 20-100 Å in diameter, this material is well-suited to be a host for novel nanomaterials. Indeed, researchers have reported a variety of nanochemistry within the channels and it has been used recently to template nanosized rhodium oxide particles.\textsuperscript{11-12}

\begin{equation*}
\begin{array}{ccc}
\text{Fe} & \text{Si}^\text{mR} & \text{R} \\
\text{R} & \text{Si}^\text{mR} & \text{R}
\end{array}
\end{equation*}

1 (R = Me) \xrightarrow{\text{heat}}

\begin{equation*}
\begin{array}{ccc}
\text{Fe} & \text{Si}^\text{n} & \text{R} \\
\text{R} & \text{Si}^\text{n} & \text{R}
\end{array}
\end{equation*}

2

In our laboratory, we have been investigating the ring-opening polymerization (ROP) of [1]silaferrocenophanes (e.g. 1) to yield soluble, high molecular-weight
macromolecules 2.\textsuperscript{13,14} When pyrolyzed, polymer 2 forms a ferromagnetic ceramic in 22\% yield that shows hysteresis in its field-dependent magnetization curve at room temperature.\textsuperscript{15} To improve the ceramic yield, we have been exploring the use of spirocyclic [1]ferrocenophane 3 to crosslink poly(ferrocenes).\textsuperscript{16-17} The crosslinked network 4 formed from the homopolymer of 3 can be pyrolyzed at 600 °C to give a superparamagnetic ceramic in 90\% yield.\textsuperscript{18}

\[
\begin{array}{c}
\text{Fe} \\
\text{Si} \\
\text{Fe}
\end{array}
\xrightarrow{\text{heat}}
\begin{array}{c}
\text{Fe} \\
\text{Si}
\end{array}
\]

Pyrolysis of poly(ferrocenes) in MCM-41 is desirable as a route to control the particle size of nanomaterials. Whereas Fe particles obtained from bulk pyrolysis of poly(ferrocenylsilanes) gives large particles,\textsuperscript{15} the growth of Fe particles may be limited by the channel diameter in MCM-41. This size control has already been employed in the synthesis of a few nanomaterials.\textsuperscript{11} Bein and coworkers have demonstrated the encapsulation of conducting polyaniline and graphitic nanowires inside MCM-41.\textsuperscript{19} Mallouk, Ozin, and coworkers have prepared extractable polyphenol-formaldehyde nanofibres inside MCM-41.\textsuperscript{20} Chomski \textit{et al.} impregnated MCM-41 with disilane to form luminescent silicon clusters in the channels.\textsuperscript{21}

The [1]silaferrocenophane 1 has been used to derivatize the surface of amorphous silica and MCM-41 via ring-opening addition of silanol OH groups to the Si-Cp bond of the ferrocenophane.\textsuperscript{22,23} We have recently reported preliminary studies of the ROP of 1
inside mesoporous silica and the subsequent pyrolysis to afford a composite with Fe nanoparticles inside the channels of MCM-41.\textsuperscript{24}

In this chapter, we report full details of our studies of the synthesis and characterization of composites made from mesoporous silica containing 1 and 3. Furthermore, studies of the pyrolysis including the first magnetization data for nanoparticles inside mesoporous silica are reported.

\section*{7.3 Experimental Section}

\subsection*{7.3.1 General Comments.}

The \([1]\text{silaf}errocenophanes 1 and 3 were prepared by literature methods.\textsuperscript{13,16} They were both recrystallized then sublimed multiple times prior to use. Well-ordered MCM-41. CPM-MCM and ODA-MCM. was prepared by a literature method (base-catalyzed condensation of Si(OEt)$_4$) using cetylpyridinium chloride and octadecyltrimethylammonium chloride, respectively, as the structure-directing template.\textsuperscript{25} Calcination under air at 540 °C resulted in template removal. Reflectance UV-vis / near-IR spectra were obtained on a Perkin-Elmer Lambda 900 spectrometer using a Spectralon integrating sphere. Solid-state 400.10 MHz $^1$H magic angle spinning (MAS). 100.62 MHz $^{13}$C cross-polarization (CP)-MAS and 79.50 MHz $^{29}$Si CP-MAS NMR spectra were recorded on a Bruker DSX400 spectrometer. Solid-state 39.75 MHz $^{29}$Si CP-MAS NMR spectra were obtained on a Bruker DSX200 spectrometer; all $^{29}$Si NMR spectra were recorded on this instrument unless otherwise specified. Powder X-ray diffraction
(PXRD) patterns were obtained on a Siemens D5000 X-ray diffractometer using Ni-filtered Cu Kα radiation (λ = 1.54178 Å). Transmission electron microscopy (TEM) images and electron diffraction (ED) patterns were recorded on a Phillips 430 microscope operating at 100 kV; the samples were microtomed into thin (ca. 300 Å) sections. DSC experiments were performed on a Perkin-Elmer 7 Series Analyzer equipped with a TAC controller and calibrated with the melting points of cyclohexane and indium. Samples were heated at 10 °C min⁻¹ under N₂. Magnetization data were obtained with a Quantum Design SQUID magnetometer. IR spectra were collected as KBr pellets on a Perkin Elmer Paragon 500 FT-IR spectrometer. Pyrolyses were carried out under an atmosphere of prepurified nitrogen using a 3-zone Lindberg pyrolysis oven Model No. 55035 with a 1 5/8 in. internal diameter and Thermcraft control system Model 3D1-50-115 (UP27) with type K thermocouples and independent temperature control. Ceramic precursors were lightly packed into quartz boats (ca. 2” x ½”) and inserted into a quartz pyrolysis tube. Fe analyses were obtained from Quantitative Technologies Inc. (Whitehouse, NJ). Samples were first digested in a mixture of perchloric, sulfuric, and nitric acids then analyzed by inductively-coupled plasma (ICP) emission spectroscopy.

7.3.2 Synthesis of MCM-41 / fcSiMe₂ Composites 5.

Samples of the ferrocenylsilane / silica composite were prepared with different loadings of 1 and different pore sizes of MCM-41. To prepare composite 5a, 292 mg of ODA-MCM in a Schlenk tube was heated under vacuum (ca. 10⁻¹ Torr) to 250 °C over 4 h and held there for 2 h. The sample was cooled to room temperature then transferred to a glovebox. Monomer 1 (97 mg, 0.40 mmol) was added and mixed with the silica. After
standing under vacuum for 3 d, the powder appeared homogeneous and orange. The powder was transferred to a sublimer and sublimed under dynamic vacuum (ca. 10⁻³ Torr) at room temperature for 24 h. The absence of any sublimate indicated that there was no excess monomer in the sample. Composite 5b was prepared by the same procedure as for 5a, but 310 mg of ODA-MCM and 170 mg of 1 were used. No excess monomer was sublimed from the product. Composite 5c was prepared by the same procedure as for 5a, but 424 mg of ODA-MCM and 315 mg of 1 were used. During sublimation, a small amount of excess monomer was removed. Composite 5d was prepared by the same procedure as for 5a, but 1.070 g of CPM-MCM and 1.150 g of 1 were used. During sublimation, some excess monomer was removed.

**Data for 5a.** Yellow powder. PXRD: 42.7 (MCM-41, d₁₀₀), 24.7 (MCM-41, d₁₁₀), 21.4 (MCM-41, d₂₀₀), 16.1 (MCM-41, d₂₁₀), 6.3 (br halo, [fcSiMe₂]ₙ), 4 (br halo, SiO₂) Å. ¹H MAS NMR (2.8 kHz spin rate, 2 s recycle delay): δ = 0.0 (CH₃), 0.8 (CH₃), 1.2 (CH₃), 1.8 (SiOH), 4.0 (br, Cp) ppm. ¹³C CP-MAS NMR (10.5 kHz spin rate, 1 ms contact time, 2 s recycle delay): 0.6 (CH₃), 68.0 (Cp), 72.2 (Si-Cp). ²⁹Si CP-MAS NMR (5 kHz spin rate, 3ms contact time, 10s recycle delay): -108 (br, SiO₂), -6.5 ([fcSiMe₂]ₙ), 6.4 (CpSiMe₂O) ppm. UV-vis / near-IR: 2430w, 2389w, 2317w, 1759w, 1718w, 1665m, 627w, 459s, 336s, 262vs nm. Fe analysis: 3.45% Fe.

**Data for 5b.** Yellow powder. PXRD: d = 43.1 (MCM-41, d₁₀₀), 24.8 (MCM-41, d₁₁₀), 21.6 (MCM-41, d₂₀₀), 16.0 (MCM-41, d₂₁₀), 6.3 (br halo, [fcSiMe₂]ₙ), 4 (br halo, SiO₂) Å. ¹H MAS NMR (9 kHz spin rate, 10 s recycle delay): δ = 0.2 (CH₃), 1.7 (OH), 4.0 (Cp)
ppm. $^{13}$C CP-MAS NMR (9 kHz spin rate, 1 ms contact time, 2 s recycle delay): $\delta = -0.4$ (CH$_3$), 68.1 (Cp), 71.6 (Si-Cp) ppm.

**Data for 5c.** Yellow-orange powder. PXRD: $d = 42.7$ (MCM-41, d$_{100}$), 24.4 (MCM-41, d$_{110}$), 21.2 (MCM-41, d$_{200}$), 15.9 (MCM-41, d$_{210}$), 6.3 (br halo, [fcSiMe$_2$]$_n$), 4 (br halo, SiO$_2$) Å. $^1$H MAS NMR (7 kHz spin rate, 10 s recycle delay): $\delta = 0.2$ (CH$_3$), 1.0 (CH$_3$), 4.0 (Cp) ppm. $^{13}$C CP-MAS NMR (10 kHz spin rate, 1 ms contact time, 2 s recycle delay): $\delta = 0.4$ (br, CH$_3$), 15 - 50 (ipso-Cp), 68.2 (Cp), 72.0 (Si-Cp) ppm. $^{29}$Si CP-MAS NMR (5 kHz spin rate, 3 ms contact time, 2 s recycle delay): $\delta = -107$ (br, SiO$_2$). -6.8 ([fcSiMe$_2$]$_n$), 0.3, 6.9 (CpSiMe$_2$O) ppm. UV-vis / near-IR: $\lambda = 2430$w, 2392w, 2314w, 1762w, 1714w, 1666m, 1135w, 459s, 337m, 266vs nm. IR (KBr): 3101w (vC-H), 2963w (vC-H), 2903w (vC-H), 1422w, 1381w, 1367w, 1249s, 1167m, 1083vs (vSi-O), 901m, 818s, 796m, 666m, 452s cm$^{-1}$. Fe analysis: 5.41% Fe.

**Data for 5d.** Yellow-orange powder. PXRD: $d = 37.3$ (MCM-41, d$_{100}$), 21.7 (MCM-41, d$_{110}$), 18.7 (MCM-41, d$_{200}$), 6.3 (br halo, [fcSiMe$_2$]$_n$) Å, 4 (br halo, SiO$_2$). $^1$H MAS NMR (1.85 kHz spin rate, 2 s recycle delay): $\delta = -0.5$ (CH$_3$), 1.7 (CH$_3$), 4.0 (Cp) ppm. $^{13}$C CP-MAS NMR (7 kHz spin rate, 1 ms contact time, 2 s recycle delay): $\delta = 0.2$ (CH$_3$), 68.3 (Cp), 72.2 (Si-Cp) ppm. $^{29}$Si CP-MAS NMR (5 kHz spin rate, 3 ms contact time, 10 s recycle delay): $\delta = -107$ (br, SiO$_2$). -6.6 ([fcSiMe$_2$]$_n$), 0.1, 7.6 (CpSiMe$_2$O) ppm. UV-vis / near-IR: $\lambda = 2430$w, 2392w, 2316w, 1762w, 1714w, 1666m, 1205w, 1135w, 458s, 335m, 268vs nm.
7.3.3 Polymerization of 1 Within the Channels of MCM-41 to give Composite 6.

The fully loaded composite 5c (ca. 200 mg) was placed in a Schlenk flask and heated under N₂ to 140 °C in an oil bath for 4 h. A colour change from orange to yellow was observed and a small amount of ferrocene (identified by \(^{1}H\) NMR) sublimed onto the colder part of the glassware.

**Data for 6.** PXRD: \(d = 41.8\) (MCM-41, \(d_{100}\)). \(24.2\) (MCM-41, \(d_{110}\)). \(21.1\) (MCM-41, \(d_{200}\)). \(15.9\) (MCM-41, \(d_{210}\)). \(6.3\) (br halo, \([fcSiMe_{2}]_{n}\)). \(4\) (br halo, SiO₂) Å. \(^{1}H\) MAS NMR (10 kHz spin rate, 10 s recycle delay): \(\delta = 0.1\) (CH₃), \(1.6\) (OH), \(3.8\) (Cp) ppm. \(^{13}C\) CP-MAS NMR (10 kHz, 1 ms contact time, 2 s recycle delay): \(\delta = 0.0\) (CH₃), \(68.5\) (Cp), \(71\) (sh. Si-Cp) ppm. \(^{29}Si\) CP-MAS NMR (79.50 MHz, 6 kHz spin rate, 5 ms contact time, 10 s recycle delay): \(\delta = -108\) (br. SiO₂), \(-6.7\) ([fcSiMe₂]ₙ), \(0.2, 7.2\) (CpSiMe₂O) ppm. UV-vis / near-IR: \(\lambda = 2430w, 2395w, 2318w, 1666m, 1335w, 457s, 335m, 266vs nm. IR (KBr): \(\lambda = 3436w,br (vOH), 3097m (vC-H), 2967m (vC-H), 2929m (vC-H), 2874m (vC-H), 1420w, 1384w, 1249s, 1166m, 1083s,br (vSi-O), 904w, 818m, 700w, 679w, 568w, 451m cm⁻¹.

7.3.4 Synthesis of MCM-41 / fcSi(CH₂)₃ Composite 7.

A Schlenk tube containing 1.32 g of CPM-MCM was heated to 100 °C overnight, raised to 200 °C in 1 h, then held at 200 °C for 2 h under dynamic vacuum (ca. \(10^{-4}\) Torr). After the Schlenk tube was cooled to room temperature, the silica was transferred to a glovebox where 1.38 g (5.43 mmol) of spirocyclic [1]ferrocenophane 3 was added. The
Schlenk tube was then placed under static vacuum (ca. 10^{-4} Torr) for 5 d at room temperature. The colour of the mixture was observed to change from a white and red mixture to a white and orange powder in 1 d. and to a homogeneous orange powder after 3 d. Excess monomer was removed by sublimation at 45 °C under dynamic vacuum for 6 d.

Data for 7. Yellow powder. PXRD: d = 36.5 (MCM-41, d_{100}), 21.5 (MCM-41, d_{110}), 18.6 (MCM-41, d_{200}), 14.1 (MCM-41, d_{210}), 6 (br halo, [FeSi(CH_2)_3]_n), 4 (br halo, SiO_2) Å. $^1$H MAS NMR (5 kHz spin rate, 1 s recycle delay): δ = 0.2 (CH_2), 4.1 (Cp) ppm. $^{13}$C CP-MAS NMR (5 kHz spin rate, 5 ms contact time, 10 s recycle delay): δ = 14.6 (CH_2), 17.8 (CH_3), 68.3 (Cp), 72.2 (Si-Cp) ppm. $^{29}$Si CP-MAS NMR (5 kHz spin rate, 5 ms contact time, 10 s recycle delay): δ = -107 (br. SiO_2), 8.8 ppm. UV-vis: $\lambda$ = 453s, 270vs nm. IR (KBr): 3437m,br (vO-H). 3097w (vC-H). 2967m (vC-H). 2929m (vC-H). 2874w (vC-H). 1636w. 1420w. 1384w. 1249s. 1166m. 1083vs (vSi-O). 904w. 818m. 700m. 679m. 568m. 451s cm^{-1}. Fe analysis: 4.28% Fe.

7.3.5 Polymerization of 3 Within the Channels of MCM-41 to Give Composite 8.

A sample of 7 in a Schlenk flask was heated to 280 °C in 1 h and held at that temperature for 4 h under N_2. The solid was observed to change from yellow-orange to yellow-brown.
Data for 8. PXRD: \( d = 36.3 \) (MCM-41, \( d_{100} \)). 21.3 (MCM-41, \( d_{110} \)). 18.6 (MCM-41, \( d_{200} \)). 6.3 (br halo. \([cSi(CH_3)]_n\)). 4 (br halo. SiO\(_2\)) \( \AA \). \(^{13}\)C CP-MAS NMR (6 kHz spin rate. 5 ms contact time. 2 s recycle delay): \( \delta = 16.9 \) (CH\(_2\)). 68.4 (Cp). 72 (S-Cp) ppm. \(^{29}\)Si CP-MAS NMR (4 kHz spin rate. 5 ms contact time. 10 s recycle delay): \( \delta = -107 \) (br. SiO\(_2\)). -58 (w. br). -25 (br. R\(_2\)SiO\(_2\)). 5. 9 ppm. UV-vis / near-IR: \( \lambda = 1916 \text{w.} \ 1768 \text{w.} \ 1666 \text{m.} \ 460 \text{s.} \ 270 \text{vs.} \)

7.3.6 Pyrolysis of Composites 5a-d.

Samples 5a-d were pyrolyzed under the same conditions. Sample 5a (222 mg) was placed in a small pre-weighed quartz boat. The quartz boat was placed inside a tube furnace and purged with a nitrogen atmosphere. Under a slow flow of N\(_2\) (ca. 50 mL min\(^{-1}\)). the temperature was raised from room temperature to 900 °C over 8 h and was held at 900 °C for 2 h. The product was a brown powder (yield 190 mg, 86%). During the pyrolysis. a small amount of ferrocene (identified by \(^1\)H NMR) condensed on the cold part of the quartz tube. Samples 5b-d were pyrolyzed under the same conditions to give ceramics 9b-d. respectively.

Data for 9a. Ceramic yield: 86%. Brown powder. PXRD: \( d = 40.8 \) (MCM-41, \( d_{100} \)). 23.5 (MCM-41, \( d_{110} \)). 20.4 (MCM-41, \( d_{200} \)). 15.5 (MCM-41, \( d_{210} \)). 4 (br halo. SiO\(_2\)) \( \AA \).

Data for 9b. Ceramic yield: 80%. Fine black powder. PXRD: \( d = 40.8 \) (MCM-41, \( d_{100} \)). 23.6 (MCM-41, \( d_{110} \)). 20.5 (MCM-41, \( d_{200} \)). 4 (br halo. SiO\(_2\)) \( \AA \).
**Data for 9c.** Ceramic yield: 75%. Brown-black powder. PXRD: $d = 41.5$ (MCM-41. $d_{100}$), 23.9 (MCM-41. $d_{110}$), 20.8 (MCM-41. $d_{200}$), 15.7 (MCM-41. $d_{210}$), 4 (br halo. SiO$_2$), 2.0 (br halo. Fe) Å.

**Data for 9d.** Ceramic yield: 69%. Black powder. PXRD: $d = 33.0$ (MCM-41. $d_{100}$), 20.0 (MCM-41. $d_{110}$), 17.5 (MCM-41. $d_{200}$), 4 (br halo. SiO$_2$), 2.02 ($\alpha$-Fe, $d_{110}$) Å.

### 7.3.7 Pyrolysis of Composite 7.

Ceramic **10a** was prepared from the pyrolysis of 7 at 500 °C. A sample of 7 (206 mg) was placed in a quartz boat inside a tube furnace. The atmosphere was then purged with nitrogen. Under a slow flow of N$_2$ (*ca.* 50 mL min$^{-1}$), the sample was heated from room temperature to 500 °C in 4 h and maintained at 500 °C for 6 h. After cooling naturally to room temperature, the sample was weighed. Ceramic **10a** appeared as a light brown powder (161 mg, 78% yield). Ceramics **10b-e** were prepared by an identical procedure starting with 200-300 mg of 7, but the pyrolysis temperature and time was varied as listed in Table 1. Ceramic **10d** was prepared using a different sample of composite 7, one prepared under identical conditions.
Table 1. Pyrolysis Temperature, Duration, and Ceramic Yields for 10a-h.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>10a</td>
<td>500</td>
<td>6</td>
<td>78%</td>
</tr>
<tr>
<td>10b</td>
<td>600</td>
<td>6</td>
<td>81%</td>
</tr>
<tr>
<td>10c</td>
<td>800</td>
<td>6</td>
<td>84%</td>
</tr>
<tr>
<td>10d</td>
<td>900</td>
<td>6</td>
<td>80%</td>
</tr>
<tr>
<td>10e</td>
<td>1000</td>
<td>6</td>
<td>79%</td>
</tr>
<tr>
<td>10f</td>
<td>1000</td>
<td>1</td>
<td>85%</td>
</tr>
<tr>
<td>10g</td>
<td>1000</td>
<td>24</td>
<td>73%</td>
</tr>
<tr>
<td>10h</td>
<td>900</td>
<td>2(^a)</td>
<td>76%</td>
</tr>
</tbody>
</table>

\(^a\) Ramp to 900 °C in 8 h (for comparison with ceramics 5a-d)

**Data for 10a.** Light brown powder. PXRD: \(d = 37.2\) (MCM-41. \(d_{100}\)). 21.3 (MCM-41. \(d_{110}\)). 18.5 (MCM-41. \(d_{200}\)). 4 (br halo. SiO\(_2\)). Å.

**Data for 10b.** Dark brown powder. PXRD: \(d = 37.0\) (MCM-41. \(d_{100}\)). 21.5 (MCM-41. \(d_{110}\)). 18.6 (MCM-41. \(d_{200}\)). 4 (br halo. SiO\(_2\)). 2.2 (br halo. Fe) Å.

**Data for 10c.** Black powder. PXRD: \(d = 36.7\) (MCM-41. \(d_{100}\)). 21.0 (MCM-41. \(d_{110}\)). 18.4 (MCM-41. \(d_{200}\)). 4 (br halo. SiO\(_2\)). 2.1 (br halo. Fe) Å.

**Data for 10d.** Black powder. PXRD: \(d = 35.1\) (MCM-41. \(d_{100}\)). 20.4 (MCM-41. \(d_{110}\)). 17.8 (MCM-41. \(d_{200}\)). 4 (br halo. SiO\(_2\)). 2.1 (br halo. Fe) Å.
Data for 10e. Black powder. PXRD: \( d = 35.3 \) (MCM-41, \( d_{100} \)). 20.6 (MCM-41, \( d_{110} \)). 17.9 (MCM-41, \( d_{200} \)). 4 (br halo, SiO\(_2\)). 2.52 (Fe\(_3\)O\(_4\), \( d_{311} \)). 2.08 (\( \gamma \)-Fe, \( d_{111} \)). 2.03 (\( \alpha \)-Fe, \( d_{110} \)) Å.

Data for 10f. Black powder. PXRD: \( d = 35.0 \) (MCM-41, \( d_{100} \)). 20.5 (MCM-41, \( d_{110} \)). 17.7 (MCM-41, \( d_{200} \)). 4 (br halo, SiO\(_2\)). 2.5 (br halo, Fe\(_3\)O\(_4\), \( d_{311} \)). 2.07 (\( \gamma \)-Fe, \( d_{111} \)). 2.02 (\( \alpha \)-Fe, \( d_{110} \)). 1.79 (\( \gamma \)-Fe, \( d_{200} \)) Å.

Data for 10g. Gray powder. PXRD: 4.25 (quartz, \( d_{100} \)). 4.04 (cristobalite, \( d_{101} \)). 4 (br halo, SiO\(_2\)). 3.34 (quartz, \( d_{101} \)). 2.96 (Fe\(_3\)O\(_4\), \( d_{220} \)). 2.52 (Fe\(_3\)O\(_4\), \( d_{311} \)). 2.45 (quartz, \( d_{110} \)). 2.28 (quartz, \( d_{102} \)). 2.23 (quartz, \( d_{111} \)). 2.12 (quartz, \( d_{200} \)). 2.06 (\( \gamma \)-Fe, \( d_{111} \)). 2.02 (\( \alpha \)-Fe, \( d_{110} \)). 1.98 (quartz, \( d_{301} \)). 1.82 (quartz, \( d_{112} \)). 1.79 (Fe\(_3\)O\(_3\), \( d_{220} \)). 1.67 (quartz, \( d_{202} \)). 1.66 (quartz, \( d_{103} \)). 1.54 (quartz, \( d_{211} \)). 1.45 (quartz, \( d_{113} \)) Å.

Data for 10h. Black powder. PXRD: \( d = 35.4 \) (MCM-41, \( d_{100} \)). 20.6 (MCM-41, \( d_{110} \)). 17.8 (MCM-41, \( d_{200} \)). 2.53 (Fe\(_3\)O\(_4\), br \( d_{311} \)). 2.1 (br halo, Fe) Å.
7.3.8 Fitting Magnetization Data to the Langevin Function.

When superparamagnetic particles are present in a system, the isothermal magnetization vs. magnetic field data should obey the Langevin function (1):

\[
\frac{M}{M^S} = \coth\left(\frac{\mu H}{kT}\right) - \frac{kT}{\mu H} \tag{1}
\]

where \(M\) is the magnetization of the sample, \(M^S\) is the saturation magnetization, \(\mu\) is the average magnetic moment of the particles, \(H\) is the magnetic field, \(k\) is Boltzmann’s constant, and \(T\) is the temperature.\(^6\) When a distribution of particles with different magnetic moments, \(\mu\), is present, the magnetization may be represented as a sum of the individual Langevin functions.\(^6\) For example, if a bimodal distribution is present (small and large particles), then the data sets may be fit to the sum of two Langevin functions, equation (2):

\[
M = M^S_s \left[ \coth\left(\frac{\mu_s H}{kT}\right) - \frac{kT}{\mu_s H} \right] + M^S_l \left[ \coth\left(\frac{\mu_l H}{kT}\right) - \frac{kT}{\mu_l H} \right] \tag{2}
\]

where \(M^S_s\), \(M^S_l\), \(\mu_s\), and \(\mu_l\) distinguish the saturation magnetization and magnetic moment of the small and large particles, respectively.

\(M\) vs. \(H\) data obtained at 300 K for 9b-d were imported into SigmaPlot Version 3.02. As the magnetization data for each of the samples fit very poorly to equation (1), they were fit to equation (2). Initial estimates for \(M^S_s\), \(M^S_l\), \(\mu_s\), and \(\mu_l\) were made by solving a system of 4 equations in Mathcad 5.0 using representative data points. The variables were then refined by least squares to minimize \(\Sigma_i w_i(M_{\text{exp}} - M_{\text{calc}})^2\), where the weighting factor \(w_i\) for the \(i^{th}\) data point was equal to \(H_{i+1} - H_{i-1}\) (to compensate for the
uneven density of data points collected as a function of magnetic field). The points at highest and lowest field were weighted with $w_i$ equal to $2(H_i - H_{i-1})$ and $2(H_{i+1} - H_i)$, respectively. The curves fit well to two Langevin equations as signified by low $\chi^2$ values and correlation coefficients ($R^2$) close to 1. Each of the two components was resolved from the function and best-fit values of $M^S$, $M^L$, $\mu_S$, and $\mu_L$ are listed in Table 2.

If the particles are assumed to be spherical, to have the same density as the bulk phase, and to possess the same saturation magnetization as the bulk phase ($M^S_B$), then the average magnetic particle diameter, $D_{mag}$, can be calculated from the magnetic moment $\mu$ as follows:  

$$D_{mag} = \left( \frac{6 \mu}{\pi M^S_B} \right)^{1/3}$$  \hspace{1cm} (3)$$

For the calculations reported in this paper, the saturation magnetization values of Fe and Fe$_3$O$_4$ were assumed to be 1700 G and 480 G, respectively.

The histogram of particle size distribution was obtained by measuring about 150 particles in a TEM image. The standard deviation, $\sigma$, was calculated as the square root of the variance using the following equation:

$$\sigma = \sqrt{\frac{1}{N} \sum (D_i - D)^2}$$

where $D$ and $N$ are the average diameter and the number of particles, respectively. A single particle that was about twice the size of any other particle in the image was neglected. Moreover, particles smaller than ca. 2 mm in the image (2 nm) were not
included as they could not be easily distinguished from the sample roughness and granularity of the image.

7.4 Results and Discussion

7.4.1 Synthesis and Characterization of fcSiMe₂ / MCM-41 Composites 5.

The reaction of MeOH with [1]silaferrocenophane 1 leads to ring-opening addition of 1 to give FcSiMe₂OMe as shown in Scheme 1.²² This methodology has subsequently been used to derivatize amorphous and mesoporous silica, anchoring 1 to the reactive ≡SiOH sites present on the surface of the silica.²²,²³ O'Brien et al. treated MCM-41 with a pentane solution of 1 to obtain a maximum loading of 65 wt% 1 in the hydrated host.²³ Alternatively, ferrocenophane 1 may be introduced into MCM-41 by vapour deposition. Thus, dehydrated MCM-41 was combined with monomer 1 in a Schlenk tube under vacuum to allow the monomer to sublime into the channels. Initially, the heterogeneous mixture contained white powder and red crystals but changed to a homogeneous orange powder over several days. The products obtained after subliming excess monomer 1 at room temperature were investigated by Fe analysis, PXRD, solid-state ¹H MAS, ¹³C CP-MAS, and ²⁹Si CP-MAS NMR, IR, and reflectance UV-vis / near-IR spectroscopies.

From the synthesis of several samples, the maximum loading appeared to occur when a weight ratio of 74% (e.s.d. 5%) of 1 to host MCM-41 was used. Fe analysis of a representative sample that was completely loaded with 1 inside ODA-MCM (5c)
indicated that it contained 5.4 wt % Fe, corresponding to an organometallic content of only 24 wt % (31 mg of 1 per 100 mg of host). This is substantially less than the loading reported by O’Brien et al. where approximately 40 wt % of the organometallic species could be introduced into the MCM-41. A sample prepared starting with ca. 33 mg of guest per 100 mg of hydrated host (5a) was also analyzed. Fe analysis indicated that it contained 3.45 wt % Fe, corresponding to an organometallic content of 15 wt % (ca. 18 mg of guest 1 per 100 mg of host).

![Chemical structures]

Scheme 1

PXRD confirmed that all the samples contained no excess crystalline monomer. Moreover, the positions of the reflections assigned to calcined MCM-41 were essentially unchanged, indicating that the long-range hexagonal order of the mesoporous host was maintained. Samples prepared with mesoporous silica templated by both octadecyltrimethylammonium (ODA-MCM) and cetylpyridinium chloride (CPM-MCM) displayed a decrease in peak intensity upon filling the material with monomer 1 (Figure 1). This phenomenon results from a reduction in the electron contrast between the channel walls and channel interior and is consistent with loading of the channels in the
mesoporous material.\textsuperscript{27} Moreover, in the region of $2\theta = 12$-$16^\circ$, a new amorphous halo emerged that is characteristic of bulk amorphous poly(ferrocenylsilanes) (Figure 2).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Low-angle PXRD patterns of (i) 5c and (ii) calcined ODA-MCM illustrate the decreased intensity observed in the hexagonal reflections upon introducing 1 into the mesoporous silica host.}
\end{figure}

IR spectroscopy of the samples showed absorptions expected for vibrations of ferrocenylsilane moieties (e.g. Cp C-H stretching (3100 cm$^{-1}$), methyl C-H stretching (2963, 2903 cm$^{-1}$), C-C stretching (1422, 1381, 1367 cm$^{-1}$), C-H bending (1167 cm$^{-1}$)) and the silica framework (e.g. Si-O stretching (1083, 452 cm$^{-1}$, broad)). Upon further loading, the intensity of the peaks attributed to C-H stretching was noticed to increase relative to the Si-O stretching peak. Furthermore, the broad O-H stretching peak near
3400 cm\(^{-1}\) was noticeably more intense in the partially loaded sample 5a compared with the fully loaded sample 5c.

![Figure 2](image)

**Figure 2.** High-angle PXRD patterns of (i) ODA-MCM, (ii) sample 5c, and (iii) amorphous polymer 2.

Reflectance UV-vis spectra of the orange-yellow solids 5a-d were all very similar, showing an intense band near 260-270 nm, a weak band at 335-7 nm, and a strong band at 458-9 nm. The first band is attributed to a charge transfer band, while the latter two bands are d-d transitions characteristic of the ferroceny1 moieties. The frequency of the low-energy transition is blue shifted relative to monomer 1 (\(\lambda_{\text{max}} = 487\))
nm in CH$_2$Cl$_2$). characteristic of ring-opened ferrocenophanes.$^{28}$ Although sample 5e showed a small amount of unreacted monomer in the solid-state NMR, its d-d absorption is similar to the others: there is probably only a very small amount of free monomer in the material. The presence of a weak absorption at 627 nm in 5a signaled the presence of trace ferrocenium moieties. possibly generated from protonation of Fe(II) from acidic silanol groups within the sample. Reflectance near-IR spectroscopy showed resonances at ca. 1666 nm (6000 cm$^{-1}$), 1715 nm (5830 cm$^{-1}$), and 1762 nm (5675 cm$^{-1}$), corresponding to the first overtone for vC-H stretching for Cp, CH$_3$ (sym), and CH$_3$ (asym), respectively.

Solid-state $^1$H MAS, $^{13}$C CP-MAS, and $^{29}$Si CP-MAS NMR were important for monitoring the loading of 1 into the MCM-41. Figure 3 shows the $^1$H MAS NMR spectra of the composites as 1 was loaded into the channels of ODA-MCM. The partially loaded composite, 5a, shows several peaks that are attributed to protons of ferrocenyl, methyl, and O-H groups in the channels of MCM-41. Upon full loading with 1, nearly all of the O-H sites have reacted with monomer to form ring-opened species. The $^{13}$C CP-MAS NMR spectra of the same series is shown in Figure 4. A partially loaded sample (5a) of MCM-41 showed resonances consistent with ring-opened species, showing only a broad methyl resonance near 0 ppm, a free Cp resonance at 68.0 ppm, and other Cp resonances near 72 ppm. When loaded with excess monomer, several new resonances emerged between 16-50 ppm and are attributed to the ipso-C of the Cp ligands in 1 present in different chemical environments in the composite.
Figure 3. $^1$H MAS NMR spectra of (i) 5a, (ii) 5b, and (iii) 5c.

Figure 4. $^{13}$C CP-MAS NMR spectra of (i) 5a, (ii) 5b, and (iii) 5c.
$^{29}$Si CP-MAS NMR spectra of each of the samples examined showed resonances at 100-120 ppm, near 7 ppm, and near -7 ppm. $^{29}$Si CP-MAS NMR spectra of composites 5a and 5c are shown in Figure 5. Q3 (SiO$_3$(OH)) and Q4 (SiO$_4$) resonances of silica are observed at 100-120 ppm. There was a noticeable decrease in the intensity of resonances assigned to Q3 silicon atoms (ca. -100 ppm) upon loading the channels with monomer 1. This would be expected if monomer 1 reacted with the silanol groups on the surface. Although the use of cross-polarization limits the quantification of these Si assignments, the same observation has been made by others. The chemical shift of 7 ppm is assigned to CpSiMe$_2$O environments by comparison with similar species in the literature.$^{29}$ These sites are attributed to either ferrocenophane 1 attached to the silica via ring-opening addition of a silanol group to the Si-Cp bond, or to oligomers attached to the surface of the silica via an Si-O-Si linkage. The narrow resonance at ca. -7 ppm is assigned to oligomers and polymer 2, [fcSiMe$_2$]$_n$ (cf. $^{29}$Si NMR of [fcSiMe$_2$]$_n$: $\delta = -6.4$ ppm in C$_6$D$_6$).$^{13}$ In all of the spectra, the resonance near -7 ppm is much narrower than the one near 7 ppm. This disparity has been attributed to enhanced motion of the Si atoms in the oligomer and polymer components compared with the ring-opened monomer tethered to the channel wall.$^{23b}$ Samples 5c and 5d also showed a smaller resonance near 0 ppm, a signal that was not observed in the partially loaded sample 5a. We have not been able assign this peak with certainty, but we speculate that it could arise from (FeSiMe$_2$)$_2$O trapped inside the channels ($^{29}$Si NMR of (FeSiMe$_2$)$_2$: $\delta = 0.4$ ppm).$^{30}$ This compound could form in the presence of any water in the silica (Scheme 2) and would be retained in the pores. Ferrocenophane 1 would be expected to react much faster with acidic silanol groups inside the channel than with water, explaining why the partially
loaded sample, which still contained a substantial number of O-H groups, did not show this disiloxane species. In addition, O’Brien et al. did not observe the disiloxane by solid-state NMR because it would have been washed from the sample in the solution phase preparation.²³

![Scheme 2](attachment:scheme2.png)

**Figure 5.** $^{29}$Si CP-MAS NMR spectra of (i) 5a and (ii) 5c.
Our evidence suggests that ring-opened species and oligomeric products, bound to the SiO₂, are present inside the channels of MCM-41 (Scheme 3). This is consistent with the NMR and EXAFS results of O’Brien et al. At very high loading, free monomer can be trapped inside the channels. We investigated the polymerization of free 1 within the channels of MCM-41.

Scheme 3
7.4.2 Polymerization of 1 in MCM-41.

When 1 was heated at 10 °C min⁻¹ in a differential scanning calorimeter, the ferrocenophane was observed to melt near 75 °C and then undergo exothermic ROP ($\Delta H_{\text{ROP}} = -330(20)$ J g⁻¹). When a sample of 5e was investigated by DSC, a broad exotherm corresponding to ring-opening polymerization of 1 was observed between 75 and 200 °C (Figure 6). The absence of an endothermic melting transition for 5e indicates that the free monomer was not crystalline, in contrast to bulk 1. This is consistent with the absence of high-angle diffraction peaks in the PXRD of 5e. Monomer trapped within the narrow channels of MCM, where ring-opened monomeric and oligomeric species are tethered to the walls, would probably be unable to crystallize. The breadth of the ROP exotherm may result from the inhomogeneity of the trapping sites of 1 inside MCM. Integration of the curve from DSC scans of 5e indicated an enthalpy change of 6(2) J g⁻¹. Given that the enthalpy of polymerization of 1 is ca. -330 J g⁻¹ (refs. 13, 31) and that 5e contained ca. 31 mg of 1 per 100 mg of host (from Fe analysis), sample 5e contained approximately 2 wt % of free monomer 1 (i.e., ca. 8% of monomer 1 introduced into the channels of MCM-41 was present as free monomer).
To examine the bulk polymerization, a sample of $5c$ was heated at 140 °C under N$_2$ for 4 h to give a yellow solid. 6. $^1$H MAS NMR, $^{29}$Si CP-MAS NMR, and PXRD of the polymerized sample were essentially identical to those for sample $5c$. Moreover, the reflectance UV-vis / near-IR spectrum of 6 was nearly the same as that of $5c$, with the d-d transition observed at 457 nm. However, the $^{13}$C CP-MAS NMR spectrum of the polymerized sample showed no $ipso$-C atoms present using the same NMR acquisition parameters as for $5c$. These results are consistent with the ROP of a very small amount of excess 1 within the channels of MCM-41.
7.4.3 Synthesis and Characterization of FeSi(CH₂)₃ / MCM-41 Composite 7.

We have recently shown that ceramic yields from poly(ferrocenyisilanes) are drastically improved when the polymer is crosslinked.¹⁸ When a sample of 3 was polymerized and subsequently pyrolyzed, the polymer was transformed into a ceramic in 90% yield.¹⁸ Incorporation of 3 into MCM-41 should give an improved ceramic precursor if it undergoes crosslinking, perhaps facilitating the synthesis of extractable ceramic nanofibres in the channels. The composites were prepared by vapour deposition using a similar procedure to that used to incorporate 1 into MCM-41. Initial attempts to remove excess monomer by room-temperature sublimation showed crystalline monomer in the powder X-ray diffractogram and Fe-containing material on the outside of the MCM-41 in TEM images of the pyrolyzed composite. However, sublimation at ca. 45 °C removed all excess monomer from the product. Fe analysis of a representative sample indicated that the sample contained 4.3 wt % Fe, corresponding to an organometallic content of 20 wt % (i.e. 24 mg of 3 per 100 mg of host). The composite was investigated by PXRD, ¹H MAS NMR, ¹³C CP-MAS NMR, ²⁹Si CP-MAS NMR, reflectance UV-vis, and IR spectroscopies.

PXRD confirmed that the long-range order of the hexagonal mesoporous material was maintained. Like 5a-d, composite 7 showed decreased PXRD intensities when compared to the calcined MCM-41, consistent with impregnation of the monomer into the channels. A broad halo observed at 10-20° 2θ is characteristic of amorphous poly(ferrocenyisilanes).

Figure 7 shows the results of solid-state NMR studies of 7. The ¹H MAS NMR spectrum of 7 showed a single broad resonance near 4 ppm. It is noteworthy that the
peak is substantially narrower than the same peak observed in polymerized 3, indicative of enhanced mobility. In the $^{13}$C CP-MAS NMR spectrum of 7, broad peaks centered at 17.8 ppm and 14.6 ppm are assigned to the silacyclobutane group. Peaks at 68.3 ppm and 72.2 ppm are assigned to Cp and SiCp resonances, respectively. The presence of a free Cp ligand is consistent with ring-opening addition of silanol groups to the Si-Cp bond of monomer 3 inside MCM-41. $^{29}$Si CP-MAS NMR of 7 showed broad resonances at 8.8 ppm and 107.6 ppm, assigned to Si from ring-opened 7 and MCM-41, respectively. The NMR results are consistent with monomer that has been ring-opened by the silanol groups to afford ring-opened monomeric and oligomeric species within the mesoporous host. For comparison, the $^{29}$Si NMR resonance for [FcSi(CH$_2$)$_3$]$_2$O is observed at 0.54 ppm in C$_6$D$_6$.

Reflectance UV-vis spectroscopy was useful to understand the state of monomer 3 in composite 7. Whereas 3 shows an absorption at 478 nm for a d-d transition, the corresponding peak is observed at 453 nm in 7. The apparent blue shift of this absorption is consistent with the ring-opening of the [1]ferrocenophane.$^{28}$ For comparison, [FcSi(CH$_2$)$_3$]$_2$O, which structurally resembles ring-opened monomer 3 attached to silica, has $\lambda_{\text{max}}$ = 451 nm in CH$_2$Cl$_2$.$^{32}$ A charge transfer band observed at 299 nm in monomer 3 was observed at 270 nm in composite 7, consistent with a substantial structural change in the ferrocenyl moiety upon incorporation into MCM-41.
Figure 7. (a) $^1$H MAS NMR spectra, (b) $^{13}$C CP-MAS NMR spectra, and (c) $^{29}$Si CP-MAS NMR spectra of monomer 3, polymer 4, and composite 7.

Diagram showing various NMR spectra with peaks at different ppm values.
IR spectroscopy of 7 was consistent with the presence of ferrocenylsilane moieties inside MCM-41. Modes attributed to vC-H stretching were observed at 3097 cm\(^{-1}\) for the Cp ligands and 2967 cm\(^{-1}\), 2929 cm\(^{-1}\), and 2874 cm\(^{-1}\) for the methylene groups. The high frequency of the first aliphatic C-H stretch is characteristic of a closed silacyclobutane ring in which the symmetric vC-H stretching frequency is elevated due to the ring strain.\(^{33}\) For comparison, monomer 3 shows aliphatic vC-H stretching modes at 2970 cm\(^{-1}\), 2943 cm\(^{-1}\), 2924 cm\(^{-1}\), and 2867 cm\(^{-1}\).

These results are consistent with the presence of ring-opened monomer 3 and oligomers tethered to the walls of the mesoporous host with the silacyclobutane rings intact. To clarify whether the silacyclobutane rings were still closed, a bulk polymerization of 7 was undertaken.

### 7.4.4 Polymerization of 3 in MCM-41.

Our previous studies of [FcSi(CH\(_2\)]\(_3\)]\(_2\)O have indicated that this monomer undergoes thermal ROP of the silacyclobutane rings at 240 °C.\(^{32}\) To test if the silacyclobutane rings in composite 7 would undergo ROP, a sample of 7 was heated under nitrogen at 280 °C for 4 h, changing colour from yellow-orange to yellow-brown. The solid-state \(^{13}\)C CP-MAS NMR spectrum of the resulting material 8 was similar to composite 7, showing a very broad peak centred at 17 ppm (CH\(_2\) resonances) and a sharp peak at 68.4 ppm (free Cp) with a shoulder at ca. 72 ppm (Si-Cp). However, the \(^{29}\)Si CP-MAS NMR spectrum of 8 was substantially changed from that of 7, showing broad peaks at ca. -107, -58, -25, 5, and 9 ppm assigned to SiO\(_2\) (host), [RSiO\(_3\)] (host), [R\(_2\)SiO\(_2\)]
(guest). [R₃SiO] (guest) and [R₂SiO] (guest), respectively. These new peaks are consistent with ring-opening of silacyclobutane within the channels. The small amount of RSiO₃ observed likely arises from -CH₂SiO₃ groups, where a reactive silacyclobutane has reacted with a silicon of the host. All of the peaks in the NMR spectrum are broad, indicating that the species are immobile as expected for crosslinked polymers and monomers pinned to the channels. IR spectroscopy of 8 indicated small structural changes to the ferrocenylsilane encapsulated in the MCM-41. In the aliphatic C-H stretching region, peaks were observed at 2962 cm⁻¹ (ν₃ CH₃), 2932 cm⁻¹ (νₛ CH₂), and 2876 cm⁻¹ (νₛ CH₂ and CH₃). Moreover, a reduction in intensity of the O-H stretching frequency (ca. 3450 cm⁻¹, broad) was observed in 8 relative to 7. These results suggest that the silacyclobutane rings in 7 have opened after thermal treatment, but have reacted at least partially by O-H ring-opening addition to the Si-CH₂ bond, forming a propyl group on silicon (Scheme 4). This may be accompanied by ring-opening polymerization of the silacyclobutanes, but polymeric carbosilane could not be distinguished from the silacyclobutane groups ring-opened with terminal silanol groups present in the MCM-41.

Scheme 4
7.4.5 Pyrolysis Study of 5a-d.

We have previously reported the pyrolysis of poly(ferrocenylsilanes) to afford ceramics containing Fe particles inside an Si/C matrix.\textsuperscript{15} By pyrolyzing composites 5, we hoped to form iron nanostructures confined to the channels of MCM-41. Samples of 5a-d were heated at 900 °C for 2 h under a slow flow of N\textsubscript{2} to yield ceramics 9a-d. The yellow powder was transformed into a fine black powder that was attracted to a magnet. A small amount of ferrocene sublimed from the material during the pyrolysis and collected on the cold part of the pyrolysis tube. Ceramic yields of 69-86% were obtained. The highest yields for the lowest loadings of 1 in MCM as expected since pristine calcined MCM-41 shows very little mass loss up to 900 °C.
Figure 8. PXRD patterns of (i) composite 5b and (ii) ceramic 9b showing the (a) low-angle and (b) high angle transformations that occur.
Figure 8 shows the PXRD patterns of a composite before and after pyrolysis. At low angles, PXRD revealed a contracted interpore distance resulting from the condensation polymerization of residual SiOH groups in the silica channels. An enhanced peak intensity relative to the loaded sample is consistent with a structural improvement of the channel walls and the loss of considerable electron density from within the channels as the polymer was transformed into a ceramic. At higher angles, the amorphous halo attributed to the ferrocenylsilane polymer ($2\theta = 14^\circ, d = 6.3 \text{ Å}$) has disappeared from the ceramic and a new broad peak near $2\theta = 45^\circ$ ($d = 2.03 \text{ Å}$) has emerged. This latter peak is assigned to the (110) reflection of $\alpha$-Fe. As a consequence of the very small $\alpha$-Fe particle sizes in the sample, the peak is substantially broader (e.g. full width at half maximum (FWHM) for $9b$ was $\Delta\theta = 6.2(4)^\circ$) than for bulk $\alpha$-Fe (FWHM $\sim 0.18^\circ 2\theta$). The Scherrer equation (4) was employed to calculate the particle size of the Fe nanocrystallites:\textsuperscript{34}

$$L_{hkl} = \left[0.9 \frac{\lambda}{B \cos \theta}\right]$$ (4)

where $L_{hkl}$ is the average diameter of the crystallites, $B = \left[B_{\text{measured}}^2 - B_{\text{standard}}^2\right]^{1/2}$ is the root mean square difference between the angular FWHM for the sample with respect to a powder Fe standard (in radians), $\lambda$ is the wavelength of the X-ray radiation, and $\theta$ is the Bragg angle for the reflection (in radians). Fe$_3$O$_4$ and Fe were evident in $9a$, but only Fe was evident by PXRD in $9b$-$d$. It was assumed that the Fe nanoparticles were only $\alpha$-Fe, though the peaks were broad enough to hide the 111 reflection of $\gamma$-Fe. Peaks were fitted several times with standard peak fitting software to give an estimate of the error in the FWHM. Using the Scherrer equation, we calculated particle sizes of 28(2), 31(2), and
41(5) Å for samples 9b, 9c, and 9d, respectively. The nanoparticles in 9b and 9c are virtually identical in size and appear to be confined to the channels of the mesoporous host. As the pore diameter of the silica in 9d is smaller than in 9b and 9c, but the Fe particles are larger, the nanoclusters may have grown out of a single channel in 9d.

It is worth noting how the pyrolysis of the poly(ferrocenylsilane) within the ordered channels of mesoporous silica differs from the bulk pyrolysis of 2. The Fe nanoparticles obtained in MCM-41 are substantially smaller than the particles obtained from the bulk pyrolysis. Also, neither graphite nor α-Si₃N₄ were observed in the pyrolyses, compositions that were obtained from the bulk pyrolysis of 2.¹⁵

The samples were imaged by transmission electron microscopy (TEM) and electron diffraction (ED). Figure 9 shows a TEM image of ceramic 9d. Fe nanoparticles are confined to the channels, though some "appear" to be larger than a single channel. A particle size distribution could not be determined from the TEM images due to the difficulty of distinguishing the edges of particles from the silica walls. The mesostructured order of the MCM-41 host material was evidently maintained at even 900 °C. The walls appeared slightly thicker and showed greater electron contrast than MCM-41 itself. This is consistent with the structural improvement and contraction of the host.
Figure 9. TEM image of ceramic 9d.

An electron diffraction pattern of the ceramic composite 9e is shown in Figure 10. The observation of electron diffraction up to the third order (300) indicates the excellent structural order of the hexagonal mesostructure. From the ED pattern, the $d_{100} \approx 45 \text{ Å}$ spacing is similar to the value obtained from PXRD ($d_{100} \approx 42 \text{ Å}$).
Figure 10. Electron diffraction of 9c reflects the hexagonal order in the ceramic.

We attempted to obtain the Fe and Si distribution in samples from high-resolution TEM line scans across the channels of the host. While preliminary scans showed the Fe was inside the channels, the sample decomposed under the electron beam before a suitable signal to noise ratio could be obtained.

Powder X-ray diffraction of the samples indicated that the α-Fe particles are small enough to be superparamagnetic. To further understand the magnetic properties of these materials, we examined ceramics 9b-d by superconducting quantum interference device (SQUID) magnetometry.

7.4.6 Magnetization Measurements.

There are several experimental criteria that are used to determine if a sample contains superparamagnetic particles. The temperature-dependent magnetization will exhibit a cusp at the blocking temperature ($T_b$) in the zero-field-cooled (ZFC) magnetization. When cooled in the absence of a magnetic field (zero-field cooling), the
magnetic moments will initially be spatially locked in random orientations. When a weak external magnetic field is then applied, the moments may slowly align (Boltzmann equilibration) and will remain aligned until the temperature is increased above $T_b$. Above $T_b$, the thermal energy overpowers the ordering effect of the magnetic field and the net magnetization of the sample decreases. Thus, the magnetization curves will display hysteresis below $T_b$, but no hysteresis above $T_b$. Finally, the plots of $M$ versus $H/T$ should superimpose in the superparamagnetic regime.

Figure 11 shows the temperature-dependent magnetization data for the zero-field-cooled susceptibility of 9b-d. All of the samples show cusps in their ZFC magnetizations, with the maxima ($T_b$) centered at ca. 30 K for 9b and 9c, and ca. 45 K for 9d. A field-cooled (FC) curve of sample 9d was not superimposable upon the ZFC curve below the blocking temperature.

Field-dependent magnetization data were obtained for 9b, 9c, and 9d at several temperatures. Figure 12 shows hysteresis curves for 9c. While hysteresis was not observed at room-temperature, the materials all showed hysteresis below 40 K. Sample 9b showed essentially the same magnetization data as 9c.

Figure 13 shows a plot of $M$ vs. $H/T$ for 9c at 100 K, 200 K, and 300 K. The curves match very closely at low field, but deviate substantially from perfect superposition at higher field.
Figure 11. Zero-field-cooling (ZFC) curves of (a) 9b, (b) 9c, and (c) 9d at 100 G.
Figure 12. Isothermal magnetization curves of ceramic 9c at (a) 5 K, (b) 25 K, (c) 40 K, and (d) 300 K.
Figure 13. Plot of \( M \) vs. \( H/T \) for \textbf{9c} at 100 K, 200 K, and 300 K.

The absence of both saturation at high magnetic fields and room-temperature hysteresis in the magnetization curves indicated the particles were superparamagnetic and the magnetization should be described by the Langevin equation (1). In a distribution of particles sizes, the low-field component of the Langevin function is primarily affected by large particles and the high-field component is most sensitive to the small particles in the system.\(^6\) The magnetization data for the superparamagnetic materials were fit to a Langevin function assuming the particles were essentially monodisperse within the channels. As the data fit poorly to a single Langevin function, the data were fit to a sum of two Langevin functions (eq. 2). Honda \textit{et al.} have used this equation in their treatment
of Fe nanoparticles in alumina and silica substrates. This extension of the Langevin function is reasonable when a bimodal distribution of grain sizes is present or when particles of two magnetic materials are present.

To analyze the data, it was essential to make some approximations, which may not necessarily be valid. First, the particles were assumed to be precisely bimodal, spherical, and to possess isotropic magnetization, though the inherent geometry of the silica channels and the iron structure may introduce a large degree of magnetic anisotropy. They were also assumed to be isolated, non-interacting particles. There may be a variety of magnetic phases in the material (e.g. FeC, Fe3O4, FeSi3Oy, Fe5Si2, and FeN,) that could contribute to the magnetization, but these were ignored. In addition, the diamagnetism of the silica and pyrolyzed organosilicon products were assumed to be negligible.
Figure 14. Magnetization data for 9c (at 300 K) fit to the Langevin function. The upper trace shows the data points (○) and the fit curve (solid). The two Langevin components of the fit are shown below (dashed).

Figure 14 shows the plot of M versus H at 300 K along with the components of the Langevin function (2) for ceramic 9c. Magnetization parameters are summarized in Table 2. Figure 15 illustrates two possible models to explain the bimodal nature of the particle distribution. As only α-Fe was observed in the PXRD patterns of 9b-d, it was first assumed that the particles were α-Fe. From the calculated fit to the bimodal Langevin function (2), the largest Fe particles had diameter 50-64 Å and the smaller
particles had diameter 28-36 Å (Table 3). If a bimodal distribution of Fe nanoparticles is in fact present, the particles sizes approximately represent clusters confined to a single channel (ca. 40 Å) and to two channels. The latter could form if the silica between two particles in adjacent channels was disrupted.

**Table 2.** Summary of Magnetization Parameters for 9b-d From Fitting to the Langevin Function.

<table>
<thead>
<tr>
<th></th>
<th>9b</th>
<th>9c</th>
<th>9d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data Points</td>
<td>34</td>
<td>23</td>
<td>31</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9995</td>
<td>0.9997</td>
<td>0.9993</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>0.021</td>
<td>0.0032</td>
<td>0.067</td>
</tr>
<tr>
<td>$M_s$ (emu g$^{-1}$)</td>
<td>0.66(2)</td>
<td>0.52(2)</td>
<td>1.84(7)</td>
</tr>
<tr>
<td>$\mu_s / kT$ (G)</td>
<td>0.00051(2)</td>
<td>0.00047(2)</td>
<td>0.00103(4)</td>
</tr>
<tr>
<td>$M_I$ (emu g$^{-1}$)</td>
<td>0.63(2)</td>
<td>0.50(2)</td>
<td>1.44(7)</td>
</tr>
<tr>
<td>$\mu_I / kT$ (G)</td>
<td>0.0028(1)</td>
<td>0.0027(1)</td>
<td>0.0057(4)</td>
</tr>
</tbody>
</table>

**Table 3.** Fe Particle Sizes and Oxide Thickness.

<table>
<thead>
<tr>
<th></th>
<th>9b</th>
<th>9c</th>
<th>9d</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{mag}$ (Å) of Small Fe Particles</td>
<td>28.7(0.4)</td>
<td>28.0(0.5)</td>
<td>36.3(0.5)</td>
</tr>
<tr>
<td>$D_{mag}$ (Å) of Large Fe Particles</td>
<td>50.9(0.7)</td>
<td>50.0(1.0)</td>
<td>64.4(1.4)</td>
</tr>
<tr>
<td>Oxide Thickness (Å)</td>
<td>4.5(0.8)</td>
<td>4.4(1.0)</td>
<td>5.8(1.4)</td>
</tr>
</tbody>
</table>

More likely, the smaller superparamagnetic contribution may arise from an oxide layer on the Fe particles (Figure 15b). If a spherical surface coating of Fe$_3$O$_4$ (the only
oxide phase observed in any of our experiments) is assumed, then the particles possess oxide layers that are 4-6 Å in thickness (Table 3). This oxide layer could simply be the Fe-SiO₂ interface between the nanoparticles and the channel wall. Other researchers have noted that magnetic particle sizes (D_{mag}) may overestimate the particle size measured by TEM by up to 40% due most likely to particle interactions.¹c Thus, the Fe nanoparticles for 9b-c (D_{mag} ~ 50 Å in diameter) may actually be confined to a single channel (diameter of ~ 40 Å). There are clearly larger particles present in 9d that could form by merging particles in adjacent channels of MCM-41. These results are in agreement with the data obtained from PXRD (Table 4).

Table 4. Comparison of Particle Sizes Determined by PXRD and Magnetization.

<table>
<thead>
<tr>
<th></th>
<th>9b</th>
<th>9c</th>
<th>9d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe Particle Size From PXRD (Å)²</td>
<td>28(2)</td>
<td>31(2)</td>
<td>41(5)</td>
</tr>
<tr>
<td>Fe Particle Size From Magnetization (Å)</td>
<td>50.9(0.7)</td>
<td>50.0(1.0)</td>
<td>64.4(1.4)</td>
</tr>
<tr>
<td>Channel Diameter From PXRD (Å)³</td>
<td>47</td>
<td>48</td>
<td>38</td>
</tr>
</tbody>
</table>

² From Scherrer equation

³ This is calculated from a₀ = 2d_{100} / √3 for a hexagonal lattice. Note that the quoted channel diameter does not account for the width of the silica wall.
Figure 15. Two proposed models to explain the observed magnetization data for magnetic particles in MCM-41. (a) A bimodal distribution of Fe nanoparticles and (b) Fe nanoparticles contained in an iron-silicate shell.

The magnetization behaviour of samples 9b and 9c were remarkably similar, suggesting that the choice of host silica affected the magnetic particles obtained from the pyrolysis. Moreover, the calculated particle sizes for 9b-c were smaller than for 9d, in agreement with the observation of a lower blocking temperature by zero-field-cooling magnetization measurements for 9b-c. The particle sizes calculated from the Langevin function are consistent with the relative blocking temperatures and particle sizes calculated from PXRD for 9b-d.
7.4.7 Pyrolysis Study of 7.

Samples of 7 were pyrolyzed under nitrogen for various times to examine the changes that occur to the ceramic: conditions are summarized in Table 1. After pyrolysis, powders (10) were obtained in 73-85% yields.

The pyrolysis of 10 was monitored by PXRD. Figure 16 shows the PXRD patterns of 10a-e in low 2θ and high 2θ regions. Though the silica underwent contraction during heating, the hexagonal mesoporous structure of the host silica was maintained up to 1000 °C. PXRD indicated that the ferrocenylsilane guest had already undergone a large structural transformation by 500 °C as the broad amorphous halo at d = 6.3 Å, a signature of ferrocenylsilanes, had disappeared, leaving only the amorphous halo at d = 4 Å characteristic of SiO₂. A peak that has been assigned to the d₄₁₀ of α-Fe first emerged at 600 °C and grew to 900 °C. In the PXRD pattern of the sample prepared at 1000 °C (10e), peaks assigned to both the high temperature bcc Fe (γ) and low temperature fcc Fe (α) were apparent, as well as a peak due to magnetite, Fe₃O₄.

Figure 17 shows TEM images of 10b and 10e. The ceramic prepared at 600 °C (10b) shows very small Fe nanoparticles that appear confined to single channels. In the sample prepared at 1000 °C, however, the particles are much larger and nearly round. The particles visible in the TEM image were counted and are plotted in a histogram in Figure 17c. The particles size distribution is monomodal and the average particle size was calculated to be 10.8 ± 3.9 nm (histogram in Figure 17c). Using the Scherrer equation, the size of the Fe particles were ca. 20-40 nm in diameter. This clearly overestimates the size observed in the TEM micrograph. There may be larger particles, which were not observed by TEM, that contribute significantly to the particle size.
determined by PXRD. The Fe$_3$O$_4$ observed in the PXRD pattern may exist as a surface coating on the Fe particles.

Samples were pyrolyzed at 1000 °C for different lengths of time and examined by PXRD (Figure 18). After 6 h at 1000 °C, the mesoporous structure was still present in the sample (10f), though the intensity of the peaks was suppressed relative to the sample prepared for 2 h (10e). Both α-Fe and γ-Fe as well as Fe$_3$O$_4$ were present in this sample. After 24 h of pyrolysis at 1000 °C, however, an enormous change had occurred to the composite structure. No evidence for mesoporosity was apparent in the PXRD pattern of the material. 10g. Moreover, the amorphous halo at d = 4 Å, attributed to SiO$_2$, was less intense, giving way to crystalline quartz and cristobalite in the sample. Both forms of Fe as well as magnetite were still present in the sample. This is, to our knowledge, the first observation of the transformation of mesoporous silica to quartz.

Finally, a sample of 7 was pyrolyzed under the same conditions as 9d was prepared. Although the ceramic yield was slightly higher for 10h than for 9d, there appears to be no substantial difference between the products prepared when monomer 1 or 3 is inside the mesoporous silica. Ceramic 10h showed a broad halo near 2.1 Å, consistent with α-Fe and some Fe$_3$O$_4$. 
**Figure 16.** PXRD patterns for calcined CPM-MCM, composite 7, and ceramics 10a-e at (a) low angles and (b) high angles. (Note that 10d was prepared using a different sample of composite 7 from the others.)
Figure 17. TEM images of (a) ceramic 10b prepared at 600°C and (b) ceramic 10e prepared at 1000 °C which show Fe nanoparticles in the ordered channels of MCM-41. (c) A histogram of the particle distribution as measured from a TEM image of sample 10e.
Figure 18. PXRD patterns for ceramics 10e-g at (a) low angles and (b) high angles.
7.5 Conclusions

Composite materials of mesoporous silica and poly(ferrocenylsilanes) have been prepared and characterized. The monomer fcSiMe₂ (1) is ring-opened by surface silanol groups to form ring-opened monomeric, oligomeric, and polymeric species as well as trapped monomeric species in the channels of MCM-41. These composites may be pyrolyzed to generate Fe nanoclusters embedded in the mesoporous silica. A combination of PXRD, TEM, ED, and SQUID magnetization measurements has provided compelling evidence that the organometallic polymer and superparamagnetic Fe nanoclusters are encapsulated inside the ordered structure of MCM-41. Moreover, magnetization data suggests that the Fe nanoclusters in the channels are capped with a thin oxide layer from the silica wall.

Spirocyclic [1]ferrocenophane 3 has also been incorporated into the channels of MCM-41. The transformation of the inorganic-organometallic composite material to a magnetic ceramic was investigated by PXRD. Between 600 and 900 °C, α-Fe nanoparticles formed inside the mesoporous silica. At 1000 °C, γ-Fe and magnetite (Fe₃O₄) were also apparent in the material. After 24 h at 1000 °C, the material had lost all hexagonal mesoporosity and transformed into crystalline quartz, cristobalite, magnetite, and iron.

We have shown that the size of Fe nanoparticles obtained from the pyrolysis of poly(ferrocenylsilanes) can be controlled with a mesostructured host. Whereas very large, ferromagnetic Fe particles were obtained from the bulk pyrolysis of 2 (R = Me).
only superparamagnetic Fe nanoparticles were observed when the pyrolysis was performed inside the channels of hexagonal MCM-41. This demonstrates that the dimensions of the silica channels control the nucleation and growth processes of the nanostructured Fe particles.

7.6 References


(18) MacLachlan, M. J.; Ginzburg, M.; Raju, N. P.; Greedan, J. E.; Ozin, G. A.; Manners.

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375.


CHAPTER 8

Over the Horizon

From the introduction and body of this thesis, it should be apparent that there have been many exciting developments in the area of polymer-solid state composite materials. As this union is still in its infancy, it is intriguing to imagine the future discoveries that will help to shape the field. I think that self-assembly and templating will remain key to creating materials in the near future. Morphological control and structural control over multiple length scales will be important to the advanced materials of the future.

Polymer mesofibres extracted from the inside of mesoporous silica (hexagonal, cubic) could be used to template solid state materials that cannot be formed in a lyotropic liquid crystalline phase. After calcination to remove the template, the mesoporous solid state material could be used for applications such as sensors, catalysts, and electronics.

Mesoporous polymer replicas may be interesting hosts for solid state materials and ceramics. For example, incorporation of Fe$_3$O$_4$ into the mesoporous polymer could give aligned magnetic particles that resemble the chains of magnetosomes present in magnetotactic bacteria. Moreover, in a magnetic field the polymer mesofibers could align to give high strength polymer bundles. Templating the mesoporous polymer replicas with shaped mesoporous silica followed by dissolution of the silica would give a polymer with shaped pores.
Crosslinking polymers around a crystal colloid array of silica, followed by dissolution of the silica in aqueous HF, could give "plastic molecular sieves". This class of lightweight periodic macroporous materials may be useful as thermal and acoustic insulation, catalyst supports, or electronic and food packaging. Also, it could be an excellent host for the growth of solid state materials with novel architectures. For example, rigid platinum mesh with high surface area may be formed using this template and may find utility in fuel cell electrodes.

Macroporous inorganic polymer replicas (from the compounds described in chapters 4-6, for example) of the silica nanospheres may be formed by a similar route. After removing the template, the material may be pyrolyzed to yield macroporous magnetic ceramics. These may have unusual magnetic and mechanical properties.

An interesting idea is to template a crystal colloid silica array with a lightly crosslinked poly(ferrocenylsilane) then to dissolve the silica to leave a macroporous poly(ferrocenylsilane) crystal. Oxidation with iodine should give a semiconducting structure. Filling the pores with an n-doped semiconductor could generate a periodic n-p junction device with an enormous surface area between the materials. Materials of this sort may have unique optical and electronic properties. Further, electrochemical oxidation of a macroporous poly(ferrocenylsilane) could provide a tunable electrical filter for macromolecules and biomolecules as well as a controlled delivery vehicle for drugs, herbicides, and perfumes.

The growth of other inorganic polymers in host templates should be explored. Investigations of nanofibres and nanoparticles of poly(thiazyl) ([SN]ₙ), which is a superconductor at low temperature, may elevate the superconducting transition to more
practical values. Mesoscale patterned polysilane may display novel photoconductivity behaviour while macroscale imprinted polysilane may be of interest for photonic band gap applications.

There is a bright future ahead for the field of polymer-solid state hybrid materials. It is apparent that materials with new architectures and novel properties will be discovered by research at the interface of the two mature fields.
APPENDICES

The appendices are divided into two sections: Appendix 1 (Tables From Chapter 5) and Appendix 2 (Tables From Chapter 6).


Table 1. Summary of Crystal Data and Data Collection Parameters for 3 - 6.

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a Weight = 1/[σ²(F₀)² + (a*P)² + 0.000*P], where P = (Max(F₀², 0) + 2*F_c²)/3
Table 2. Selected Bond Lengths (Å) and Angles (°) for 3.

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<td>C37-C36-C40</td>
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<td>C37-C38-C39</td>
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<td>C12-C11-C15</td>
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<td>C38-C39-C40</td>
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Table 6. Selected Bond Lengths (Å) and Angles (°) for 5.

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<th>Angles</th>
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<td><strong>Si(1)-C(13)-C(12)</strong></td>
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<td><strong>C(1)-Si(1)-C(11)</strong></td>
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<td><strong>C(1)-Si(1)-C(13)</strong></td>
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<td><strong>C(6)-Si(1)-C(11)</strong></td>
<td>118.15(7)</td>
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<td><strong>C(6)-Si(1)-C(13)</strong></td>
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<td><strong>C(11)-Si(1)-C(13)</strong></td>
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Table 8. Infrared Bands of 3 and 4.

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<td>3095w</td>
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<td>3081w</td>
<td>(\nu) C-H</td>
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<td>1292m</td>
<td>(\delta) C-H(_{ip})</td>
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<td>1182s</td>
<td>1154w</td>
<td>(\delta) C-H(_{ip})</td>
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<td>1021s</td>
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<td>(\delta) C-H(_{oop})</td>
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<td>(\delta) C-H(_{ip})</td>
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<td>815w</td>
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<td>661m</td>
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<td>(\delta) C-C(_{oop})</td>
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<tr>
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<td>531m</td>
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<td>510s</td>
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\(^a\) \(\nu\) = stretch; \(\delta\) = bend; ip = in-plane; oop = out-of-plane
Table 9. Raman Bands of 3, 4, 6, and Ferrocene.

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<th>Assignment&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>1065m</td>
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## Appendix 2. Tables for Chapter 6.

**Table 1.** Observed Infrared and Raman Frequencies for Selected Vibrational Modes of 4 and 5.

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<th>4 Raman$^c$ (cm$^{-1}$)</th>
<th>5 IR$^b$ (cm$^{-1}$)</th>
<th>5 Raman, (cm$^{-1}$)</th>
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<td>νO-H (H-bonded)</td>
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<td>3105(s), 3083(s)</td>
<td>3102-3071(s)</td>
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$^a$ ν = stretch; δ = bend; ip = in-plane; oop = out-of-plane; w = weak; m = medium; s = strong

$^b$ Nujol mull

$^c$ Crystalline sample
Table 2. Crystal Data for Compounds 4, 5, and the Cocrystal.

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<td>(\text{C}<em>{60}\text{H}</em>{54}\text{Fe}<em>{6}\text{O}</em>{3}\text{Si}<em>{3}-(\text{CH}</em>{2}\text{Cl})_{0.5})</td>
<td>(\text{C}<em>{40}\text{H}</em>{38}\text{Fe}<em>{4}\text{O}</em>{3}\text{Si})</td>
<td>(\text{C}<em>{201}\text{H}</em>{216}\text{C}<em>{16}\text{Fe}</em>{18}\text{O}_{12}\text{Si})</td>
</tr>
<tr>
<td>(M_r)</td>
<td>1284.86</td>
<td>846.28</td>
<td>4294.55</td>
</tr>
<tr>
<td>temperature (K)</td>
<td>110.0(1)</td>
<td>293(2)</td>
<td>203(2)</td>
</tr>
<tr>
<td>wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
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<tr>
<td>crystal system</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Rhombohedral</td>
</tr>
<tr>
<td>space group</td>
<td>P-1</td>
<td>Cc</td>
<td>R3</td>
</tr>
<tr>
<td>a, Å</td>
<td>13.6449(7)</td>
<td>17.8040(3)</td>
<td>32.6448(4)</td>
</tr>
<tr>
<td>b, Å</td>
<td>20.3600(13)</td>
<td>14.6140(4)</td>
<td>32.6448(4)</td>
</tr>
<tr>
<td>c, Å</td>
<td>20.6260(12)</td>
<td>13.4620(2)</td>
<td>15.5290(2)</td>
</tr>
<tr>
<td>(\alpha, \text{deg})</td>
<td>113.068(1)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(\beta, \text{deg})</td>
<td>90.290(1)</td>
<td>94.777(3)</td>
<td>90</td>
</tr>
<tr>
<td>(\gamma, \text{deg})</td>
<td>94.286(1)</td>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td>(V, \text{Å}^3)</td>
<td>5253.5(5)</td>
<td>3490.48(12)</td>
<td>14331.84(18)</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>(D_{\text{calc}}, \text{g cm}^{-3})</td>
<td>1.624</td>
<td>1.610</td>
<td>1.493</td>
</tr>
<tr>
<td>(\mu(\text{Mo K}\alpha), \text{mm}^{-1})</td>
<td>1.780</td>
<td>1.737</td>
<td>1.518</td>
</tr>
<tr>
<td>(F(000))</td>
<td>2628</td>
<td>1736</td>
<td>6642</td>
</tr>
<tr>
<td>crystal size (mm)</td>
<td>0.20 x 0.15 x 0.12</td>
<td>0.32 x 0.31 x</td>
<td>0.4 x 0.4 x 0.4</td>
</tr>
<tr>
<td>(\theta) range collected, deg</td>
<td>4.15 to 26.46</td>
<td>4.34 to 26.40</td>
<td>1.95 to 28.26</td>
</tr>
<tr>
<td>total no. of reflns</td>
<td>37536</td>
<td>13591</td>
<td>21800</td>
</tr>
<tr>
<td>no. of unique reflns</td>
<td>19878</td>
<td>6805</td>
<td>11648</td>
</tr>
<tr>
<td>(R_{\text{int}})</td>
<td>0.050</td>
<td>0.0538</td>
<td>0.0261</td>
</tr>
<tr>
<td>absorption correction</td>
<td>Denzo-SMN</td>
<td>Denzo-SMN</td>
<td>None</td>
</tr>
<tr>
<td>(wR_2) (all data)</td>
<td>0.1584</td>
<td>0.1186</td>
<td>0.1219</td>
</tr>
<tr>
<td>(R_1) (I&gt;2\sigma(I))</td>
<td>0.0562</td>
<td>0.0342</td>
<td>0.0417</td>
</tr>
<tr>
<td>GOF</td>
<td>1.020</td>
<td>1.153</td>
<td>1.476</td>
</tr>
<tr>
<td>absolute structure parameter</td>
<td></td>
<td>0.23(2)</td>
<td>0.023(16)</td>
</tr>
<tr>
<td>no. of params</td>
<td>1298</td>
<td>444</td>
<td>676</td>
</tr>
<tr>
<td>res. el density (e Å(^{-3}))</td>
<td>+0.720, -1.160</td>
<td>+0.396, -0.465</td>
<td>+1.583, -1.295</td>
</tr>
<tr>
<td>extinction coeff.</td>
<td>0.0018(2)</td>
<td>0.0027(4)</td>
<td>0</td>
</tr>
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</table>
Table 3. Selected Bond Lengths (Å) and Bond Angles (°) for Cyclotrisiloxane 4.

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(1A)-O(1A)</td>
<td>1.641(4)</td>
<td>Si(1B)-O(1B)</td>
<td>1.638(4)</td>
</tr>
<tr>
<td>Si(1A)-O(3A)</td>
<td>1.633(3)</td>
<td>Si(1B)-O(3B)</td>
<td>1.629(4)</td>
</tr>
<tr>
<td>Si(1A)-C(1A)</td>
<td>1.837(6)</td>
<td>Si(1B)-C(1B)</td>
<td>1.839(6)</td>
</tr>
<tr>
<td>Si(1A)-C(11A)</td>
<td>1.838(6)</td>
<td>Si(1B)-C(11B)</td>
<td>1.835(6)</td>
</tr>
<tr>
<td>Si(2A)-O(1A)</td>
<td>1.634(4)</td>
<td>Si(2B)-O(1B)</td>
<td>1.634(4)</td>
</tr>
<tr>
<td>Si(2A)-O(2A)</td>
<td>1.638(4)</td>
<td>Si(2B)-O(2B)</td>
<td>1.632(4)</td>
</tr>
<tr>
<td>Si(2A)-C(21A)</td>
<td>1.843(6)</td>
<td>Si(2B)-C(21B)</td>
<td>1.835(6)</td>
</tr>
<tr>
<td>Si(2A)-C(31A)</td>
<td>1.832(6)</td>
<td>Si(2B)-C(31B)</td>
<td>1.836(6)</td>
</tr>
<tr>
<td>Si(3A)-O(2A)</td>
<td>1.639(4)</td>
<td>Si(3B)-O(2B)</td>
<td>1.641(4)</td>
</tr>
<tr>
<td>Si(3A)-O(3A)</td>
<td>1.640(4)</td>
<td>Si(3B)-O(3B)</td>
<td>1.642(4)</td>
</tr>
<tr>
<td>Si(3A)-C(41A)</td>
<td>1.842(6)</td>
<td>Si(3B)-C(41B)</td>
<td>1.838(6)</td>
</tr>
<tr>
<td>Si(3A)-C(51A)</td>
<td>1.830(6)</td>
<td>Si(3B)-C(51B)</td>
<td>1.830(6)</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Angles</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(1A)-O(1A)-Si(2A)</td>
<td>133.2(2)</td>
<td>Si(1B)-O(1B)-Si(2B)</td>
<td>133.3(2)</td>
</tr>
<tr>
<td>Si(1A)-O(3A)-Si(3A)</td>
<td>133.8(2)</td>
<td>Si(1B)-O(3B)-Si(3B)</td>
<td>133.6(2)</td>
</tr>
<tr>
<td>Si(2A)-O(2A)-Si(3A)</td>
<td>133.7(2)</td>
<td>Si(2B)-O(2B)-Si(3B)</td>
<td>133.7(2)</td>
</tr>
<tr>
<td>O(1A)-Si(1A)-O(3A)</td>
<td>106.43(19)</td>
<td>O(1B)-Si(1B)-O(3B)</td>
<td>106.41(19)</td>
</tr>
<tr>
<td>O(1A)-Si(2A)-O(2A)</td>
<td>106.5(2)</td>
<td>O(1B)-Si(2B)-O(2B)</td>
<td>106.6(2)</td>
</tr>
<tr>
<td>O(2A)-Si(3A)-O(3A)</td>
<td>106.02(19)</td>
<td>O(2B)-Si(3B)-O(3B)</td>
<td>105.81(19)</td>
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<tr>
<td>C(1A)-Si(1A)-C(11A)</td>
<td>116.2(3)</td>
<td>C(1B)-Si(1B)-C(11B)</td>
<td>116.0(3)</td>
</tr>
<tr>
<td>C(21A)-Si(2A)-C(31A)</td>
<td>115.7(3)</td>
<td>C(21B)-Si(2B)-C(31B)</td>
<td>114.9(3)</td>
</tr>
<tr>
<td>C(41A)-Si(3A)-C(51A)</td>
<td>114.9(2)</td>
<td>C(41B)-Si(3B)-C(51B)</td>
<td>115.2(3)</td>
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Table 4. Selected Bond Lengths (Å), Intermolecular Distances (Å), and Bond Angles (°) for Disiloxanediol 5

<table>
<thead>
<tr>
<th>Bond Lengths</th>
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<tbody>
<tr>
<td>Si(1)-O(1)</td>
<td>1.635(4)</td>
<td>Si(2)-O(2)</td>
<td>1.644(4)</td>
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<tr>
<td>Si(1)-O(3)</td>
<td>1.606(4)</td>
<td>Si(2)-O(3)</td>
<td>1.621(3)</td>
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<tr>
<td>Si(1)-C(1)</td>
<td>1.845(5)</td>
<td>Si(2)-C(11)</td>
<td>1.834(5)</td>
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<tr>
<td>Si(1)-C(21)</td>
<td>1.843(6)</td>
<td>Si(2)-C(31)</td>
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<table>
<thead>
<tr>
<th>Intermolecular Distances</th>
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</thead>
<tbody>
<tr>
<td>O(1)---O(2)</td>
<td>2.931(4)</td>
<td>O(1)---O(1)</td>
<td>2.921(4)</td>
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<table>
<thead>
<tr>
<th>Angles</th>
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</thead>
<tbody>
<tr>
<td>O(1)-Si(1)-O(3)</td>
<td>107.7(2)</td>
<td>O(2)-Si(2)-O(3)</td>
<td>110.9(2)</td>
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<tr>
<td>C(1)-Si(1)-C(21)</td>
<td>112.0(2)</td>
<td>C(11)-Si(2)-C(31)</td>
<td>114.8(2)</td>
</tr>
<tr>
<td>Si(1)-O(3)-Si(2)</td>
<td>157.1(3)</td>
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Table 5. Selected Bond Lengths (Å) and Bond Angles (°) for Cyclotrisiloxane 4 in the Cocrystal.

<table>
<thead>
<tr>
<th>Bond Lengths</th>
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<tbody>
<tr>
<td>Si(1)-C(6)</td>
<td>1.859(8)</td>
<td>Si(1)-C(11)</td>
<td>1.828(8)</td>
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<td>Si(1)-O(21)</td>
<td>1.636(5)</td>
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<table>
<thead>
<tr>
<th>Angles</th>
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</thead>
<tbody>
<tr>
<td>Si(1)-O(21)-Si(1B)</td>
<td>133.4(3)</td>
<td>O(21)-Si(1)-O(21A)</td>
<td>106.6(3)</td>
</tr>
<tr>
<td>C(6)-Si(1)-C(11)</td>
<td>114.5(3)</td>
<td></td>
<td></td>
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Table 6. Selected Bond Lengths (Å) and Bond Angles (°) for Disiloxanediol 5 in the Cocrystal.

<table>
<thead>
<tr>
<th>Bond Lengths</th>
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<tr>
<td>Si(2)-O(71)</td>
<td>1.643(5)</td>
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<tr>
<td>Si(2)-O(72)</td>
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<td>Si(2)-C(36)</td>
<td>1.856(7)</td>
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<td>Si(2)-C(46)</td>
<td>1.849(7)</td>
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<table>
<thead>
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<th>Intermolecular Distances</th>
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<tbody>
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<td>O(71)---O(73)</td>
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<td>O(71)---O(71)</td>
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<tr>
<td>O(71)---Cl(1)</td>
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<td>O(71)---C(91)</td>
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<tbody>
<tr>
<td>O(71)-Si(2)-O(72)</td>
<td>109.4(3)</td>
</tr>
<tr>
<td>C(36)-Si(2)-C(46)</td>
<td>107.0(3)</td>
</tr>
<tr>
<td>Si(2)-O(72)-Si(3)</td>
<td>157.1(3)</td>
</tr>
</tbody>
</table>