Stabilization of low-valent group 14 element

Rajoshree RoyChowdhury

University of Windsor

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Stabilization of Low-valent group 14 element

by

Rajoshree Bandyopadhyay
(née RoyChowdhury)

A Dissertation
Submitted to the Faculty of Graduate Studies
through the Department of Chemistry and Biochemistry
in Partial Fulfillment of the Requirements for
the Degree of Doctor of Philosophy at the
University of Windsor

Windsor, Ontario, Canada

2012

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Stabilization Of Low-Valent Group-14 Elements

by

Rajoshree Roychowdhury

APPROVED BY:

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Faculty of Education

April 9, 2012
Declaration of Co-Authorship / Previous Publication

I. Co-Authorship Declaration

I hereby declare that this thesis incorporates material that is result of joint research, as follows:

**Chapter 2 of this thesis incorporates the outcome of a joint research undertaken in collaboration between Dr. Kim M. Baines (University of Western Ontario) and Dr. Charles L.B. Macdonald groups. The experiments and data analysis were performed by Paul A. Rupar (graduate student of Dr. Baines) and me. X-ray crystallography was done by Benjamin F.T. Cooper. Michael R. Stinchcombe had run $^{19}F$ NMRs of these compounds. Dr. Ragogna had contributed with valuable suggestions.**

**Chapter 4 of this thesis incorporates the outcome of a joint research undertaken in collaboration with Dr. Robert W. Schurko and Dr. Charles L.B. Macdonald. The $^{119}Sn$ solid state NMR spectroscopy was carried out by Aaron Rossini from Dr. Schurko’s group. I have contributed in synthesizing $[Sn([15]crown-5)_{2}][OTf]_{2}$ and $[Sn([12]crown-4)_{2}][OTf]_{2}$ and recrystallizing them. Benjamin F.T. Cooper synthesized $[Sn([18]crown-6)-OTf][OTf]$ and solved all the crystals obtained in this project.**

**Chapter 5 of this thesis is focused on various characterizations of all the complexes isolated in Chapter 4. Additional Sn[OTf]$_{2}$ complexes of the glymes were isolated by Warren W. Friedl which were crystallographically solved by Benjamin F.T Cooper. This joint research was undertaken in collaboration with Dr. Robert W. Schurko, Dr. Rolfe H. Herber, Dr. H. S. Eichhorn and Dr. Charles L.B. Macdonald. The $^{119}Sn$ solid state NMR spectroscopy was carried out by Aaron J. Rossini from Dr. Schurko’s group. Mössbauer Spectroscopy was run by Dr. Herbert. Dr. Eichhorn contributed with important suggestions regarding cyclic voltammetry analysis. I have contributed in running cyclic voltammetry on all the Sn(II) complexes.**

I am aware of the University of Windsor Senate Policy on Authorship and I certify that I have properly acknowledged the contribution of other researchers to my thesis, and have obtained written permission from each of the co-author(s) to include the above material(s) in my thesis.
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II. Declaration of Previous Publication

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<td>Experimental and computational insights into the stabilization of low-valent main group elements using crown ethers and related ligands &lt;i&gt;Journal of American Chemical Society, 2012, 134&lt;/i&gt;, 4332-4345</td>
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Abstract

This thesis concerns the synthesis and study of the phenomenal ligand properties of crown ethers and glymes in stabilizing germanium and tin complexes in low oxidation states supported by either chlorides or triflates as the counter-anions. The abbreviated nomenclature for the ligands presented can be generalized by the form [x]crown-y, where [x] describes the total number of atoms and y, the total number of donor atoms of the ligand. Four differently-sized crown ethers, [12]crown-4, [15]crown-5, [18]crown-6 and benzo[18]crown-6 have been used in this dissertation. Crowned Ge(II) and Sn(II) complexes exhibit several unprecedented structural motifs that depend both on the size of the crown ether and the nature of the counter anions. Triglyme and tetruglyme have been used to stabilize Sn(II) complexes. The crowned Ge(II) molecules were characterized in the solid state by single crystal X-ray diffraction, NMR spectroscopy and IR spectroscopy. The Sn(II) complexes were characterized by a variety of methods including Mössbauer spectroscopy, Solid State NMR spectroscopy, and electrochemical studies. Extensive use of Mössbauer spectroscopy was also employed to gain insight into the s-character of the lone-pair on the tin centers. Subtle changes in ligands showed a pronounced effect on the symmetry of the complexes. To compare the results obtained from the observations and from experimental investigations, a series of density functional theory calculations are done on all the crowned Ge(II) and Sn(II) complexes in order to assess whether the structural features that are observed for the cationic fragments experimentally are consistent with the minimum energy structures in their gas phase.
Dedicated to my spiritual gurus:

Swami Bhuteshananda ji
&
Rev. Swami Swahananda ji
Acknowledgements

My journey in University of Windsor began in the summer of 2007. It was after the completion of my M.Sc. at Memorial University of Newfoundland, from the cold Atlantic regions of St.John’s, that I was warmly welcomed by Dr. Charles L. B. Macdonald. I would like to thank Professor Macdonald for giving me the opportunity to work for him. Under his guidance, the last few years have been a great period to learn chemistry. Apart from being my supervisor, he has been my mentor and has been very understanding and cooperative. He corrected my mistakes in very polite ways. I also wish to acknowledge my committee members: Dr. Stephan J. Loeb, Dr. Holger S. Eichhorn and Dr. Barbara Zielinski.

Thanks to Dr. Mike Fuerth and Dr. Matt Revington for their guidance on NMR. Thanks to Dr. Robert W. Schurko, Dr. Aaron J. Rossini, Dr. Holger S. Eichhorn, Dr. R. H. Herber, Dr. Kim Baines, Dr. Paul A. Rupar and Dr. Paul J. Ragogna for collaborating with me.

I would like to thank all the past and present members of Professor Macdonald’s group and Professor Johnson’s group for making the lab environment and the office environment so much more of an interesting place to work. My collaboration with everyone will always remain a memorable experience in my life. I would like to thank Marlene Bezaire for being so affectionate and caring in various ways.

Heartfelt gratitude to my parents, my dearest sister Shreyashi, and my baby brother Krishnendu who have been cheering me up from miles away. Last but not the least my loving husband, Saptarshi for whom I think every word would be insufficient to express my gratitude. Big thanks to Saptarshi and his parents for being so supportive.

Finally, I would like to thank my creator whom I really cannot thank enough. He has been endlessly showering me with blessings of immense love, strength and patience and I am so grateful to have Him beside me every moment of my life.

“Courage and perseverance have a magical talisman before which difficulties disappear and obstacles vanish into air” – John Quincy Adams.
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<td>cm</td>
<td>centimeter</td>
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<tr>
<td>mm</td>
<td>millimeter</td>
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<td>pm</td>
<td>pico meter</td>
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<td>mg</td>
<td>milligram</td>
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<td>milliliter</td>
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<td>g</td>
<td>gram</td>
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<td>s</td>
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<td>minute</td>
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<td>ppm</td>
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<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
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<td>diethylether</td>
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<td>cyclic voltammetry</td>
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<td>ME</td>
<td>Mössbauer effect</td>
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<td>[18]crown-6</td>
<td>1,4,7,10,13,16-hexaoxacyclooctadecane</td>
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<td>[12]crown-4</td>
<td>1,4,7,10-tetraoxacyclododecane</td>
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<td>Triflate</td>
<td>trifluoromethylsulphonate</td>
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<td>Mes*</td>
<td>2,4,6-tri-t-butylphenyl</td>
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<tr>
<td>Dis</td>
<td>bis(trimethylsilyl)methyl</td>
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<td>Tbt</td>
<td>2,4,6-tris(bis(trimethylsilyl)methyl)phenyl</td>
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<td>Tip</td>
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<td>2,4,6-tris(1-ethylpropyl)phenyl</td>
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<tr>
<td>VCAP</td>
<td>variable-amplitude cross-polarization</td>
</tr>
<tr>
<td><strong>MS</strong> = mass spectrometry</td>
<td><strong>CP</strong> = cross polarization</td>
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<tr>
<td><strong>FTIR</strong> = Fourier transformation infrared</td>
<td><strong>H-L</strong> = HOMO-LUMO</td>
</tr>
<tr>
<td><strong>MS</strong> = mass spectrometry</td>
<td><strong>HOMO</strong> = highest occupied molecular orbital</td>
</tr>
<tr>
<td><strong>MW</strong> = molecular weight</td>
<td><strong>LUMO</strong> = lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td><strong>m/z</strong> = mass-to-charge ratio</td>
<td><strong>LP</strong> = lone pair</td>
</tr>
<tr>
<td><strong>QS</strong> = quadrupolar splitting</td>
<td><strong>Ω</strong> = span</td>
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<tr>
<td><strong>EFG</strong> = electron field gradient</td>
<td><strong>δ</strong> = chemical shift</td>
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<td><strong>SSNMR</strong> = solid state nuclear magnetic resonance</td>
<td><strong>IS</strong> = isomer shift</td>
</tr>
<tr>
<td><strong>MAS</strong> = magic angle spins</td>
<td><strong>WBI</strong> = Wiberg Bond Index</td>
</tr>
<tr>
<td><strong>VT</strong> = variable temperature</td>
<td><strong>NBO</strong> = natural bond orbital</td>
</tr>
<tr>
<td><strong>pXRD</strong> = powder x-ray diffraction</td>
<td><strong>XPS</strong> = X-ray photoelectron spectroscopy</td>
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Chapter 1

Introduction to various polyethers and Group-14 elements

1.1 Introduction

Crown ethers and the related cryptands belong to a class of very interesting and important ligands. These ligands are derived from ethylene glycol and substituted ethylene glycol. The synthesis of this family of polyethers was discovered by Charles Pedersen in 1967, along with their greater ability to selectively bind alkali and alkaline earth ions.\(^1\)\(^,\)\(^2\) Many interesting complexes have been generated using crown ethers and cryptand ligands, including species known as 'alkalides'\(^3\)\(^,\)\(^4\) and 'electrides'\(^5\) that contained particularly unexpected anions. The chemical literature provides ample evidence of crown ethers coordinating with s-block and to a lesser extent of d-block elements. In contrast, the investigation of crown ether ligations of p-block elements has remained under-explored. In addition to metal complexation, these ligands have generated a novel family of salts with various kinds of complex ions.\(^6\)\(^-\)\(^9\) Studies over the past 30 years have demonstrated that crown ethers and cryptands can play interesting roles in many chemical and physical processes. They have interesting applications models for biomolecules,\(^10\) in supramolecular chemistry,\(^11\) and crystal engineering; and they can function as components for building intricate macromolecules.\(^12\) In fact, supramolecular chemistry has attracted the interests of many scientists;\(^13\)\(^-\)\(^15\) the importance of this work was
highlighted by the award of the 1987 Nobel Prize in Chemistry to Charles Pedersen, along with Jean-Marie Lehn and Donald J. Cram, for their pioneering work in the area of supramolecular chemistry. This introductory chapter explores the progress made in the chemistry of crown ethers and related cryptands over the past 30 years, followed by a brief review of the chemistry of group 14 elements, especially in relatively low oxidation states.

1.2 Coronands and Podands

Vögtle and Weber coined the term ‘coronands’ for crown ethers and ‘coronates’ for their complexes. Non-cyclic crown ethers are termed as ‘podands’ and their complexes are called ‘podates’. Structurally, crowns are macrocyclic polyethers in which the ethereal O-atoms are separated by two methylene (-CH₂) groups. Crown ethers are abbreviated as \(m\)-C-\(n\) where \(m\) is the size of the ring and \(n\) is the number of ethereal O-atoms. However, in this thesis, the crowns have been denoted as crown-\(n\). Some examples of crown ethers are given in Figure 1.1.

Figure 1.1 Types of crown ethers: a.[12]crown-4, b.[15]crown-5, c.benzo[15]crown-5

Glymes and polyethylene glycols are examples of podands. The nomenclature of glymes is also based on the number of oxygen atoms present but it must be noted that because the parent glyme has 2 oxygen atoms, there is always one more oxygen atom present than
suggested by the numerical prefix. The two types of glymes used in this dissertation are triglyme (4 oxygen atoms) and tetraglyme (5 oxygen atoms) (Figure 1.2).

![Diagram of glymes](image)

**Figure 1.2** Types of glymes: **a.** triglyme, **b.** tetraglyme, **c.** benzotetraglyme

A third family of related ligands, known as the ‘podando-coronands’, are commonly called lariat ethers. It is possible to construct many complexes, called ‘podando-coronates’, with lariat ethers.¹⁹

Crown ethers have been synthesized with reported $n$-values ranging from 3 to 20. Their excellent and tunable ligand properties are a result of their variable cavity sizes that can range from about 1.2 Å to 3.2 Å. More precisely, the cavity sizes for [12]crown-4, [15]crown-5, and [18]crown-6 are 60 pm, 90 pm, and 140 pm, respectively.²⁰ This variation in cavity size allows crown ethers to accommodate metal (or other) ions of appropriate size. In fact, the crown ether ligation of particular cations is so favorable that it can be used to drive improbable reactions to occur. For example, perhaps the most noteworthy chemistry of crown ethers was illustrated by reports of the high solubility of crowned cations of alkali metals in amine and ether solvents that proved to be salts of solvated electrons or alkalide anions.²¹
1.3 Applications and Uses of Crown Ether

Crown ethers also have many useful applications in organic synthesis, solvent extraction, and phase transfer catalysis, as they can stabilize the low-oxidation states of various elements, model important biomolecules,22 and enhance other unusual reactions.

As a result of Pedersen’s ground-breaking discovery, many new families of organic macrocyclic molecules were synthesized. These families include thiacrown ethers,23 azacrown ethers,24 lariat ethers,19 chiral crown ethers,25,26 cryptands,27-29 spherands,30,31 cryptahemispherands,32,33 hemispherands,34 calixarenes,35-37 cavitands,38-40 hemicarcerands,41 carcerands (molecular containers),42-44 and boron macrocycles.45-48 All of these compounds can bind to cations and anions, act as ion transport agents, stabilize unstable molecules, and participate as hosts in host-guest chemistry.

1.4 Group 14 and Common Oxidation States49

In theory, the oxidation state of an atom indicates the number of electrons directly associated with that element and therefore may determine the reactivity and structural features of the compound in which it is found. The isolation of complexes of d-block elements in their various oxidation states has many synthetic applications, such as the generation of catalysts or catalyst precursors. In the past two decades, there has been substantial progress in stabilizing p-block elements in relatively low oxidation states. Considerable effort has been required to do so because compounds containing low-oxidation state centers are usually coordinatively unsaturated – they typically feature non-bonding electrons at the low-valent centre – making such species highly reactive. In fact, it is their potential for high reactivity that inspired scientists to target such
compounds to perform “transition-metal like” chemistry such as small molecule activation.\textsuperscript{50}

Group 14 elements are also known as “tetrels” due to their valence shell configuration. These elements have a [core]\(ns^2np^2\) electron configuration which permits them to form up to four bonds with most neutral compounds. When such elements combine with elements from other groups, the tetravalent state of the tetrels often produces compound that are “electron precise”, i.e., with no “lone pairs” or vacant orbitals for the group 14 element. There are two common oxidation states for group 14 elements: +2 and +4; the +4 state is more common for carbon, silicon, and germanium, whereas tin and lead are more stable in the +2 state (in which the element has two non-bonding valence electrons). The increasing stability of the lower oxidation state down the group is attributable to the inert pair effect. Group 14 features a series of elements which have properties ranging from non-metallic to metallic. Carbon, the lightest element, is a true non-metal, which can exist in different allotropic forms (namely diamond, graphite and fullerenes). Carbon is followed in the Group 14 by the two metalloids, silicon and germanium. The heavier elements tin and lead are both metals.\textsuperscript{51} In this thesis, the elements of focus are germanium and tin and thus much of the following discussion concentrates on compounds containing these elements.

1.5 Low-valent germanium and tin chemistry

The most well-investigated class of low-valent germanium and tin compounds are the carbene analogues.\textsuperscript{52-54} Silylenes, germylenes, stannylenes and plumbylenes are the heavier congeners of carbenes and can be represented generically as \(R_2M\), where \(R\) can
be a simple organic substituent or a group bound through a heteroatom (typically O, S, or N). They are divalent species and are usually assigned a formal oxidation state +2.\textsuperscript{55}

\[ \text{\textbullet\textbullet\textbullet C} \quad \text{\textbullet\textbullet\textbullet Si} \quad \text{\textbullet\textbullet\textbullet Ge} \quad \text{\textbullet\textbullet\textbullet Sn} \quad \text{\textbullet\textbullet\textbullet Pb} \]

**Figure 1.3** Core structures of carbenes, silylenes, germynes, stannylenes, plumbylenes

\(N\)-heterocyclic carbenes or “NHCs” are cyclic carbenes in which the divalent carbon atoms is flanked by two amido substituents that render such carbenes particularly stable.\textsuperscript{56,57} In fact, the first stable crystallographically characterized carbene was an NHC prepared by Arduengo and co-workers.\textsuperscript{58} The flanking nitrogen atoms in the heterocycle donate electron density to the empty p-orbital of carbon and stabilize the electron-rich center inductively,\textsuperscript{59} thus making the system more kinetically and thermodynamically stable. The importance of NHCs lies in their broad application in organometallic chemistry, organic synthesis, and homogeneous catalysis.\textsuperscript{60,61} These applications have led to interest in the synthesis of related NHC analogues\textsuperscript{62} using heavier group 14 elements (Si,\textsuperscript{63} Ge,\textsuperscript{64} and Sn\textsuperscript{65}). Germynes are typically less reactive than analogous carbenes\textsuperscript{58,59} and silylenes,\textsuperscript{66} due to the larger energy gap between the s- and p-orbitals of germanium.\textsuperscript{67,68}

### 1.5.1 Germynes

The first stable acyclic diamidogermylene \([(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ge}\textsuperscript{69}] was reported by Lappert \textit{et al.} in 1976. This compound was exceptional in that the monomeric form existed in solution but its corresponding digermene dimeric form was found in solid crystalline state. Jutzi \textit{et al.} isolated the germylene \([(\text{Me}_3\text{Si})_3\text{C}] [(\text{Me}_3\text{Si})_2\text{CH}]\text{Ge} that is
monomeric in both solution and the solid state and characterized it crystallographically in 1991.\(^{70}\)

\[
\text{(Me}_3\text{Si)}_2\text{HC Ge : } \quad \text{(Me}_3\text{Si)}_2\text{HC Ge = Ge CH(SiMe}_3)_2
\]

**Figure 1.4** Lappert's germylene complexes in monomeric and dimeric forms\(^{66}\)

Extremely bulky aromatic groups, as illustrated in **Figure 1.5**, have also been employed to isolate very stable germynes.\(^{71-75}\)

\[
\text{F}_3\text{C} \quad \text{F}_3\text{C} \quad \text{F}_3\text{C} \quad \text{t-Bu} \quad \text{t-Bu} \quad \text{Mes} \quad \text{Mes} \quad \text{Mes} \quad \text{Tbt Ge : TIP}
\]

**Figure 1.5** Bulky aromatic groups such as \(\text{R}_3\text{C}, \text{Mes}^*, \text{terphenyl} \) and \(\text{Tbt}(2,4,6-\text{tris(bis(trimethylsilyl)methyl)phenyl})/\text{TIP}(2,4,6-\text{triisopropylphenyl})\) have been used to isolate stable germynes\(^{68-72}\).

A cyclic version, namely, the \(N\)-heterocyclic germylene \([\text{Me}_2\text{Si(Nt-Bu)}_2]\text{Ge}\),\(^{76}\) was isolated by Veith and co-workers in 1982. Furthermore, the germanium analogue of Arduengo’s carbene \((\text{t-BuNCHCHNt-Bu})\text{Ge}\)\(^{77}\) was obtained by Herrmann \textit{et al.} in 1992.\(^{78}\) Kira \textit{et al.} designed a constrained bidentate ligand to stabilize a dialkylgermylene (**Figure 1.6**) analogous to Lappert's original germylene.\(^{79}\) The literature of \(\text{Ge(II)}\) chemistry is rich and diverse with different types of germylene derivatives,\(^{80}\) which have been reviewed periodically.\(^{81,82}\)
More recently, stabilization of low-valent group 14 elements has been also accomplished by using neutral ligands. These ligands coordinate to the central atom by forming covalent or dative bonds hence filling their empty orbitals in the valence shells. Such species can range from being relatively stable to being highly reactive. There are two possible simple models, namely a dative model and more conventional covalent Lewis-type model that can represent such complexes (Figure 1.7).

In 2007, Baines et al. reported a novel Ge(II) dication where the latter is coordinated by three N-heterocyclic carbene ligands. Although the germanium-containing ion is clearly a dication, the charge on the ion is actually well-distributed onto the substituents and not really condensed on the Ge(II) center.
In fact, it should be emphasized that the introduction of a Lewis base (D) to many types of carbenoids has produced stable donor-acceptor complex. In effect, the transfer of electron density from the base to the empty $p$-orbital of Ge (or any carbenoid center, as illustrated in Figure 1.8, where the base, D can be groups like ether, imine, phosphine, carbene, etc.) both reduces the electron-deficiency of the system and fills the coordination sphere.

For example, Baines et al. demonstrated that a strong sigma donor like $N$-heterocyclic carbenes could be used to stabilize a normally highly-reactive dimesitylgemmylene through the formation of a complex. This was the first example of transient GeR$_2$ species stabilized by an NHC.

**Scheme 1.1** Synthesis of [Ge(NHC)$_3$]$^{84}$

**Figure 1.8** Donor stabilizing Ge(II) center
GeCl$_2$(1,4-dioxane), which is probably the most common starting material for Ge(II) chemistry, is also a fine example of an intermolecularly stabilized germylene, as illustrated in Figure 1.9. The germanium dichloride adducts like GeCl$_2$(1,4-dioxane) and GeCl$_2$(benzthioazole)$^{67}$ were synthesized and structurally characterized in the early 1970s, and the germylene monoiodide complex (acac)GeI (Hacac), where acac represents acetylacetone, was reported together with its structure in the late 1970s by Stobart.$^{68}$

![Structure of GeCl$_2$.dioxane](image)

**Figure 1.9** Structure of GeCl$_2$.dioxane

In fact, GeCl$_2$ has also been stabilized by different macrocyclic ligands like thioether and selenoether (Figure 1.12).$^{86}$ Typically both of the halide substituents remain covalently bonded to the Ge(II) center. These types of adducts are clearly analogous to those described for the smaller monodentate donors described above. The results obtained with other ligands, such as crown ethers with chloride and triflate salts of Ge(II) will be discussed in detail in later chapters.
A major breakthrough in the area was reported by the Baines group in 2008 with their report of the isolation of a “naked” dicationic Ge(II) ion through the use of a macrocyclic polyether, [2.2.2]-cryptand. The encapsulating ligand appeared to protect the germanium dication from any nucleophilic counterions and solvents and the charge on germanium was calculated to be 1.38. The bond distance of 5.32 Å between the germanium and oxygen of the triflate indicated that the ions were quite well-separated.

**Scheme 1.3** Synthesis of Ge$^{2+}$ by cryptand$^{87}$

### 1.5.2 Stannylenes, Distannenes

Much interest in the chemistry and preparation of stannylenes arises because they are potential precursors of many novel organotin complexes.$^{88}$ In 1976 Lappert *et al.*
isolated the first stable dialkylstannylene in solution, where it existed as a monomer–dimer equilibrium mixture although it existed as a monomer in the gas phase and a dimer in the solid state. The dimer, called a distannene, has a bond length of 276.8(1) pm and has features a trans-bent arrangement with angle of 41° between the SnC₂ plane and the Sn-Sn vector. Many distannenes that exist in the crystalline state dissociate to form stannylenes in solution (Figure 1.11).\textsuperscript{89-91}

\textbf{Figure 1.11} Lappert’s dialkylstannylene complexes in monomeric and dimeric forms\textsuperscript{84}

The first monomeric dialkyl and diaryl stannylene that were synthesized and characterized crystallographically in solid states are bis[2-pyridyl-2,2-bis(trimethylsilyl)methyl]stannylene\textsuperscript{92} and bis[2,4,6-tris(trifluoromethyl)phenyl]stannylene\textsuperscript{93,94} (Figure 1.12). The divalent tin centers in such compounds are stabilized by the presence of intramolecular interactions between the tin and neighboring nitrogen or fluorine atoms. These interactions are the consequences of the electron-rich ligand atoms that can donate electron density to the vacant 5p \(\pi\)-type orbital of the tin.
Kira et al. also used the same Dis-like bidentate ligand to isolate the first stable dialkylstannylene in its solid state (Figure 1.13). As with the germanium analogues, other bulky ligands, like 2,4,6-tri-t-butylphenyl (Mes*) groups and Tbt and Tcp (Tbt = 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl; Tcp = 2,4,6-tricyclohexylphenyl and Tpp = 2,4,6-tris(1-ethylpropyl)phenyl), also led to the successful isolation of kinetically stabilized monomeric diarylstannylenes that were characterized in the solid state (Figure 1.14).
From several of the examples of germylenes and stannylenes described above, it can be observed that $R_2E$: ($E=\text{Ge, Sn}$) fragments are sometimes more favorable than the dimeric alternatives $R_2E=ER_2$, with $R$ = bulky aryl groups. Furthermore, the digermenes and distannenes also often exhibit non-planar structures that are at odds with the expectations for the organic analogues (olefins). A rationale for both of these observations is provided by the CGMT-model (Carter-Goddard-Malrieu-Trinquier). Carbenoids can either have singlet ($S$) or triplet ($T$) states with a very small transition energy between $S \rightarrow T$. Due to the small energy difference between the $sp^2$ and $\pi$-type orbitals in carbenes, the preferred manner of the double-bond formation occurs by the combination of two oppositely positioned triplet carbene fragments.

**Scheme 1.4** Triplet state of two carbenoid fragments

Figure 1.14 Use of bulky aryl groups to stabilize stannylenes$^{89,90}$

### 1.6 Bonding and CGMT Model$^{62}$

From several of the examples of germylenes and stannylenes described above, it can be observed that $R_2E$: ($E=\text{Ge, Sn}$) fragments are sometimes more favorable than the dimeric alternatives $R_2E=ER_2$, with $R$ = bulky aryl groups. Furthermore, the digermenes and distannenes also often exhibit non-planar structures that are at odds with the expectations for the organic analogues (olefins). A rationale for both of these observations is provided by the CGMT-model (Carter-Goddard-Malrieu-Trinquier). Carbenoids can either have singlet ($S$) or triplet ($T$) states with a very small transition energy between $S \rightarrow T$. Due to the small energy difference between the $sp^2$ and $\pi$-type orbitals in carbenes, the preferred manner of the double-bond formation occurs by the combination of two oppositely positioned triplet carbene fragments.

**Scheme 1.4** Triplet state of two carbenoid fragments
In contrast, almost all germynes and stannylenes (and other heavier group 14 carbenoids) isolated have singlet ground states and feature a high S→T transition energy. The gap between these two states increases with an increasing atomic mass of the group-14 element. Thus, the approach in Scheme 1.4 may result in a destabilized Scheme 1.5 state for the two such singlet fragments. Consequently, the lone pairs of electrons generate a two-center-four-electron interaction that results in repulsion rather than in bond formation.

Scheme 1.5 Singlet state of two carbenoid fragments

However, if the two species are rotated between the two central atoms at angle $\Theta$ to each other, delocalization of the electron density from the doubly-occupied donor s orbitals occurs to the vacant p($\pi$) acceptor orbitals. This leads to a double bond formation, by a double donor-acceptor adduct formation (Scheme 1.6). This generates a trans-bent arrangement of the substituents about the E=E at angle $\Theta$. The angle $\Theta$ increases substantially on going to heavier elements.

Scheme 1.6 Trans-bent arrangement about E=E
The multiple bonding of hypervalent group 14 (Ge, Sn) compounds has been and remains a subject of significant discussion. The geometrical distortions of group 14 congeners of alkynes can be rationalized either using the CGMT approach or by invoking molecular orbital (MO) perturbations (these are simply two slightly different ways of treating the same effect). In the given MO diagram, left side represent orbitals of the linear alkyne molecule and to the right is the trans-bent ($C_{2h}$) heavier group 14 analogues. It is evident that the bent geometry of the alkyne analogues of group 14 heavier elements is a consequence of the mixing of anti-bonding ($\sigma^*$) and in-plane $\pi$-orbitals within the molecule, caused by the second order Jahn–Teller effect. This phenomenon establishes an unsymmetric non-bonding ($n_-$), lone pair character to the in-plane $\pi$-orbital, which is the HOMO, thus affecting the molecular shape. On the other hand, mixing of the s- and $\pi^*$-orbitals (both $a_g$ symmetry) weakens the $\sigma$-bond. The degree of the mixing is inversely proportional to the energy gap between the orbitals and is highest in the heavier atoms, as the weakened bonding creates a closer separation between the molecular levels (< 4 eV).\(^9\)

Figure 1.15 MO bonding comparison of alkyne analogues of heavier congeners\(^9\)
“The HOMO (π-orbital, \(a_u\)) can act as a Lewis base electron donor, whereas the virtual lone pair combination \(a_g(n_+)\) can act as a lone-pair acceptor orbital.”

1.7 Ge(I) and Sn(I) compounds

Although, this thesis concentrates on group 14 elements in the +2 oxidation state, it is worth noting that lower oxidation state species have been obtained. Schnepf et al. have reported a very exciting route to synthesize E(I) (E = Ge, Sn) by a technique called co-condensation, where E(I)Br was isolated first at temperatures above 1000 °C and high pressure in gaseous phase. Then the gaseous products are condensed at very low temperature (~196 °C) with an added solvent. The entire process is carried out in a ‘home made’ apparatus.

```
1600 °C
10^{-2} \text{ mbar}
\begin{align*}
\text{Ge(I)} &\quad + \quad \text{HBr(g)} \quad \xrightarrow{1600 \, ^\circ \text{C}} \quad \text{GeBr(g)} &\quad + \quad \text{1/2 H}_2 \,(g) \\
\text{Sn(I)} &\quad + \quad \text{HBr(g)} \quad \xrightarrow{1370 \, ^\circ \text{C}} \quad \text{SnBr(g)} &\quad + \quad \text{1/2 H}_2 \,(g)
\end{align*}
```

**Scheme 1.7 Synthesis of E(I) compounds**

Ge(I) and Sn(I) halides have been used in making novel metalloid cluster compounds of the general formulae \(E_nR_m\) with \(n>m\) (E = tetrel elements; R = ligand). The reaction (Scheme 1.8) involves bulky ligands (L) like Si(SiMe\(_3\))\(_3\). These complexes are composed of “naked” tetrel atoms have an oxidation state of 0 and the other ligated tetrels. So, on average the oxidation state of these complexes ranges between 0 and 1. Thus, these cluster compounds bridge the gap between molecular and solid state leading to interesting physical properties that may be useful for nanotechnology.
Outline of the thesis

Earlier members of our group have shown crown ethers were useful in stabilizing group 13 elements in the univalent state.\textsuperscript{103,104} Changes in the sizes of crown ethers resulted in complexes with very different structures. Furthermore, the use of different counter-anions of these In-complexes caused dramatically different reactivity and stability. This dissertation demonstrates that the properties of crown ethers make them ideal for the stabilization of low-valent group 14 elements.
Figure 1.16 Various types of synthesis using InOTf\textsuperscript{105}

Since these In(I) fragment are isoelectronic with Sn(II) and isovalent with Ge(II), similar crown chemistry was anticipated for these elements.

Figure 1.17 Structures depicting isovalent and isolobal relationships\textsuperscript{97}

Chapter 2 discusses the structural features of crowned Ge(II) complexes using chloride and triflates as their counter-anions. [12]crown-4, [15]crown-5, [18]crown-5 and benzo[18]crown-6 are the crowns that have been used. The synthesis and the
unprecedented crystallographic features are presented. This chapter also includes computational studies of the crowned complexes. Chapter 3 follows with the investigation of the reactivities of some of the crowned Ge(II) complexes. A remarkably stable water adduct of the Ge(II) complex was isolated and the synthetic and structural aspects are rationalized.

Chapter 4 and chapter 5 describe the crown ether chemistry of Sn(II) complexes. The former chapter is comprised of the synthesis and crystallographic details of the crown ether Sn(II) complexes while the latter introduces acyclic glyme complexes and presents in-depth analysis of these complexes that were not possible for the Ge(II) or In(I) analogues. Since the Sn(II) complexes are fairly air- and moisture- stable, they could be conveniently analyzed spectroscopically and physically. Furthermore, detailed spectroscopic characterization using Mössbauer spectroscopy, solid state NMR and cyclic voltammetry studies of the tin complexes provide general insight into the nature of ligand-metal interactions in such systems. The glyme-type ligands were performed to compare the differences between constrained and unconstrained macrocycles.

Finally, the last chapter concludes with suggested future work and other suggested investigations.
References


Chapter 2

Cationic Crown Ether Complexes of Germanium(II)

2.1 Introduction

Cations of germanium continue to receive considerable attention owing to the long-standing interest in their comparative chemistry with carbon and silicon.\textsuperscript{1-6} Typically, covalently bound substituents on Ge are required to provide steric and electronic stabilization to protect the positively charged germanium species from reactions with solvent and counteranions. Recently, the synthesis of 2.1, a complex of cryptand[2.2.2] with Ge\textsuperscript{2+}, highlighted the possibility of isolating reactive germanium cations using electron-rich macrobicyclic molecules to stabilize the cation with numerous weak donor acceptor interactions, rather than with any discrete two-center-two-electron bonds.\textsuperscript{7,8} Although it is well established that cryptands can sequester metallic cations, 2.1 was the first example of a cryptand non-metal cationic inclusion complex and represented a novel approach to isolating lighter p-block cations.

![Figure 2.1](image)

**Figure 2.1** [Cryptand [2.2.2] Ge][OTf]\textsubscript{2}
Crown ethers, like cryptands, are renowned for their strong ligating properties towards metallic cations. Coordination complexes with every type of metal ion in the periodic table have been described. In the p block, reported examples of crown ether complexes with metallic cations include aluminum, gallium, indium, thallium, tin, lead, and bismuth. Neutral crown ether complexes of non-metals are also known, although the nonmetal atom is usually situated outside the cavity of the macrocycle. Only a single example of a nonmetal p-block cation has been reported, namely a [15]crown-5 complex of [SbCl]^{2+}. Many different bonding modes are possible between crown ethers and guest cations; this diversity originates from the relationship between the crown ether cavity size and the ionic radius of the guest. As a consequence, complexes of the same cation with different crown ethers of varying dimensions often exhibit strikingly different structures. For example, In^+ readily fits into the cavity of [18]crown-6 but forms a crown ether sandwich with two molecules of [15]crown-5. We now report that crown ethers can also support germanium cations and allow facile access to a series of unprecedented mono- and dicationic Ge^{II} complexes. We have examined three differently sized crown ethers, [12]crown-4, [15]crown-5, and [18]crown-6, which all form complexes with cationic germanium(II), each with unique structural characteristics.

2.2 Results and Discussion

Reaction of excess [12]crown-4 in a solution of GeCl_2·dioxane in THF resulted in the formation of a white solid (Scheme 2.1).
Scheme 2.1 Synthesis of a.) \([\text{Ge([12]crown-4)}_{2}][\text{GeCl}_3]_2\), b.) \([\text{Ge([12]crown-4)}_{2}][\text{OTf}]_2\)

The structure of the product was determined to be the crown ether solvate of the salt \([\text{Ge([12]crown-4)}_{2}][\text{GeCl}_3]_2\) (2\([\text{GeCl}_3]_2\cdot[12]\text{crown-4}\)) and consists of two [12]crown-4 molecules sandwiching a Ge(II) dication (Figure 2.2).\(^{[22]}\) The two [GeCl₃] counteranions are clearly separated from Ge²⁺, and the closest Cl⁻-Ge²⁺ approach is 5.305(2) Å.

Figure 2.2 Thermal ellipsoid plot (30% probability surface) of 2.2. Hydrogen atoms, the GeCl₃ counter ions and the [12]crown-4 solvate molecule are omitted for clarity. Selected distance between atoms (Å): Ge1-O13 2.428(8), Ge1-O16 2.438(6), Ge1-O19 2.383(6), Ge1-O112 2.398(8)
The structure of 2.2 is comparable to that of 2.1, as both feature an unusual eight-coordinate germanium center; Ge\textsuperscript{II} species typically have coordination numbers of two to four. The Ge-O separations range from 2.383(6) to 2.489(7) Å, which are comparable to the Ge-O interactions in 2.1 (2.4856(16) Å) and much longer than typical Ge-O single-bond lengths, which range from 1.75 to 1.85 Å.\textsuperscript{23,24} Like 2.1, complex 2.2 does not exhibit a stereochemically active lone pair of electrons, which is most likely attributable to the highly symmetrical environment and the positive charge on the germanium ion. Solution \textsuperscript{1}H NMR spectroscopy experiments on the salt reveal distinct signals for the complexed and free crown ether molecules indicate that the dicationic complex remains intact in solution.

In light of the structural features of 2.2[GeCl\textsubscript{3}]\textsubscript{2}, we reasoned that a similar salt of the dication should be accessible for other anions. Thus, we prepared the germanium(II) triflate (triflate=OTf=O\textsubscript{3}SCF\textsubscript{3}) [12]crown-4 complex (Scheme 2.1) by the treatment of two equivalents of [12]crown-4 with one equivalent of GeCl\textsubscript{2}-dioxane and two equivalents of Me\textsubscript{3}SiOTf at room temperature.\textsuperscript{25} All of the characterization methods indicate the formation of the related salt 2.2[OTf]\textsubscript{2}, and crystallographic analysis confirms the formation of the anticipated dication.

The structure of 2.2 clearly shows the germanium center residing outside the cavity of the two [12]crown-4 moieties, suggesting that [12]crown-4 is too small to accommodate a Ge\textsuperscript{2+} ion within its cavity. To determine how a larger crown ether interacts with Ge\textsuperscript{II}, the reaction of one equivalent of [15]crown-5 with two equivalents of GeCl\textsubscript{2}-dioxane was studied (Scheme 2.2).
**Scheme 2.2** Synthesis of a.)[GeCl([15]crown-5)][GeCl₃] b.)[GeOTf([15]crown-5)][OTf] Single crystals were grown, and the product was confirmed to be [GeCl([15]crown-5)][GeCl₃] (2.3[GeCl₃]) by single crystal X-ray diffraction, elemental analysis, and spectroscopic methods. As illustrated in **Figure 2.3**, the salt 2.3[GeCl₃] consists of a \(^+\)GeCl cation encapsulated by [15]crown-5 rather than a dication as observed in 2.1 and 2.2.\(^{26,27}\) The closest Ge\(^{+}\)Cl-Cl\(^-\)anion distance of 3.387(2) Å lies well outside of the range for typical covalent bonding interactions and is consistent with a discrete cation–anion system. The Ge4-Cl4 bond length of 2.293(2) Å is comparable to typical Ge-Cl bond lengths of 2.09–2.21 Å.\(^{23}\) The crown ether adopts a folded conformation in which the plane defined by Ge4, O41, O42, and O43 is almost perpendicular to the plane defined by Ge4, O45, and O44. The \(^+\)GeCl fragment is situated closest to O42 at a distance of 2.104(6) Å, much closer than what was observed in 2.1 and 2.2; two other oxygen atoms, O41 and O43, also show close contacts of 2.363(7) and 2.433(10) Å. These can be compared to the range for typical Ge-O single bonds at 1.75–1.85 Å.\(^{23}\) The two remaining oxygen atoms, O44 and O45, are situated significantly farther away at
3.044(8) and 2.835(8) Å as a result of the folding of the ring. The adoption of a folded conformation by the [15]crown-5 ligand in 2.3 implies that the ¹GeCl fragment is too large to fit into the cavity of the crown ether and that the germanium center possesses a stereochemically active lone pair of electrons. The salt 2.3[GeCl₃] is obtained regardless of the stoichiometry employed in the reaction with [15]crown-5.

The synthesis of a germanium(II) triflate [15]crown-5 complex (Figure 2.4) was investigated to observe what effect, if any, a change in the substituent at the Ge center would produce.

**Figure 2.3** Thermal ellipsoid plot (30% probability surface) of 2.3. Only one of the four crystallographically-independent cations is illustrated; hydrogen atoms and the ¹GeCl₃ counter ion are omitted for clarity. Selected distances between atoms (Å) (average for all 4 cations in brackets): Ge4-Cl4 2.293(2) [2.308(6)], Ge4-O41 2.363(7) [2.353(18)], Ge4-O42 2.104(6) [2.128(15)], Ge4-O43 2.433(10) [2.380(13)], Ge4-O44 3.044(8) [2.985(17)], Ge4-O45 2.835(8) [2.916(15)]

One equivalent of [15]crown-5 was treated with one equivalent of GeCl₂·dioxane and two equivalents of Me₃SiOTf at room temperature.²⁵ A white powder was collected and identified as the monocationic complex [GeOTf([15]crown-5)][OTf] (2.4[OTf], Figure 2.3).²¹ The geometry of the crown ether moiety in 2.4 has changed strikingly from that in 2.3. The crown ether in 2.4 now adopts the more typical planar conformation of the
oxygen donors and the germanium center. The germanium ion is situated near the centroid of the ring, with Ge-O\textsubscript{crown} separations ranging from 2.233(5) to 2.349(6) Å. One of the triflate groups in 2.4[OTf] remains in close proximity to the germanium cation. Although the Ge-O\textsubscript{triflate} separation of 2.015(3) Å is longer than a typical Ge-O bond (1.75–1.85 Å),\textsuperscript{23} it is comparable to other known Ge-O\textsubscript{triflate} covalent interactions.\textsuperscript{28} Furthermore, the S1-O1 bond length of 1.451(3) Å is longer than the remaining two sulfur–oxygen bonds (1.416(6) and 1.423(6) Å), which is characteristic of a triflate ion with at least partial covalent bonding to a substituent.

Figure 2.4 Thermal ellipsoid plot (30% probability surface) of 2.4 Hydrogen atoms and the -OTf counterion are omitted for clarity. Selected interatomic distances [Å]: Ge–O11 2.260(4), Ge–O12 2.233(5), Ge–O13 2.308(6), Ge–O14A 2.289 (8), Ge–O15A 2.349(6), Ge–O1 2.015(3), S1–O1 1.451(3), S1–O2 1.416(6), S1–O3 1.423(6).

The second triflate group in 2.4[OTf] is present as a distinctly separate anion in the unit cell, and the closest Ge-O\textsubscript{triflate} separation is 3.169(6) Å. A possible rationale for the differences between the structures of 2.3 and 2.4 is that the Ge-O\textsubscript{triflate} bond of 2.4 is much more polarized than the Ge-Cl bond of 2.3, thus increasing the effective charge on
the Ge center in 2.4 and decreasing the size of the cation, allowing it to fit more readily into the cavity of the [15]crown-5 ligand.

In spite of the foregoing discussion, crown ethers are notoriously flexible molecules, and the observed geometrical differences between 2.3 and 2.4 could be a result of crystal packing effects rather than electronic effects. To examine complexes similar to 2.3 and 2.4 featuring a somewhat less flexible framework, the benzocrown ether derivatives of 2.3 and 2.4 (2.5 and 2.6, respectively) were synthesized and characterized. The structures obtained exhibit features virtually identical to those observed in 2.3 and 2.4: in the chloride complex 2.5, the crown ether fragment features a folded conformation, while the triflate derivative 2.6 adopts a typical planar conformation (see Appendix I). Therefore, the observed structural differences between 2.3 and 2.4 are more likely attributable to the steric and electronic effects of the type described above and not to crystal packing effects.

The direct reaction of two equivalents of GeCl₂-dioxane with [18]crown-6 (Scheme 2.3) resulted in the formation of a new complex with a stoichiometry of Ge₂Cl₄-[18]crown-6. The recrystallization of a preparation containing excess crown ether resulted in the formation of the crown ether solvate of the desired salt.
Scheme 2.3 Synthesis of a.) [GeCl([18]crown-6)]-[GeCl₃] b.) [Ge(OTf)₂([18]crown-6)]

Figure 2.7 Thermal ellipsoid plot (30% probability surface) of 2.7. Hydrogen atoms, the GeCl₃ counter ion, and the 18-crown-6 solvate molecule are omitted for clarity. Selected distances between atoms (Å): Ge1-Cl1 2.201(1), Ge1-O11 2.195(3), Ge1-O12 2.359(4), Ge1-O13 2.869(5), Ge1-O14 3.237(4), Ge1-O15 3.076(4), Ge1-O16 2.640(4)

The structure [GeCl([18]crown-6)]-[GeCl₃]-1/2[18]crown-6 (2.7[GeCl₃]-1/2[18]crown-6, Figure 2.7) shows that the larger crown ether is indeed able to ligate the Cl-Ge⁺ fragment in a planar fashion. The Ge center is offset from the centroid of the crown ether oxygen atoms. The closest germanium–oxygen separation is 2.195(3) Å for the Ge1-O11
interaction. The remaining Ge-O distances are significantly longer, ranging from 2.359(4) to 3.237(4) Å; this situation is likely a consequence of the larger cavity size of the [18]crown-6 ring being too large to bind the Ge cation in a symmetrical manner. The structure is also consistent with a stereochemically active lone pair of electrons on the germanium center pointing in a direction orthogonal to the ring, opposite the Ge1-Cl1 bond.

Finally, to observe the interaction of the larger crown ether with the triflate substituents, GeCl$_2$·dioxane was treated with [18]crown-6 and two equivalents of Me$_3$SiOTf in THF (Scheme 2.3).$^{21}$ Suitable single crystals were grown and identified as [Ge(OTf)$_2$([18]crown-6)] (2.8), which, surprisingly, consists of a symmetrical Ge(OTf)$_2$ fragment located within the cavity of [18]crown-6 (Figure 2.7). As in 2.7, the germanium atom is located away from the centroid of the oxygen atoms in the crown ether and is much closer to the O11 and O11A atoms (2.218(3) Å) than the remaining oxygen atoms (two at 2.673(3) Å and two at 3.159(4) Å).
The crown ether in 2.8 is noticeably distorted, with the oxygen atoms labeled O13 and O13A located out of the plane defined by the germanium center and the other four oxygen atoms in the ligand. The distant O atoms appear to be oriented in a manner that is not suitable for donation to the Ge center. The O\textsubscript{ triflate}-Ge bonds are long (2.204(5) Å) and, although they appear incipient towards ionization, 2.8 is clearly not an ion-separated system as observed for the salts of 2.2–2.7. The structural features of 2.8 are consistent with a stereochemically active lone pair of electrons on germanium oriented in the direction of O13 and O13A. We postulate that the triflate anions remain in contact with the Ge ion because the larger [18]crown-6 ligand allows for the lone pair of electrons to reside inside the cavity of the crown ether.  

We have shown that crown ethers are suitable ligands for the stabilization of cationic germanium(II) systems, the structural properties of which are highly dependent

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**Figure 2.8** Thermal ellipsoid plot (30% probability surface) of 2.8. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å]: Ge–O11 2.218(3), Ge–O12 2.673(3), Ge–O13 3.159(4), Ge–O12.204(5), S–O1 1.448(5), S–O2 1.422(4), S–O3 1.397(6). The crown ether and is much closer to the O11 and O11A atoms (2.218(3) Å) than the remaining oxygen atoms (two at 2.673(3) Å and two at 3.159(4) Å)
on the size of crown ether used and on the substituents on germanium. The surprising ease with which the crown ethers promote the ionization of Ge\textsuperscript{II} demonstrates the effectiveness of these macrocycles in isolating otherwise elusive cationic germanium species. The simplicity of the synthetic approach may render it applicable to the preparation of other novel nonmetal cations.

2.3 Experimental

All manipulations were carried out under an anhydrous N\textsubscript{2} atmosphere using standard Schlenk line and glove box techniques at room temperature. Benzene, tetrahydrofuran (THF), CH\textsubscript{2}Cl\textsubscript{2}, toluene, and CH\textsubscript{3}CN were dried by passing through an alumina column\textsuperscript{30} and then stored over 4 Å molecular sieves. CD\textsubscript{3}CN and CD\textsubscript{2}Cl\textsubscript{2} were distilled over CaH\textsubscript{2} and then stored over 4 Å molecular sieves. NMR chemical shifts are reported in ppm. The \textsuperscript{1}H NMR spectra were referenced internally to the residual CD\textsubscript{2}HCN resonance at 1.94 ppm or the CDHCl\textsubscript{2} resonance at 5.32 ppm. The \textsuperscript{19}F NMR spectra were referenced externally to CFCl\textsubscript{3} (0 ppm) or to C\textsubscript{6}H\textsubscript{5}F (-113.1 ppm relative to CFCl\textsubscript{3}). Elemental analysis was performed at Guelph Chemical Laboratories, Guelph, Ontario, Canada. GeCl\textsubscript{2}-dioxane\textsuperscript{31} and 2.9\textsuperscript{32} were synthesized according to literature procedures. All other chemicals were purchased from commercial sources and used without further purification. FT-Raman spectra of the bulk material are reported in cm\textsuperscript{-1} and were collected under a N\textsubscript{2} atmosphere in a sealed tube. Melting points were determined under a N\textsubscript{2} atmosphere and are uncorrected.

Synthesis of 2.2[GeCl\textsubscript{3}]\textsubscript{2}

A solution of [12]crown-4 (0.190 g, 1.08 mmol) in THF was added to a solution of GeCl\textsubscript{2}-dioxane (0.250 g, 1.08 mmol) in THF. The resultant colorless solution was left for
stirring for 2 hours after which all volatile components were removed under reduced pressure. The remaining oily product was washed in pentane (5 mL x 3) to provide a white solid which was recrystallized from CH₂Cl₂. The crystalline material was characterized as 2.2[GeCl₃]₂·([12]crown-4) (0.275 g, 80%).

¹H NMR (CD₂Cl₂): 3.69 (s, 32H, complexed crown), 3.67 (s, 16H, free crown)

¹³C NMR (CD₂Cl₂): 70.57 (s, CH₂)

M. P.: 70 – 72 °C

FT-Raman (ranked intensities): 133(3), 162(5), 284(8), 332(6), 401(16), 492(15), 525(17), 710(18), 818(10), 847(11), 899(12), 1028(13), 1142(14), 1285(9), 1451(7), 2871(4), 2907(1), 2936(2).


**Synthesis of 2.2[OTf]₂**

[12]crown-4 (0.14 mL, 0.86 mmol) was added to a GeCl₂·dioxane (0.10 g, 0.43 mmol) solution in THF (2 mL). The solution was allowed to stir for 5 min, after which Me₃SiOTf (0.15 mL, 0.86 mmol) was added. After the reaction mixture was stirred for 1 hr, hexanes (5 mL) was added. A white precipitate was formed, which was collected and then washed with Et₂O (4 mL x 2). The precipitate was identified as [Ge·[12]crown-4][OTf]₂ (2.2[OTf]₂) (0.15 g, 49 %). Crystals suitable for single x-ray diffraction were obtained by slow diffusion of pentane into a saturated THF solution of 2.2[OTf]₂. Analysis of the single crystals by X-ray diffraction showed that the solid state structure of
2.2[OTf]₂ is qualitatively similar to that of 2.2[GeCl₃]₂ but the quality of the data was poor and precludes further discussion.

³¹H NMR (CD₃CN): 3.96

¹⁹F NMR (CD₃CN): -79.4

M. P.: 156 – 160 °C

FT-Raman (ranked intensities): 313(6), 349(5), 366(12), 494(13), 573(10), 754(7), 853(4), 909(14), 1032(2), 1069(16), 1105(15), 1224(11), 1264(9), 1451(8), 2896(3), 2954(1).

ESI-MS(+ mode) m/z: 199 [([12]crown-4)∙Na, 100%] 399 [GeOTf([12]crown-4), 50%], 575 (GeOTf₂([12]crown-4), 5 %).


**Synthesis of 2.3[GeCl₃]**

A solution of [15]crown-5 (0.284 g, 1.29 mmol) in THF was added to a solution of GeCl₂·dioxane (0.600 g, 2.59 mmol) in THF. The resultant colorless solution was left to stir for 2 hours after which all volatile components were removed under reduced pressure. The oily residue was washed in pentane (5 mL x 3) to provide a white solid which was recrystallized from CH₂Cl₂. The crystalline material was characterized as 2.3[GeCl₃] (0.615 g, 94%).

³¹H NMR (CD₃CN): 3.45

¹³C NMR (CD₃CN): 70.48

M. P.: 89 – 91 °C

FTRaman (ranked intensities): 149(4), 289(5), 318(3), 850(7), 1136(9), 1268(8), 1474(6), 2887(2), 2925(1).
ESI-MS(+ mode) m/z: 221 [[15]crown-5-H, 100%], 329 [[15]crown-5-GeCl, 5%].

Anal. Calcd for C_{10}H_{20}Cl_{4}GeO_{5}: C, 23.67; H, 3.97. Found: C, 23.40; H, 3.89.

**Synthesis of 2.4[OTf]**

A solution of [15]crown-5 (0.568 g, 2.59 mmol) and Me_3SiOTf (933 uL, 5.16 mmol) in THF was added to a solution of GeCl_2.dioxane (0.600 g, 2.59 mmol) in THF. The resultant colorless solution was left to stir for 24 hours. All volatile components were then removed under reduced pressure. The oily residue was washed with pentane (5 mL x 3) to give a white solid which was recrystallized from CH_2Cl_2. The crystalline material was characterized as 2.4[OTf] (0.600 g, 39%).

^1H NMR (CD_3CN): 4.02

^13C NMR (CD_3CN): 68.93

^19F NMR (CD_3CN): -80.0

M. P.: 128 – 131 °C

FT-Raman (ranked intensities): 313(11), 348(3), 534(15), 572(12), 755(6), 764(7), 857(4), 997(10), 1030(1), 1094(14), 1138(13), 1236(9), 1473(8), 2894(5), 2965(2).

ESI-MS(+ mode) m/z: 259 [K·[15]crown-5, 100%], 443 [GeOTf·[15]crown-5, 10%].

Anal. Calcd for C_{18}H_{32}F_{6}GeO_{14}S_{2}: C, 24.39; H, 3.41; O, 29.78. Found: C, 23.92; H, 3.12; O, 30.18.

**Synthesis of 2.5[OTf]**

To a suspension of GeCl_2.dioxane (0.10 g, 0.43 mmol) in C_6H_6 (5 mL) was added benzo[15]crown-5 (0.12 g, 0.43 mmol). The mixture was stirred for 5 min after which Me_3SiOTf (157 uL, 0.86 mmol) was added. The reaction mixture was stirred for 18 hr. Pentane (10 mL) was added to complete the precipitation of a white precipitate. The
precipitate was identified as [GeCl∙benzo[15]crown-5][OTf] (2.5[OTf]) (0.19 g, 83%). Crystals suitable for single crystal x-ray diffraction were obtained by slow diffusion of Et₂O into a saturated solution THF solution of 2.5[OTf].

¹H NMR (CD₃CN): 3.97-3.99 (multiplet, 4H), 4.07-4.10 (multiplet, 4H), 4.26 (singlet, 8H), 7.03 (singlet, 4H).

¹⁹F NMR (CD₃CN): -79.3

M. P. 128 – 130 °C

FT-Raman (ranked intensities): 311(1), 465(18), 503(17), 573(9), 756(7), 777(16), 836(3), 1029(2), 1052(6), 1124(15), 1164(14), 1255(12), 1320(13), 1454(10), 1594(8), 2897(11), 2952(4), 3074(5).


Synthesis of 2.6[OTf]

To a solution of 2.5[OTf] (0.06 g, 0.11 mmol) in THF (4 mL) was added 2.9 (0.05 g, 0.11 mmol). The reaction mixture was stirred for 18 hr. A white precipitate was collected by centrifugation and washed with C₆H₆ (4 mL x 2) and then pentane (4 mL x 2). The precipitate was identified as [GeOTf∙benzo[15]crown-5][OTf], 2.6[OTf], (0.06 g, 86%). Crystals suitable for single crystal x-ray diffraction were obtained by slow diffusion of
Et₂O into a saturated solution THF solution of 2.6[OTf]. Analysis of the single crystals by X-ray diffraction showed that the solid state structure of 2.6[OTf] is qualitatively similar to that of 2.4[OTf] but the quality of the data was poor and precludes further discussion.

\(^1\)H NMR (CD₃CN): 4.14-4.16 (multiplet 4 H), 4.23-4.25 (multiplet, 4 H), 4.36-4.38 (multiplet, 4 H), 4.42-4.45 (multiplet 4 H), 7.14 (singlet, 4 H).

\(^19\)F NMR (CD₃CN): -79.3

M.P.: 128 – 130 °C

FT-Raman (relative intensity): 305(7), 349(6), 575(14), 607(13), 763(5), 830(10), 993(1), 1032(2), 1133(15), 1176(11), 1242(8), 1467(12), 1595(9), 2891(16), 2952(3), 3072(4).

ESI-MS (+ mode) \(m/z\): 269 [benzo[15]-crown-5·H, 7 %], 291 [benzo[15]crown-5·Na, 38 %], 491 [benzo[15]crown-5·GeOTf, 100 %].


**Synthesis of 2.7[GeCl\(_3\)]**

A solution of [18]crown-6 (0.341 g, 1.29 mmol) in THF was added to a solution of GeCl\(_2\).dioxane (0.600 g, 2.59 mmol) in THF. The resultant colorless solution was left to stir for 2 hours after which all volatile components were removed under reduced pressure. The oily residue was washed in pentane to provide a white solid which was recrystallized from CH\(_2\)Cl\(_2\). Resultant material was characterized as 2.7[GeCl\(_3\)] (0.720 g, 100%). Crystals of 2.7[GeCl\(_3\)]\(\cdot\frac{1}{2}\)[18]crown-6 suitable for single crystal X-ray diffraction were obtained in 82% yield by the concentration of a 2.7[GeCl\(_3\)] solution in CH\(_2\)Cl\(_2\) that contained excess [18]crown-6.

\(^1\)H NMR (CD₃CN): 3.37
\[^{13}\text{C} \text{NMR (CD}_3\text{CN)}: 75.15\]

\[\text{M. P.: } 97 – 100 \, ^\circ\text{C}\]

\[\text{ESI-MS (+ mode) } m/z: 265 \text{ [[18]crown-6-H, 90%]}, 287 \text{ [[18]crown-6-Na, 15%]}, 303 \text{ [[18]crown-6-K, 10%]}, 373\text{[[18]crown-6-GeCl, 100%]}.

\[\text{FT-Raman (ranked intensity): 134(3), 165(9), 274(7), 323(2), 348(6), 545(15), 869(10), 1074(16), 1141(14), 1245(13), 1275(12), 1367(18), 1412(17), 1466(8), 2813(11), 2851(5), 2913(4), 2946(1).}\]

\[\text{Anal. Calcd for } C_{12}H_{24}Cl_4Ge_2O_6: C, 27.94; H, 4.69. \text{ Found: C, 27.43; H, 4.55.}\]

**Synthesis of 2.8**

A solution of [18]crown-6 (0.681 g, 2.76 mmol) and Me$_3$SiOTf (933 uL, 5.16 mmol) in THF was added to a solution of GeCl$_2$.dioxane (0.600 g, 2.59 mmol) in THF. The resultant colorless solution was to stir for 24 hours, and then all volatile components were removed under reduced pressure. The oily residue was washed with pentane (3 times) to give white solid which was recrystallized from CH$_2$Cl$_2$. The crystalline material was characterized as 2.8 (0.726 g, 44%).

\[^{1}\text{H NMR (CD}_3\text{CN): } 3.83\]

\[^{13}\text{C NMR (CD}_3\text{CN): } 71.04\]

\[^{19}\text{F NMR (CD}_3\text{CN): } -80.0\]

\[\text{M. P.: } 85 – 89 \, ^\circ\text{C}\]

\[\text{ESI-MS } m/z: 487 \text{ [[18]crown-6-GeOTf, 100%].}\]

\[\text{FT-Raman (ranked intensity): 118(13), 287(18), 318(8), 347(1), 572(16), 753(12), 763(15), 874(11), 1027(4), 1145(17), 1244(14), 1277(9), 1471(7), 2817(10), 2856(5), 2888(6), 2918(2), 2952(3).}\]
References


(18)  Thiocrown ether complexes of GeX₂ were reported with the germanium coordinated to the periphery of the macrocycle. See F. Cheng, A. L. Hector, W. Levason, G. Reid, M. Webster, W. Zhang *Chem. Commun.* 2008, 5508.

(20) 1,4-Dioxane is never called "[6]crown-2" but it is the smallest member of the cyclic (C$_2$H$_4$O)$_n$ ether family. The solid state structure of GeCl$_2$·dioxane consists of GeCl$_2$ moieties linked together by dioxane, forming a 1-D coordination polymer. See M. K. Denk, M. Khan, A. J. Lough, K. Shuchi, *Acta Cryst.* **1998**, C54, 1830.

(22) The [12]crown-4 moiety showed disorder but was successfully modeled as a superposition of two molecules. Only one of the superpositions is discussed.


(24) The distance between Ge and oxygen in GeCl$_2$·dioxane is 2.399 (1) Å. See reference.

(25) In effect, Ge(OTf)$_2$ is generated *in situ* with the concomitant formation of Me$_3$SiCl. Ge(OTf)$_2$ has been reported previously but was not structurally characterized. See M. H. Castany, H. Lavayssière, G. Dousse, *Synth. React. Inorg. Met.-Org. Chem.* **1998**, 28, 781.

(26) It is also interesting to note that the reactivity of GeCl$_2$·dioxane with [15]crown-5 mirrors that of SnCl$_2$ with [18]crown-6. See ref [Error! Bookmark not defined.].

(27) Four cation/anion pairs are found in the asymmetric unit, all with very similar metrical parameters, and therefore, only one ion pair is discussed.

Chapter 3

Stabilization of Germanium(II) center by water

3.1 Introduction

The chemistry of compounds containing heavier group 14 elements (tetrels) has been a very active area of main group chemical research for several decades. Because of the importance and ubiquity of organic chemistry, the resultant compounds of the heavier tetrels are often compared to and contrasted with appropriate carbon analogues. The structural and chemical properties of many of these compounds are often quite distinct from those of the carbon congeners.\textsuperscript{1-7} Many recent investigations have focused on the preparation and chemistry of low-valent germanium complexes,\textsuperscript{8,9} multiple bonds, and some of these studies have yielded compounds that have no precedent in carbon chemistry (e.g. Zintl ions). In the most notable recent example, Baines and co-workers discovered that an unambiguously metal-based dication of germanium can be stabilized by the [2.2.2]-cryptand ligand.\textsuperscript{10} More recently, our group, in collaboration with the Baines group and simultaneously with the Reid group, have demonstrated that crown ethers are also appropriate ligands for the stabilization of unambiguous Ge(II) dications.\textsuperscript{11,12} In that work, we reasoned that the less restrictive binding of the divalent germanium center by the crown ether ligands [15]crown-5 and [18]crown-6 (in comparison to the [2.2.2]cryptand or the bis [12]crown-4 sandwich complexes) should facilitate the interaction of the metal with other reagents. In order to evaluate this
postulate, we have undertaken an investigation into the reactivity of the Ge(II) crown ether complexes with a variety of simple reagents. In this work, we present the first results of our studies regarding the simple coordination chemistry of the Ge(II) dication which include the remarkable formation of a crystallographically-characterized water adduct!

3.2 Results and Discussions

In particular, the addition of 1.0 µL of water (or D₂O) to a solution [GeOTf[15]crown-5][OTf] in CH₂Cl₂ generates the complex [Ge[15]crown-5•H₂O][OTf]₂, 3.1,([Ge[15]crown-5•D₂O][OTf]₂, 3.2) (Scheme 3.1) as assessed by ¹H NMR spectroscopy in solution. Removal of all volatile components yields a colorless solid characterized as 3.1 by microanalysis and spectroscopic analyses.

![Scheme 3.1](image)

**Scheme 3.1** Synthesis of water complex of [Ge[15]crown-5•H₂O][OTf]₂

Recrystallized material suitable for analysis by single crystal X-ray diffraction was obtained through the slow evaporation of a dichloromethane solution of the crude product.

Complex 3.1 crystallizes in the triclinic space group P-1 with one molecule in the asymmetric unit, as illustrated in Figure 3.1. The molecular structure of 3.1 confirms the
proposed composition and reveals some important details. The germanium atom sits within the cavity of the [15]crown-5 ligand almost exactly at the centroid of the 5 O-atoms. The oxygen atom of the H₂O molecule (O(1)) is bound to the Ge atom in a position that is essentially perpendicular to the crown ether (0.384(1)° from the normal to the O₅ plane). The Ge-O(1)) distance of 2.003(4) Å is considerably longer than typical covalent Ge-O bonds (1.75-1.85 Å);¹³ the range of 1.70 to 1.90 Å covers the majority of compounds reported in the Cambridge Structural Database. It must be noted that these distances mostly correspond to Ge(IV) compounds and one would anticipate that the distances Ge(II)-O distances should be somewhat longer because of the larger ionic radius(Ge(II), 87 pm; Ge(IV), 67 pm).¹⁴ However, reported distances for the 11 neutral compounds with dicoordinate Ge atoms featuring a Ge-O bond also range from1.765 Å¹⁵ to 1.869 Å.¹⁶ The Ge-O_crown bonds range from 2.265(4)-2.361(3) Å which are comparable to those observed in the starting material [GeOTf[15]crown-5][OTf]. The O(1)-H bond lengths were constrained to be ca.0.79 Å; the O(1)···O_triflate distances are 2.631(7) and 2.681(5) Å and are thus well within the accepted range for the inter-oxygen distances (ca. 2.7 Å) in hydrogen bonded species.¹⁷ Examination of the three S-O bond lengths in each triflate group reveals that the S-O bond to the oxygen atom closest to the water (i.e. O(11) and O(21)) is somewhat longer than the remaining two. Together, these data clearly suggest that the triflate anions are both H-bonded to the H₂O fragment in the solid state. The geometry about the oxygen atom in the water molecule appears to be best-described as modestly pyramidal, with a sum of the angles at O of 357°, as illustrated for the heavy water analogue in Figure 3.1(b).
The isolation of a well-characterized water complex of Ge(II) is remarkable and perhaps unexpected given the considerable reactivity exhibited by most divalent germanium compounds. Roesky demonstrated the preparation of LGeOH complexes with β-diketiminate ligands, but the ready preparation and isolation of 3.1 is surprising. There are a handful of structurally characterized Ge(IV) water complexes but such species are rather rare too.

**Figure 3.1** (a) [Ge[15]crown-5•H₂O][OTf]₂ (b) [Ge[15]crown-5•D₂O][OTf]₂

FTIR spectra of the protio and deuterio complexes, illustrated in **Figure 3.2**(a.) and (b.) respectively, clearly show the presence of H-bonded O-H and O-D stretches at 3458 and 1971 cm⁻¹, respectively.
The $^1$H and $^{13}$C NMR peaks have shown the presence of a crown peak at 4.0 ppm and 68.93 ppm respectively. The resonance for the proton at 8.02 ppm in CD$_3$CN indicates that the proton of the water molecule has become highly acidic; the corresponding resonance for free water in the same solvent is 2.13 ppm. The potential synthetic utility of this acidic water complex is examined below.

Given the remarkable stability of the water complex 3.1, we sought to determine in other simple elements hydrides might also be accessible. Gratifyingly, the treatment of [GeOTf[15]crown-5][OTf] with NH$_3$ and H$_2$S both result in the formation of colorless species for which there is evidence of complex formation. Although we have not yet been
able to obtain crystal structures for either of the compounds, NMR and IR studies and microanalysis confirm the formation of the proposed adducts. For example, the $^1H$ NMR spectrum of the reaction mixture of [GeOTf[15]crown-5][OTf] with NH$_3$ features a 1:1:1 triplet signal at 1.94 ppm that is attributable to the coupling of the protons to the $^{14}$N ($I = 1$) nucleus. The FTIR spectrum of the solid (Figure 3.3) contains a peak at 3197 cm$^{-1}$ which corresponds to the N-H stretch and the elemental analysis is consistent with a 1:1 adduct of [GeOTf[15]crown-5][OTf] and NH$_3$, 3.3. The $^1H$ NMR spectrum of the reaction mixture [GeOTf[15]crown-5][OTf] with H$_2$S features a singlet at 5.5 ppm attributable to the adduct, 3.4.

Figure 3.3 FTIR spectrum of the adduct obtained from the treatment of [GeOTf[15]crown-5][OTf] with NH$_3$.

3.3 Computational Investigations

Because we were unable to obtain crystal structures for either of the adducts, 3.3 or 3.4, we employed DFT calculations to assess the likely structures of the materials. The computed structure of the water adduct 3.1', illustrated in Figure 3.4, reproduces the structure obtained experimentally quite accurately so it is likely that the computed
structures of the adducts 3.3' and 3.4' are reasonable models for the ammonia and hydrogen sulfide adducts.

![DFT optimized structures for adducts of 3.3', 3.1', 3.4'](image)

**Figure 3.4** DFT optimized structures for adducts of 3.3', 3.1', 3.4'

**Table 3.1** Selected Computational Data for the Ge(II) adduct models and free Lewis bases

<table>
<thead>
<tr>
<th>Model</th>
<th>Donor-Acceptor Complex</th>
<th>Free Donor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dist. (Å)</td>
<td>Snapping Energy (kJ/mol)</td>
</tr>
<tr>
<td>3.1'</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge-O</td>
<td>2.10573</td>
<td>-144.64</td>
</tr>
<tr>
<td>O-H1</td>
<td>0.96984</td>
<td></td>
</tr>
<tr>
<td>O-H2</td>
<td>0.96952</td>
<td></td>
</tr>
<tr>
<td>3.3'</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge-N</td>
<td>2.09883</td>
<td>-200.68</td>
</tr>
<tr>
<td>N-H1</td>
<td>1.01839</td>
<td></td>
</tr>
<tr>
<td>N-H2</td>
<td>1.02011</td>
<td></td>
</tr>
<tr>
<td>N-H3</td>
<td>1.01850</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ge-S</td>
<td>-111.05</td>
</tr>
<tr>
<td>-----</td>
<td>-------</td>
<td>---------</td>
</tr>
<tr>
<td>3.4'</td>
<td>Ge-S</td>
<td>2.59895</td>
</tr>
<tr>
<td></td>
<td>S-H1</td>
<td>1.34697</td>
</tr>
<tr>
<td></td>
<td>S-H2</td>
<td>1.34696</td>
</tr>
</tbody>
</table>

The above table demonstrates that 3.3' has a much stronger bond between Ge-N and this is attributable to the higher Lewis basicity of NH₃ compared to OH₂. Repeated attempts were made to recrystallize the 3.4'. Interestingly, every time the crystal structure of 3.1' was obtained. This could be a consequence of the relatively high snapping energy of 3.1' in comparison to that of 3.4'. The other interesting result is the difference in the charges on the H-atoms of N, O and S-atoms in complexes 3.1', 3.3', and 3.4' when compared to those of free NH₃, H₂O and H₂S. In every case, the charges of the H-atoms in their complexed form increases making these protons slightly acidic; this is consistent with the observed deshielding of the proton NMR signals upon complexation.

The term “snapping energy” was coined by Thomas Ziegler, which actually directly refers to the energy required to break the bond between two fragments of a molecule. However, this energy should not be mistaken with bond dissociation energies since the latter is associated with reorientation of molecules.²⁰

3.4 Other Results

We have also sought to elaborate such adduct chemistry using alcohols such as methanol, ethanol and also with phenol. Somewhat surprisingly, the alcohols did not
yield isolable adducts as yet however phenol did produce a crystalline complex that was suitable for analysis by single-crystal X-ray diffraction. The structure of this salt \([\text{Ge}[15]\text{crown-5}\cdot\text{phenol}][\text{OTf}]_2\), 3.5, is presented in Figure 3.5.

![Figure 3.5](image)

**Figure 3.5** Crystal structure of phenol-complex of Ge(II)

In summary, we have discovered that crown ether stabilized germanium(II) triflate can be used to produce remarkably stable complexes of simple hydrides, including the first structurally characterized complex of water with Ge(II). The synthetic potential of these hydride adducts is currently being pursued.

### 3.5 Experimental

All manipulations were carried out under an anhydrous \(\text{N}_2\) atmosphere using standard Schlenk line and glove box techniques at room temperature. \(\text{CH}_2\text{Cl}_2\) was dried by passing through an alumina column\(^1\) and then stored over 4 Å molecular sieves. \(\text{CD}_3\text{CN}\) was distilled over CaH\(_2\) and then stored over 4 Å molecular sieves. \(\text{H}_2\text{O}\) and \(\text{D}_2\text{O}\)
were stored under oxygen-free condition. NMR chemical shifts are reported in ppm. The $^1$H NMR spectra were referenced internally to the residual CD$_2$HCN resonance at 1.94 ppm. The $^{19}$F NMR spectra were referenced externally to CFCl$_3$ (0 ppm) or to C$_6$H$_5$F (-113.1 ppm relative to CFCl$_3$). Elemental analysis was performed at University of Windsor, Ontario, Canada and Atlantic Microlab Inc., Atlanta, USA. GeCl$_2$-dioxane was synthesized according to literature procedures. All other chemicals were purchased from commercial sources and used without further purification. FTIR spectra of the bulk material are reported in cm$^{-1}$ and were collected as Nujol mulls between KBr plates. Melting points were determined under a N$_2$ atmosphere and are uncorrected.

**Synthesis of [Ge[15]crown-5•H$_2$O][OTf]$_2$, 3.1**

To a solution of [GeOTf[15]crown-5][OTf] (0.545 g, 92.2 mmol) in CH$_2$Cl$_2$, 1:1 equivalence of H$_2$O was added. The resultant colorless solution was left to stir for 24 hours. All volatile components were then removed under reduced pressure. The white solid was recrystallized from CH$_2$Cl$_2$. The crystalline material was characterized as [Ge[15]crown-5•H$_2$O][OTf]$_2$, 3.1 (0.509 g, 91%).

$^1$H NMR (CD$_3$CN): 4.02 (s, 10H, CH$_2$); 8.02 (s, 2H, OH)

$^{13}$C NMR (CD$_3$CN): 68.93

$^{19}$F NMR (CD$_3$CN): -80.0

M. P.: 140 – 145 °C

FTIR: O-H = 3456 cm$^{-1}$
Anal. Calcd C_{12}H_{22}O_{12}GeF_{6}S_{2}: C, 23.66; H, 3.64; Found: C, 22.46; H, 4.22.

\[[\text{Ge}(\text{C}_{10}\text{H}_{20}\text{O}_{5})\text{H}_{2}\text{OOH}]^+] = m/z \ 325/327/329/331 \text{ and} \]

\[[\text{Ge}(\text{C}_{10}\text{H}_{20}\text{O}_{5})\text{OH}]^+] = 307/9/11/13

**Synthesis of** \([\text{Ge}[15]\text{crown}-5\cdot\text{D}_{2}\text{O}][\text{OTf}]_{2} \text{, 3.2} \)

To a solution of \([\text{GeOTf}[15]\text{crown}-5][\text{OTf}] \) (0.545 g, 92.2 mmol) in CH$_2$Cl$_2$, 1:1 equivalence of D$_2$O was added. The resultant colorless solution was left to stir for 24 hours. All volatile components were then removed under reduced pressure. The white solid was recrystallized from CH$_2$Cl$_2$. The crystalline material was characterized as \([\text{Ge}[15]\text{crown}-5\cdot\text{D}_{2}\text{O}][\text{OTf}]_{2}, 3.2. \)

$^1$H NMR (CD$_3$CN): 4.02

$^{13}$C NMR (CD$_3$CN): 68.93

$^{19}$F NMR (CD$_3$CN): -80.0

FTIR (peaks): O-D = 1970 cm$^{-1}$

**Synthesis of** \([\text{Ge}[15]\text{crown}-5\cdot\text{NH}_3][\text{OTf}]_{2} \text{, 3.3} \)

To a solution of \([\text{GeOTf}[15]\text{crown}-5][\text{OTf}] \) (0.545 g, 92.2 mmol) in CH$_2$Cl$_2$, NH$_3$ solution in methanol (1.0 uL, 0.6x10$^{-3}$ mmol) was added. The resultant colorless solution was left to stir for 24 hours. All volatile components were then removed under reduced pressure. The white solid was characterized as \([\text{Ge}[15]\text{crown}-5\cdot\text{NH}_3][\text{OTf}]_{2}, 3.3. \)
$^1$H NMR (CD$_3$CN): 6.3(t, 3H), 4.02(s, 20H)

$^{13}$C NMR (CD$_3$CN): 68.93

$^{19}$F NMR (CD$_3$CN): -80.0

M. P.: 180 – 185 °C

FTIR (peaks): N-H= 3197 cm$^{-1}$

Anal. Calcd for C$_{12}$H$_{23}$O$_{11}$GeF$_6$S$_2$N: C, 22.72; H, 3.16; N, 1.97. Found: C, 23.70; H, 3.18, N, 2.30.

References

Chapter 4

Crown ether complexes of Tin(II)

Trifluoromethanesulfonate

4.1 Introduction

The phenomenal ligand properties of the family of macrocyclic polyethers known as crown ethers has been used since the late 1960's in order to isolate numerous remarkable complexes for elements from throughout the periodic table.\(^1\) In spite of the often interesting nature of the compounds obtained using elements from the s- and d-blocks, the crown ether chemistry of the p-block elements has not been examined nearly as extensively.\(^2\) Recently, we found that differently-sized crown ethers allow for the ready isolation of Ge\(^{II}\) cations, including dications that do not feature any covalent bonds to the semi-metal center;\(^3\)-\(^5\) these results complement the observations of systems with the related cryptand ligands\(^6\) and suggest that the use of such macrocyclic ligands should provide for a rich and interesting chemistry for even more of the p-block elements. In fact, we had previously found that crown ether ligation of our indium(I) trifluoromethanesulfonate (triflate) reagent In\(^{I}\)O\(_3\)SCF\(_3\) (In\(^{I}\)OTf)\(^7\) allows for the isolation of stable and isolable monomeric indium(I) complexes that exhibit unusual and perhaps useful modes of reactivity.\(^8\)-\(^11\)

In light of the isovalent or isoelectronic relationship of Sn\(^{II}\) with Ge\(^{II}\) and In\(^{I}\), respectively, and as part of our continuing investigation of the chemistry of crown ether complexes of p-block elements in low oxidation or valence states,\(^12\) we were interested in
examining the crown ether chemistry of tin(II) analogues. It should be noted that Nicholson and co-workers prepared crystalline crown ether complexes of Sn\textsuperscript{II} halides in the 1980's as part of investigations about the nature of stereochemically-active “lone pairs” of electrons,\textsuperscript{13,14} some of which had been investigated spectroscopically prior to elucidation of their structural features,\textsuperscript{15,16} and [18]crown-6 was employed recently by Feldmann and co-workers to prepare an interesting mixed-valent tin iodide salt.\textsuperscript{17} It should also be emphasized that our investigations of In\textsuperscript{I} and Ge\textsuperscript{II}, in conjunction with other well-known behavior, demonstrate that there are sometimes significant difference between the chemistry of main group element halides and the corresponding triflate analogues in terms of both relative stability and the structures of the complexes that may be isolated. Given the foregoing, in the present work, we detail the results of experimental and computational studies of tin(II) triflate with crown ethers of three different sizes.

### 4.2 Results and Discussion

**Experimental Investigations**

The treatment of equimolar amounts of [18]crown-6 with Sn\textsuperscript{II}OTf\textsubscript{2} in toluene or THF results in the formation of a colorless solution that provides upon concentration crystalline material in excellent yield characterized by microanalysis, multinuclear NMR spectroscopy and single crystal X-ray diffraction as [Sn([18]crown-6)OTf][OTf], \textbf{4.1}[OTf]. The salt \textbf{4.1}[OTf] crystallizes in the space group \textit{P}-1 with one formula unit in the asymmetric unit, which is illustrated in \textbf{Figure 4.1}. The structure of the salt is best-described as consisting of a mono-cationic fragment composed of the crowned tin(II) center, which appears to be bound to one of the triflate groups, and a separate triflate
anion. The covalent radii of Sn and O are 1.40 Å and 0.73 Å, respectively and the ionic radii for Sn(2+) and O(-2) are 0.93 Å and 1.40 Å, respectively.\textsuperscript{18} It thus appears as if only the Sn-O bond to the closest triflate anion, at a distance of 2.282(9) Å, could possibly be treated as a "normal" single bond. The shortest Sn-O distance for the other triflate fragment is 2.596(9) Å, which falls within the sum of the van der Waals radii for Sn (2.19 Å) and O (1.52 Å), but is far longer than a typical single bond. For comparative purposes, it should be noted that the Sn\textsuperscript{II}-OTf distances in the Cambridge Structural Database (CSD)\textsuperscript{19} range from 2.253-3.074 Å (average: 2.544 Å) however the longer distances are certainly best described as being mostly ionic in nature. Furthermore, although the estimated standard deviations (esd) are relatively large, the various S-O distances in 4.1[OTf] are also consistent with description above of the two different types of triflate fragments: the “bound” triflate fragment exhibits the two short S-O bonds and one long S-O bond anticipated, whereas the “free” triflate has a smaller range of S-O distances.
Figure 4.1 Solid state structure of [Sn([18]crown-6)OTf][OTf], 4.1[OTf] – hydrogen atoms are omitted for clarity. Selected metrical parameters including distances (Å) and angles (°): Sn-O(11), 2.282(9); Sn-O(21), 2.596(9); Sn-O(1), 2.506(6); Sn-O(2), 2.767(5); Sn-O(3), 3.026(6); Sn-O(4), 3.013(6); Sn-O(5), 2.712(6); Sn-O(6), 2.464(6); S(1)-O(11), 1.449(9); S(1)-O(12), 1.409(8); S(1)-O(13), 1.416(7); S(2)-O(21), 1.437(9); S(2)-O(22), 1.432(7); S(2)-O(23), 1.414(8).

Overall, the structure is clearly related to the halide complexes reported by Nicholson of the form [Cl-Sn([18]crown-6)][A] (A = SnCl₃ and ClO₄⁻) in that it contains a monocationic Sn²⁺ fragment in which the substituent bonded to the tin atom lies nearly normal to the crown ether. In the case of the chlorinated cation, the face opposite the substituent does not feature unusually close contacts and appears to suggest the presence of a stereochemically-active "lone pair" of electrons and the results of Mössbauer spectroscopy suggest that this is perhaps a reasonable description, although the data
suggest that the "lone pair" has a very high 5s-character.\textsuperscript{13} However, in the case of \textbf{4.1}[OTf], the relatively close distance of the second triflate renders the situation somewhat more ambiguous; the nature of cation is examined in more detail below using computational methods.

In spite of the structural features observed in the solid state, the \textsuperscript{19}F NMR spectrum of \textbf{4.1}[OTf] in CD\textsubscript{2}Cl\textsubscript{2} solution features only a single peak and could thus be consistent either with the complete dissociation of the salt into [Sn([18]crown-6)]\textsuperscript{+2} and two anionic triflate ions or, more likely, the rapid exchange of the free and bound triflate groups on the NMR timescale. None of the other NMR spectra exhibit any features that are worthy of note.

In light of the similarity of the cationic fragment \textbf{4.1} with In([18]crown-6), and the previous results of Nicholson,\textsuperscript{14} we reasoned that the smaller [15]crown-5 should likely produce a "crown sandwich" and thus the reaction was undertaken using a 2:1 ratio of crown ether to tin. The reaction in THF proceeded as anticipated and generated [Sn([15]crown-5)\textsubscript{2}][OTf]\textsubscript{2}, \textbf{4.2}[OTf]\textsubscript{2}, in virtually quantitative yield upon removal of the volatile components, however the material often contained residual solvent. Recrystallization of the material from CH\textsubscript{2}Cl\textsubscript{2} produced crystalline material that was generally of poor quality in terms of its suitability for analysis by single crystal X-ray diffraction. Several samples were twinned and disordered significantly and, although they confirmed the proposed connectivity, they provided extremely low-quality solutions. The solution for the highest quality data set we obtained is illustrated in \textbf{Figure 4.2}. Again, the data were of poor quality but were adequate to confirm that the structure does, in fact, contain an unambiguously dicationic "crown sandwich" of Sn\textsuperscript{II} that does not appear to
bear a stereochemically-active "lone pair" of electrons. Given the low-quality of the data, the values obtained for the metrical parameters are not suitable for extensive discussion but they are consistent with those reported by Nicholson and co-workers for [Sn([15]crown-5)2][SnCl3]2.14

Figure 4.2 Solid state structure of [Sn([15]crown-5)2][OTf]2, 4.2[OTf]2 – hydrogen atoms are omitted for clarity. Selected metrical parameters including distances (Å) and angles (°): Sn-O(11), 2.53(2); Sn-O(12), 2.59(1); Sn-O(13), 2.76(1); Sn-O(14), 2.75(1); Sn-O(15), 2.59(1); Sn-O(21), 2.83(1); Sn-O(22), 2.98(1); Sn-O(23), 2.87(1); Sn-O(24), 2.77(1); Sn-O(25), 2.83(1); centroid(O11-O15)-Sn-centroid(O21-O25), 175.3(1); plane(O11-O15) plane(O21-O25), 2.4(1).

Finally, the treatment of tin(II) triflate with two equivalents of [12]crown-4 in THF provided the 2:1 crown ether complex [Sn([12]crown-4)2][OTf]2, 4.3[OTf]2 in excellent yield upon concentration. Recrystallization of the material generated colorless crystals suitable for examination by single crystal X-ray diffraction. The salt crystallizes
in the monoclinic space group \( P2_1/c \) with one formula unit located in the asymmetric unit, the contents of which is illustrated in **Figure 4.3.** The structure of \( 4.3[\text{OTf}]_2 \) is best described as consisting of a bent-sandwich-like dicationic \([\text{Sn([12]crown-4)}_2]^+\) fragment and two anionic triflate ions. Although it may appear as if the triflate group containing the oxygen atom labeled O(11) may be in close proximity to the open wedge of the cation, the Sn-O(11) distance of 3.119(4) Å is more than 0.5 Å longer than the Sn-O distance to the "anionic" OTf group in \( 4.1[\text{OTf}] \) and it is longer than any of the Sn-O distances for triflate groups in the CSD. Furthermore, the S-O distances to S(1) are virtually equivalent to each other and to those of the "free" triflate ion containing S(2) thus suggesting that both of the fragments should described as ionic triflate species. Although the tin complex and the closest triflate ion may perhaps exist as some form of contact ion pair, the extreme length of the Sn-O interaction appears to render such a description implausible.

**Figure 4.3** Solid state structure of \([\text{Sn([12]crown-4)}_2][\text{OTf}]_2\), \( 4.3[\text{OTf}]_2 \) – hydrogen atoms are omitted for clarity. Selected metrical parameters including distances (Å) and angles (°): Sn-O(11), 3.119(4); Sn-O(31), 2.476(4); Sn-O(32), 2.495(3); Sn-O(33), 2.741(4); Sn-O(34), 2.813(3); Sn-O(41), 2.475(4); Sn-O(42), 2.474(3); Sn-O(43), 2.629(3); Sn-O(44),

66
2.676(3); S(1)-O(11), 1.430(4); S(1)-O(12), 1.425(4); S(1)-O(13), 1.441(4); S(2)-O(21), 1.426(4); S(2)-O(22), 1.432(4); S(2)-O(23), 1.440(4); centroid(O(31)-O(34))-Sn-centroid(O(41)-O(44)), 153.95(2); plane(O(31)-O(34))\( \angle \)plane(O(41)-O(44)), 40.7(1).

The dication \textbf{4.3} features four relatively short Sn-O bonds ranging from 2.474(3) to 2.495(3) Å (two from each of the crown ethers) and four substantially longer bonds ranging from 2.629(3) to 2.813(3) Å; the bent geometry of the sandwich is further evident from the angle between the O\(_4\) planes in the two heterocycles (40.7(1)°) and the 153.95(2)° angle at the tin atom between the O\(_4\) centroid on each of the crown ethers. The bent arrangement of \textbf{4.3} contrasts sharply with the more conventional centrosymmetric sandwich observed for the germanium(II) analogue \([\text{Ge}([12]\text{crown-4})_2]^{+2},^3\) as one might perhaps anticipate on the basis of the greater size of Sn\(^{II}\) versus Ge\(^{II}\), and again may imply the presence of a stereochemically-active "lone pair" of electrons on the tin center. However, it should be noted that the \textit{bis}([12]\text{crown-4}) complexes of potassium cations, which cannot possibly have any non-bonding valence electrons, also exhibit structures in which the two macrocycles appear to be canted so as to expose a face of metal atom. In fact, the centroid-K-centroid angles for the complexes reported in the CSD range from roughly 155° to the perhaps anticipated 180° and the angles between the best-fit O\(_4\) planes on the two rings range from 0° to almost 30° so the geometrical parameters of the complex do not appear to be an especially reliable indicator as to the presence of a stereochemically-active "lone-pair" of electrons on the encapsulated metal center. Given the foregoing, the reason(s) for the bent arrangement of \textbf{4.3} is not clear and the experimental observations we have obtained are not sufficient to allow for an unambiguous conclusion in that regard.
Computational Investigations

In light of the questions arising from the observations obtained from experimental investigations, we performed a series of density functional theory (DFT) calculations in order to assess whether the structural features that we have observed for the cationic fragments experimentally are consistent with the minimum energy structures that one would find in the gas phase or if the peculiarities of the structures are best attributable to the consequences of crystal packing effects. We also endeavored to gain insight into the nature of non-bonding electrons on the tin(II) atoms in such complexes through the analysis of the electron distribution in reasonable model compounds. The geometries of suitable model compounds for each of the cations were optimized in the absence of any constraints using the method described in the Experimental Section. The optimized structures obtained for each of the model compounds containing [18]crown-6 ligands are presented in Figure 4.4 and those containing the smaller crown ethers are depicted in Figure 4.5; a summary of pertinent electronic and structural information is collected in Table 4.1.
As illustrated in Figure 4.4, the optimized structure of the model $[\text{Sn}([18]\text{crown-6})-\text{OTf}]^{+1}$ cation is very similar to the structure of the monocationic fragment observed experimentally in the solid state with two notable deviations: (1) the tin atom is predicted to reside in the center of the crown ether roughly 0.2 Å above the O₆ centroid opposite the triflate fragment while the tin atom in the crystal structure is located toward one side of the ring; and, (2) the calculated Sn-O distance of 2.125 Å to the triflate ligand is significantly shorter than the 2.282(9) Å observed experimentally. In contrast, the triflate-
free dication model \([Sn([18]crown-6)]^{+2}\) features a very distorted crown ether that does not resemble any of the structures that have ever been reported experimentally. Overall, these observations suggest that although the monocationic model \([Sn([18]crown-6)-OTf]^{+1}\) is certainly more appropriate, the interaction of the anionic triflate with the monocationic fragment in the real compound is clearly sufficient to perturb the system noticeably.

As for the analysis of the electronic structure of the \([18]\text{crown-6}\) model systems, we wish to note that the Wiberg Bond Index of around 0.29 for the \(Sn-OTf\) bond is significantly larger than the corresponding value of 0.11 found for the isoelectronic indium(I) model, as one would anticipate given the higher electronegativity and charge of \(Sn^{II}\) versus \(In^{I}\); this observation is also consistent with the interpretation of \([Sn([18]crown-6)-OTf]^{+1}\) as being bound relatively tightly. Nevertheless, we wish to emphasize that in spite of the significant interaction between the tin atom and the triflate group, the non-bonding pair of electrons on the tin atom remains almost exclusively (ca. 96\%) \(5s\) in character, as expected on the basis of the results of the Mössbauer experiments performed on the related halide cations.
Table 4.1 Selected calculated quantities from the DFT optimized structures of model compounds for tin and indium crown ether complexes; distances are reported in Å units.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$N_{imag}^a$</th>
<th>Q(M)$^b$</th>
<th>LP(M)</th>
<th>LP(M) $^{c}$% 5s</th>
<th>WBI$^d$ (M-O$^{ring}$) range</th>
<th>WBI$^d$ (M-OTf)</th>
<th>WBI$^d$ (M) total</th>
<th>R (M-O$^{ring}$) range</th>
<th>r(M-OTf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L= [18]crown-6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[SnL]$^{+}$</td>
<td>0</td>
<td>1.50</td>
<td>97.49</td>
<td>0.1132-0.1729</td>
<td>-</td>
<td>0.9928</td>
<td>2.426-2.636</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>[Sn-OTf]$^{+}$</td>
<td>0</td>
<td>1.44</td>
<td>95.96</td>
<td>0.1007-0.1117</td>
<td>0.2883</td>
<td>1.0899</td>
<td>2.692-2.760</td>
<td>2.125</td>
<td></td>
</tr>
<tr>
<td>In-OTf</td>
<td>0</td>
<td>0.74</td>
<td>95.72</td>
<td>0.0446-0.0530</td>
<td>0.1136</td>
<td>0.6065</td>
<td>2.805-2.962</td>
<td>2.253</td>
<td></td>
</tr>
<tr>
<td>[SnL$_2$]$^{-}$</td>
<td>0</td>
<td>1.36</td>
<td>99.88</td>
<td>0.0857-0.1193</td>
<td>-</td>
<td>1.2268</td>
<td>2.620-2.994</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>L= [12]crown-4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[SnL$_2$]$^{+}$ bent</td>
<td>0</td>
<td>1.43</td>
<td>98.26</td>
<td>0.0967-0.1396</td>
<td>-</td>
<td>1.1398</td>
<td>2.484-2.767</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>[SnL$_2$]$^{+}$ linear</td>
<td>1$^e$</td>
<td>1.42</td>
<td>100.00</td>
<td>0.1181-0.1185</td>
<td>-</td>
<td>1.1535</td>
<td>2.630-2.634</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Number of imaginary frequencies in the Hessian matrix
$^b$NBO charge on the metal atom
$^c$NBO percentage of s character in the "lone pair" orbital on the metal atom
$^d$NBO Wiberg Bond Index for the bonds indicated
$^e$This transition state is less stable than the bent geometry by ca. 17 kJ/mol; the imaginary frequency has a value of -29.1 cm$^{-1}$.

The optimized structure of the model [Sn([15]crown-5)$_2$]$^{+2}$, as depicted in Figure 4.5, is completely consistent with those observed in the solid state both in this work and in the previous report and requires no additional comment. As one would predict on the basis of the roughly centrosymmetric coordination environment about the tin atom, the non-bonding valence electrons on tin are predicted to reside in an orbital that is essentially exclusively of 5s character.
Figure 4.5 DFT optimized structures for model compounds containing the [15]crown-5 and [12]crown-4 ligands.

For the [12]crown-4 complexes, the geometry optimizations provided two different possible dicationic [Sn([12]crown-4)_2]^{2+} model compounds illustrated in Figure 4.5; one having a roughly centrosymmetric arrangement of crown ether ligands (labeled "linear" in the figure) and one having a "bent" geometry more similar to the structure observed experimentally. Frequency analyses on the two optimized structures reveal that whereas the bent structure is a true minimum, the linear structure exhibits one imaginary frequency (albeit of only \(-29.1 \text{ cm}^{-1}\)) and is approximately 17 kJ/mol less stable than the bent model. Thus it is clear that the adoption of a bent geometry is not simply an effect of crystal packing but is an integral feature of this complex. Furthermore, it should be noted that the optimized model structure matches the experimental one almost perfectly, as illustrated in Figure 4.6, which suggests that the apparent interaction between the sandwich complex and the triflate anion does not actually affect the structure of the dication in a significant manner. Regardless of the geometry adopted by the sandwich
complex, the non-bonding electrons are again found to reside in an orbital that is more than 98% 5s character.

Figure 4.6 Overlay of the DFT optimized structure (dotted) and the experimental structure (solid) for the [12]crown-4 complexes.

4.3 Conclusions

The treatment of Sn$^{II}$OTf$_2$ with crown ethers produces coordination complexes of Sn$^{II}$ featuring dramatically different structural features depending on the size of the ligand. The largest ligand, [18]crown-6 is sufficiently large enough to encircle the metal and produces a monocationic salt of the form [Sn([18]crown-6)-OTf][OTf], the cation of which appears to feature a stereochemically-active "lone pair" of electrons. A single [15]crown-5 macrocycle is too small to ligate the Sn$^{II}$ center and instead a centrosymmetric sandwich-like dicationic complex is generated of the form [Sn([15]crown-5)$_2$][OTf]$_2$ that appears to have a "lone pair" that is stereochemically-
inactive. Finally, the smallest of the macrocycles, [12]crown-4, also produces a 2:1 complex of the form [Sn([12]crown-4)₂][OTf]₂, however the structure of the dication is bent and again appears to be consistent with a stereochemically-active pair of non-bonding electrons. Computational investigations predict the observed structures quite well and suggest that the non-bonding valence electrons on tin are always almost exclusively 5s in character regardless of the gross structural features of the complex.

As a final observation, we wish to note that in stark contrast to the related In¹ species, none of the Sn² complexes appear to undergo insertion chemistry into the C-Cl bonds of chlorocarbon solvents. In fact, as indicated above, several of the complexes are actually recrystallized from such solvents.

4.4 Experimental

General Methods

All work was carried out using standard inert-atmosphere techniques. All reagents and solvents were obtained from Aldrich or Strem and were used without further purification. Solvents were dried on a series of Grubbs‘-type columns and were degassed prior to use.²⁰ C₆D₆, CD₃CN and CD₂Cl₂ were distilled over CaH₂ and then stored over 4 Å molecular sieves. Unless otherwise noted in the text, NMR spectra were recorded at room temperature on either a Bruker DPX 300 MHz spectrometer or a DRX 500 MHz spectrometer. Chemical shifts are reported in ppm, relative to external standards (SiMe₄ for ¹H and ¹³C; CFCl₃ for ¹⁹F; SnMe₄ for ¹¹⁹Sn). Melting points were obtained using an Electrothermal® melting point apparatus on samples sealed in glass capillaries under dry nitrogen. Elemental analysis was performed at Guelph Chemical Laboratories, Guelph, Ontario, Canada.
**Synthesis of [SnOTf([18]crown-6)][OTf], 4.1[OTf]**

A solution of [18]crown-6 (0.634 g, 2.40 mmol) in toluene was added to a solution of Sn(OTf)$_2$ (1.00 g, 2.64 mmol) in toluene. The resultant colorless solution was left to stir for 24 hours. Slow evaporation of the solvent produced a colorless crystalline material which was identified as [SnOTf([18]crown-6)][OTf] (1.53 g, 93%). Please note that while this compound was reported in the supporting information (Appendix I) of our preliminary communication about Ge$^{II}$ complexes,$^3$ the data are included here for completeness.

$^1$H NMR (CD$_2$Cl$_2$): 3.12

$^{13}$C NMR (CD$_2$Cl$_2$): 70.57 (s, CH$_2$)

$^{19}$F NMR (CD$_2$Cl$_2$): -78.4

D. P.: ca. 210 °C

Anal. Calcd for C$_{14}$H$_{24}$F$_6$SnO$_{12}$S$_2$: C, 24.69; H, 3.55; O, 28.18. Found: C, 24.22; H, 3.19; O, 27.70.

**Synthesis of [Sn([15]crown-5)$_2$][OTf]$_2$, 4.2[OTf]$_2$**

A solution of [15]crown-5 (0.20 mL, 0.214 g, 0.972 mmol) in THF was added to a solution of Sn(OTf)$_2$ (0.200 g, 0.480 mmol) in THF. The resultant colorless solution was left for stirring for 2 hours after which all volatile components were removed under reduced pressure. The remaining white solid product was washed with pentane (5 mL) to yield a colorless solid characterized as [Sn([15]crown-5)$_2$][OTf]$_2$ (0.401 g, 0.468 mmol, 97%). Single crystals suitable for X-ray diffraction studies were obtained through the
evaporation of a CH$_2$Cl$_2$ solution of this solid; the crystalline material was identified as and characterized as [Sn([15]crown-5)$_2$][OTf]$_2$ (0.200 g, 49% crystalline yield).

$^1$H NMR (CD$_2$Cl$_2$): 3.851 (s, CH$_2$)

$^{13}$C NMR (CD$_2$Cl$_2$): 69.4 (s, CH$_2$)

$^{19}$F NMR (CD$_2$Cl$_2$): -79.3

M. P.: 100 – 105 °C

Anal. Calcd for C$_{22}$H$_{40}$F$_6$SnO$_{16}$S$_2$: C, 30.82; H, 4.70; O, 29.86. Found: C, 34.34; H, 5.52; O, 33.25 – this is consistent with [Sn([12]crown-4)$_2$][OTf]$_2$ · 2THF.

**Synthesis of [Sn([12]crown-4)$_2$][OTf]$_2$, 4.3[OTf]$_2$**

A solution of [12]crown-4 (0.15 mL, 0.166 g, 0.943 mmol) in THF was added to a solution of Sn(OTf)$_2$ (0.200 g, 0.479 mmol) in THF. The resultant colorless solution was left for stirring for 2 hours after which all volatile components were removed under reduced pressure. The remaining white solid product was washed with pentane (5 mL) and dried under reduced pressure to yield a colorless solid characterized as [Sn([12]crown-4)$_2$][OTf]$_2$ (0.355 g, 0.465 mmol, 96%). Single crystals suitable for X-ray diffraction studies were obtained through the evaporation of a CH$_2$Cl$_2$ solution of this solid; the crystalline material was identified as [Sn([12]crown-4)$_2$][OTf]$_2$ (0.125 g, 0.162 mmol, 34% crystalline yield).

$^1$H NMR (CD$_2$Cl$_2$): 3.834 (s, CH$_2$)

$^{13}$C NMR (CD$_2$Cl$_2$): 69.5 (s, CH$_2$)

$^{19}$F NMR (CD$_2$Cl$_2$): -79.4

M. P.: 149 – 152 °C
Anal. Calcd for C$_{18}$H$_{32}$F$_6$SnO$_{14}$S$_2$: C, 28.10; H, 4.19; O, 29.12. Found: C, 28.48; H, 4.46; O, 29.60.
References


Chapter 5

Experimental and computational insights into the stabilization of low-valent main group elements using crown ethers and related ligands

5.1 Introduction

The chemistry of main group elements in low oxidation or valence states has been an area of active research and discovery over the last few decades that has contributed significantly to the "renaissance" of main group chemistry, and is projected to play a significant role in the future of the field. Low oxidation state compounds are of interest because the unusually electron-rich nature of the species often results in dramatically different chemical behavior and structural features in comparison to analogous compounds that contain the element in a more typical oxidation state. In fact, their unique properties can render low oxidation state species appropriate for uses ranging from new reagent and ligand chemistry, to catalysis (or as models for catalysts) and even to function as materials precursors or as models for the formation of nano-scale and bulk materials.

As has often been the case for low-coordinate and/or highly-reactive species, the judicious design of ligands has proven crucial to the successful isolation of species under typical laboratory conditions. Most of the ligands designed to stabilize otherwise-reactive molecular fragments have featured the use of either steric bulk (e.g. terphenyl ligands) to provide a kinetic barrier to reactivity or donor groups to provide electron density to
formally vacant orbitals. Often, as in the case of α-diimino ligands, β-diketiminate ligands and related nitrogen-based chelating ligands, both steric and electronic stabilization may be provided by the ligand.\textsuperscript{13-17}

As an alternative approach to the stabilization of low-valent main group species, we have recently investigated the use of multi-dentate ligands featuring numerous weak donors and no strong covalent bonds. In particular, we have explored the use of crown ethers as ligands for the stabilization and solubilization of low-valent species from groups 13 and 14, and others have also found that such ligands may be used to isolate interesting mixed-valent\textsuperscript{18} and higher valent species.\textsuperscript{19} During the course of our investigations, we have made a number of surprising and sometimes puzzling observations. For example, as illustrated in Scheme 5.1, whereas the free salt [In][OTf] is stable in the presence of halocarbon solvents such as CH\textsubscript{2}Cl\textsubscript{2} and CHCl\textsubscript{3},\textsuperscript{20} the [18]crown-6 ligated variant of the salt [In([18]crown-6)][OTf] rapidly inserts into the C-Cl bonds of such solvents.\textsuperscript{21,22} However, the corresponding salt [In([15]crown-5)\textsubscript{2}][OTf], containing the sandwich-like cation, appears to be inert to such oxidative addition chemistry.\textsuperscript{23} In contrast, while [In][OTf] decomposes rapidly in THF, the crown-ether complexes are stable in that solvent. Furthermore, whereas [In([18]crown-6)][OTf] is a stable and readily-isolated salt that exists as a contact ion pair in the solid state,\textsuperscript{21,24} all attempts to ligate indium(I) halides using crown ethers, either starting from the halides or by generating them \textit{in situ}, results in the rapid disproportionation of the material. In fact, fragments of the form "In-X([18]crown-6)" have only been isolated as the donor component in adducts of the type X-([18]crown-6)In→InX\textsubscript{3}.\textsuperscript{25}
Some observed reactivity patterns of monovalent indium halides and triflate salts and their crown ether complexes (X = Cl, Br, I; R = H, Cl). Similarly, our studies of the chemistry of the isovalent germanium species revealed marked differences between the corresponding triflate and halide analogues, as illustrated in Scheme 5.2. The use of the [12]crown-4 ligands resulted in the formation of salts containing sandwich-like dications of the form [Ge([12]crown-4)₂]^{2+} that, like the related [2,2,2]-cryptand encapsulated germanium dication, exhibit no unusual interaction with the counter anions. In stark contrast, the use of the larger crown ethers provided products in which the nature and type of cation-anion interactions have a pronounced effect. For example, whereas the [15]crown-5 adduct of GeOTf₂ contains a cation of the form [Ge([15]crown-5)-OTf]⁺ that features a crown ether with a typical
conformation, the cation in the related salt [GeCl([15]crown-5)][GeCl$_3$] exhibits a crown ether that appears to be "folded".\textsuperscript{26}

\begin{center}
\includegraphics[width=0.8\textwidth]{scheme_5.2.png}
\end{center}

**Scheme 5.2** Illustrations of the structures of the complexes observed from the treatment of divalent germanium halides or triflates with differently sized crown ethers.

In this work we investigate a series of stable tin complexes that are isovalent with the indium(I) and analogous to the germanium(II) complexes described above, and whose spectral and physical properties allow us to obtain valuable insight into their chemistry and electronic structure. We also examine the properties of related complexes of tin(II) with the more flexible glyme-type podand ligands, which are the acyclic analogues of crown ethers, in order to determine if they are suitable for the stabilization and/or solubilization of low-valent species. More generally, the conclusions we can draw from these studies provide for a deeper understanding of the factors that contribute to the
stabilization (or activation) of low-valent species, thereby allowing for improvements in the design of ligands suitable for the desired reactivity.

5.2 Experimental Section

5.2.1 General Methods

All work was carried out using standard inert-atmosphere techniques. All reagents and solvents were obtained from Aldrich or Strem and were used without further purification. Complexes \( \text{Sn(OTf)}_2 \cdot [18\text{-Crown-6}] \) (5.1), \( \text{Sn(OTf)}_2 \cdot ([15\text{-Crown-5}})_2 \) (5.2), and \( \text{Sn(OTf)}_2 \cdot ([12\text{-Crown-4}})_2 \) (5.3) were prepared as described previously.\(^{29}\) The salt \([\text{SnCl([18]crown-6][SnCl}_3]\) (5.6) was prepared by a modification of the reported procedure.\(^{30,31}\) Solvents were dried on a series of Grubbs’-type columns and were degassed prior to use.\(^{32}\) \(\text{C}_6\text{D}_6\) and \(\text{CD}_2\text{Cl}_2\) were distilled over \(\text{CaH}_2\) and then stored over 4 Å molecular sieves. Unless otherwise noted, solution NMR spectra were recorded at room temperature on either Bruker DPX 300 MHz or DRX 500 MHz spectrometers. Chemical shifts are reported in ppm, relative to external standards (SiMe\(_4\) for \(^1\text{H}\) and \(^{13}\text{C}\); CFCl\(_3\) for \(^{19}\text{F}\); SnMe\(_4\) for \(^{119}\text{Sn}\)). Elemental analyses were performed at the Centre for Catalysis and Materials Research at the University of Windsor.

5.2.2 Synthetic Procedures

Each of the glyme complexes was prepared using the following procedure. A solution of the desired glyme in acetonitrile (ca. 1 mL) was added dropwise to a solution of \(\text{SnOTf}_2\) in the same solvent (50 mL). The resultant colorless solution was stirred overnight and subsequently all volatile components were removed under reduced pressure to afford a colorless liquid. The liquid was rinsed and sonicated with a 1:5 mixture of ether: pentane to yield a cream colored solid characterized in each case as the
target 1:1 glyme complex. Crystalline material suitable for examination by single crystal X-ray diffraction was obtained by the slow evaporation of a saturated solution of this material from a 50:50 mixture of THF and toluene.

**Data for Sn(OTf)$_2$-triglyme 5.4**

Reagents: triglyme (0.304 mL, 1.68 mmol); SnOTf$_2$ (350 mg, 0.840 mmol). Product: Sn(OTf)$_2$-triglyme (5.4) (405 mg, 0.524 mmol, 62%). Anal. Calcd. for C$_{10}$H$_{18}$F$_6$O$_{10}$S$_2$Sn (fw 595.05 g mol$^{-1}$): C, 20.14; H 3.04. Found: C, 20.08; H, 3.11. $^1$H NMR (CD$_3$CN, $\delta$, ppm): 3.56 (s, 6H), 3.76 (m, 4H), 4.02 (m, 8H). $^{13}$C NMR{$^1$H} (CDCl$_3$, $\delta$, ppm): 58.4 (s), 69.5 (s), 69.8 (s), 71.5 (s), 119.8 (q). $^{19}$F{$^1$H} NMR (CD$_3$CN, $\delta$, ppm): -79 ppm (s).

**Data for Sn(OTf)$_2$-tetraglyme 5.5**

Reagents: tetraglyme (0.211 mL, 0.960 mmol); SnOTf$_2$ (400 mg, 0.960 mmol). Product: Sn(OTf)$_2$-tetraglyme (5.5) (554 mg, 0.868 mmol, 90%). Anal. Calcd. for C$_{12}$H$_{22}$F$_6$O$_{11}$S$_2$Sn (fw 639.10 g mol$^{-1}$): C, 22.50; H 3.46. Found: C, 22.06; H, 3.60. $^1$H NMR (CD$_3$CN, $\delta$, ppm): 3.47 (s, 6H), 3.72 (m, 4H), 3.94 (m, 8H), 4.02 (m, 4H). $^{13}$C{$^1$H} NMR (CDCl$_3$, $\delta$, ppm): 58.0 (s), 69.0 (s), 70.0 (s), 70.2 (s), 70.8 (s), 120.0 (q). $^{19}$F{$^1$H} NMR (CD$_3$CN, $\delta$, ppm): -79 ppm (s).

**5.2.3 X-ray Crystallography**

The subject crystals were covered in Nujol$^\text{®}$ or Paratone-N$^\text{®}$, mounted on a goniometer head and rapidly placed in the dry N$_2$ cold-stream of the low-temperature apparatus (Kryoflex) attached to the diffractometer. The data were collected using the SMART$^{33}$ software on a Bruker APEX CCD diffractometer using a graphite monochromator with MoK$_{\alpha}$ radiation ($\lambda = 0.71073 $ Å). A hemisphere of data was
collected for each crystal using a counting times ranging from 10 to 30 seconds per frame at -100 °C. Details of crystal data, data collection and structure refinement are listed in Table 5.1. Data reduction was performed using the SAINT-Plus software and the data were corrected for absorption using SADABS. The structures were solved by direct methods using SIR97 and refined by full-matrix least-squares on $F^2$ with anisotropic displacement parameters for the non-disordered heavy atoms using SHELXL-97 and the WinGX software package and thermal ellipsoid plots were produced using SHELXTL. The space group assignments and structural solutions were evaluated using PLATON. One of the triflate groups in 5.4 was disordered and this disorder was refined using a 2-site model in which the corresponding thermal parameters and bond distances in each of the two components were restrained to be similar; the refinement revealed that the occupancy of the most common site is approximately 70%. Powder X-ray diffraction (pXRD) experiments that confirm that the bulk materials are consistent with the single crystal structures were performed with a Bruker D8 Discover diffractometer equipped with a Hi-Star area detector using Cu Kα radiation ($\lambda = 1.54186 \text{ Å}$).
Table 5.1 Summary of crystallographic data for the compounds in this work.

<table>
<thead>
<tr>
<th>Compound</th>
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<th>[Sn(tetraglyme)][OTf][Sn(tetraglyme)][OTf]_2</th>
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<td>5.5</td>
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<td>C_{12}H_{22}F_{6}O_{11}Sn</td>
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<td>P2_1/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>8.7518(8)</td>
<td>14.1583(19)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>16.1270(14)</td>
<td>10.1383(14)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>14.8106(13)</td>
<td>17.040(2)</td>
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<tr>
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<td>90</td>
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<tr>
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<tr>
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<tr>
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<td>1.752-27.50</td>
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<tr>
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<td>5166 / 0 / 291</td>
</tr>
<tr>
<td>Goodness-of-fit, S = F² (all data)</td>
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<td>1.198</td>
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<td>Final R indices</td>
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<tr>
<td>wR² indices (all data)</td>
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<tr>
<td>Largest diff. peak and hole (e Å⁻³)</td>
<td>1.019 and -0.587</td>
<td>1.586 and -1.005</td>
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</tbody>
</table>

*S = \left[ \sum w(F_o^2 - |F_c|^2) \right] / (n-p)^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of parameters used.} \quad ^b R1(F) = \sum(|F_o| - |F_c|)/\sum|F_o|, \text{ for reflections with } F_o > 4(\sum (F_o)). \quad wR²(F^2) = \left\{ \sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2 \right\}^{1/2}, \text{ where } w \text{ is the weight given each reflection.}

5.2.4 Mössbauer Spectroscopy

Temperature-dependent $^{119}$Sn Mössbauer effect (ME) spectra were acquired in transmission geometry using a 2mCi $^{119m}$Sn source (CaSnO₃) as described previously.⁴¹
All isomer shifts (IS) are with respect to the centroid of a room temperature BaSnO$_3$ absorption spectrum, and spectrometer calibration was effected as usual.$^{42}$ Temperature monitoring over the extended data acquisition intervals was effected using the Daswin program of Glaberson.$^{43}$ In order to monitor the temperature-dependence of the recoil-free fraction ($-d\ln A/dT$), the transmission rate was recorded both before and after each temperature point data acquisition. It should be noted that all of the ME spectra show the presence of an Sn(IV) impurity with a signal at around 0 mm·s$^{-1}$, which is almost certainly a tin(IV) oxide that appears to arise as a results of sample preparation in air.$^{44}$

5.2.5 **Solid-state NMR Spectroscopy**

$^{119}$Sn and $^{13}$C solid-state NMR (SSNMR) spectra were acquired on a Varian Infinity Plus spectrometer with an Oxford 9.4 T wide-bore magnet [$\nu_0(^1\text{H}) = 399.73$ MHz]. Tin chemical shifts were referenced to neat liquid Me$_4$Sn ($\delta_{\text{iso}} = 0.0$ ppm).$^{45}$ Carbon chemical shifts were referenced to tetramethylsilane ($\delta_{\text{iso}} = 0.0$ ppm) by using the high-frequency peak of adamantane as a secondary reference ($\delta_{\text{iso}} = 38.56$ ppm).$^{46}$

All SSNMR experiments were performed on triple resonance 4 mm HXY or double-resonance 4 mm HX Varian/Chemagnetics probes. Magic-angle spinning (MAS) $^{119}$Sn SSNMR spectra were acquired with either direct excitation of $^{119}$Sn ($\pi/2$-acquire) or with variable-amplitude cross-polarization (VACP) from $^1$H.$^{47,48}$ Static (i.e., stationary sample) $^{119}$Sn SSNMR spectra were acquired with a variety of pulse sequences which are indicated in the Figures: (i) direct excitation spin echo ($\pi/2-\tau-\pi-\tau$-acquire), (ii) quadrupolar Carr-Purcell Meiboom-Gill (QCPMG),$^{49}$ (iii) CP spin echo, (iv) cross-polarization/Carr-Purcell-Meiboom-Gill (CP/CPMG).$^{50,51}$ Echo reconstructed CPMG spectra were obtained by summing the whole echoes of the FIDs in the time domain,
followed by Fourier transform and magnitude calculation. CP experiments were optimized directly on the individual samples. All spectra were acquired with $^1$H decoupling using the TPPM decoupling scheme. All $^1$H-$^{119}$Sn CP experiments employed 2.15 μs $\pi/2$ proton pulses, Hartman-Hahn matching fields of approximately 40 kHz, contact times between 5 and 10 ms and recycle delays between 2 to 8 s. $^{119}$Sn{$^1$H} direct excitation experiments employed recycle delays of 10 to 20 s and $\pi/2$ pulses of 1.55 μs, and between 80 and 2000 transients were collected. Static and MAS $^{119}$Sn SSNMR spectra were simulated with the WSolids program, which includes Herzfeld-Berger analysis of MAS spectra. The anisotropic CS tensor parameters ($\Omega$ and $\kappa$) and $\delta_{bs0}$ were initially obtained from simulations of the MAS $^{119}$Sn SSNMR spectra (Figure S1) and refined via simulations of static $^{119}$Sn SSNMR spectra. For 5.6, the CS tensor parameters were obtained exclusively from simulations of the MAS $^{119}$Sn SSNMR spectrum. The MAS $^{13}$C SSNMR spectra are presented exclusively in the Supporting Information (Appendix IV).

5.2.6 Cyclic Voltammetry

Cyclic voltammetry experiments were conducted using a Bioanalytical Systems Electrochemical Analyzer BAS100B/W instrument employing a one-compartment, three electrode cell with a 3 mm diameter glassy carbon working electrode, a platinum counter electrode and an Ag/AgNO$_3$ (0.1 M in MeCN) reference electrode. The voltammograms were recorded for solutions of each of the complexes in dichloromethane using electrochemical grade [NBu$_4$][PF$_6$] (0.1 M) as the supporting electrolyte. A variety of scan rates were examined and the results reported herein were recorded at 100 mVs$^{-1}$. 
5.2.7 Computational Investigations

DFT and MP2 Calculations of Electronic Structure and Population Analyses. All of the computational investigations were performed using the Shared Hierarchical Academic Research Computing Network (SHARCNET) facilities (www.sharcnet.ca), with either the Gaussian03\textsuperscript{57} or Gaussian09\textsuperscript{58} program suites. Geometry optimizations have been calculated using density functional theory (DFT), specifically implementing the B3PW91 method\textsuperscript{59,60} in conjunction with Stuttgart/Dresden (SDD) quasi-relativistic effective core pseudopotential and basis set for Sn\textsuperscript{61} and the 6-31G(d) basis set for all other atoms. The geometry optimizations were not subjected to any symmetry restrictions and each stationary point was confirmed to be a minimum having zero imaginary vibrational frequencies. Single point calculations were conducted at the MP2 level using the same basis set on models in which the heavy atom positions were those observed in the solid state structures and hydrogen atoms were placed in appropriate geometrically-calculated positions (with C-H bond lengths set to 1.07 Å) using Gaussview 3.0. Population analyses were conducted using the Natural Bond Orbital (NBO)\textsuperscript{62} implementation included with the Gaussian packages. The magnitudes of the lowest-energy electronic transitions were computed using time-dependent DFT (TD-DFT) at the B3PW91/dgdzvp\textsuperscript{63,64} level of theory using the single point geometries. Plots of molecular orbitals and electron densities were generated using MOLDEN.\textsuperscript{65}

DFT Calculations of $^{119}$Sn NMR Parameters. Theoretical calculations were performed with the EPR and NMR module\textsuperscript{66-68} of the Amsterdam Density Functional (ADF) program suite.\textsuperscript{69-71} The VWN-BP functional was used for electron exchange and correlation for all calculations.\textsuperscript{72-74} Relativistic effects (including spin-orbit) were taken
into account with the zeroth-order regular approximation (ZORA).\textsuperscript{75-79} All-electron gauge including atomic orbitals (GIAO)\textsuperscript{80} triple-\(\zeta\) doubly-polarized (TZ2P) basis sets were employed on all atoms. Additional calculations employing an all electron quadruple-\(\zeta\) quadruple polarized (QZ4P) basis set on Sn and the TZ2P basis set on all other atoms were also attempted. The calculations were performed using the single point models described above or, where indicated, using the B3PW91 geometry optimized structures. The NMR calculations on the models of the [12]crown-4 and [15]crown-5 tin(II) triflate complexes \textsuperscript{5.2} and \textsuperscript{5.3} included only the coordinated crown ether ligands and carried an overall +2 charge (i.e., the triflate anions were not included). NMR calculations on the model for the [18]crown-6 tin(II) triflate complex \textsuperscript{5.1} were performed on a neutral unit including the crown ether ligand and the two nearest triflate ligands. The isotropic magnetic shielding (\(\sigma_{\text{iso}}\)) values of SnMe\(_4\) (at the B3PW91 optimized geometry) calculated at the corresponding level of theory were used to convert the calculated principal magnetic shielding values (\(\sigma_{ii}\)) to chemical shift (\(\delta_{ii}\)) values (see Table \textsuperscript{5.3}).

\section*{5.3 Results and Discussion}

\subsection*{5.3.1 Syntheses and structural details}

As we noted previously, well-defined, crystalline complexes of SnOTf\(_2\) with crown ethers are readily prepared through the treatment of tin(II) triflate with the appropriate stoichiometry of the cyclic poly-ethers [18]crown-6, [15]crown-5, or [12]crown-4 (Figure \textsuperscript{5.1}). Although a detailed description of the structures has been reported,\textsuperscript{29} a summary of the important features of these structures is presented so that the reader may appreciate the structure-property relationships that are inferred from the
physical, spectroscopic and computational investigations presented in the following sections.

![Solid state structures of [Sn([18]crown-6)OTf][OTf], [Sn([15]crown-5)2][OTf]2, and [Sn([12]crown-4)2][OTf]2, illustrating the different structural types adopted by the differently-sized cyclic poly-ether ligands. Dashed lines are used to emphasize coordination environment of the tin atom attributable to the oxygen atoms of the crown ether ligand and the dotted lines indicate the closest tin-anion contacts.]

The 1:1 adduct of SnOTf2 with [18]crown-6, exhibits a structure in which the tin atom is "belted" by the crown ether in a manner reminiscent of s-block metal crown ether complexes. Overall, the complex appears to exist as a salt of the form [Sn([18]crown-6)OTf][OTf], in which there is one tin-bound triflate substituent (Sn-O: 2.282(6) Å) and one "free" triflate anion (Sn-O: 2.596(9) Å); such an arrangement is at least superficially similar to the structure of [Sn([18]crown-6)Cl][SnCl3].

The smaller crown ethers, [15]crown-5 and [12]crown-4, are too small to accommodate the tin atom within the crown ether cavity and thus both form 2:1 sandwich-like complexes with the divalent metal. In the case of [Sn([15]crown-5)2][OTf]2, there appears to be
no interactions between the triflate anions and tin atom in the roughly centrosymmetric $[\text{Sn([15]crown-5)}_2]^2^+$. In contrast, in salt 5.3, the smaller [12]crown-4 ligands are not large enough to completely encapsulate the tin atom and the cation is best described as being a bent "crown"-sandwich complex. The open wedge of the cation appears to allow for the interaction of the tin atom with an adjacent triflate anion; however, the very long Sn-O distance of 3.119(4) Å and the metrical parameters of both the cation and the triflate group suggest that this is a very weak interaction that does not noticeably perturb the structures of the component ions.29

Given that the size of the crown ether ring clearly plays a role in the composition and structure adopted by low-valent complexes from groups 13 and 14, we rationalized that glyme-type podand ligands might be superior for the stabilization and/or solubilization of low-valent species: the absence of the constraints associated with being cyclic renders glymes more flexible so that they may adjust their binding to the most favorable arrangement. In this vein, we observed that the treatment of SnOTf$_2$ with triglyme or tetraglyme in acetonitrile results in the formation of the 1:1 complexes Sn(OTf)$_2$·triglyme, 5.4, or Sn(OTf)$_2$·tetraglyme, 5.5, in quantitative yield on the basis of NMR spectroscopy and isolated in reasonable crystalline yield and high purity (as assessed by microanalysis and pXRD). It is noteworthy that, in contrast to all of the crown ether complexes described above, the $^1$H and $^{13}$C NMR signals for the glyme ligand are markedly different upon complexation and confirm the formation of complex in solution. However, like all of the crown ether complexes, no identifiable $^{119}$Sn solution NMR signals for the complexes could be detected.
**Figure 5.2** Solid state structures of Sn(OTf)$_2$-triglyme, 5.4, and Sn(OTf)$_2$-tetraglyme, 5.5; thermal ellipsoids are drawn to depict the 30% probability surface and all hydrogen atoms are omitted for clarity. For compound 5.4, only highest-occupancy component of the disordered triflate group (containing S(1), O(11), etc.) is depicted. Selected metrical parameters including distances (Å) and angles (°): 5.4: Sn-O(11), 2.331(6); Sn-O(21), 2.741(6); Sn-O(31), 2.511(3); Sn-O(32), 2.378(3); Sn-O(33), 2.454(3); Sn-O(34), 2.725(3); S(1)-O(11), 1.471(5); S(1)-O(12), 1.401(5); S(1)-O(13), 1.430(15); S(2)-O(21), 1.425(4); S(2)-O(22), 1.420(4); S(2)-O(23), 1.436(3); O(11)-Sn-O(21), 166.4(4). 5.5: Sn-O(11), 2.408(5); Sn-O(21), 2.519(6); Sn-O(31), 2.664(6); Sn-O(32), 2.436(4); Sn-O(33), 2.396(4); Sn-O(34), 2.568(5); Sn-O(35), 2.968(5); S(1)-O(11), 1.466(5); S(1)-O(12), 1.421(5); S(1)-O(13), 1.430(5); S(2)-O(21), 1.443(6); S(2)-O(22), 1.416(5); S(2)-O(23), 1.415(5); O(11)-Sn-O(21), 145.2(2).
Crystals suitable for examination by X-ray diffraction were obtained by the slow evaporation of solutions of \textit{5.4} or \textit{5.5} in 1:1 mixtures of THF and toluene; \textit{5.4} crystallizes in the space group \textit{P2}_1/\textit{n} with one formula equivalent comprising the asymmetric unit (Figure 5.2). Examination of the pertinent metrical parameters suggests that complex \textit{5.4} appears to be similar to the [18]crown-6 complex \textit{5.1} in several ways. The compound is a 1:1 complex in which the ligand binds the tin atom in a belt-like manner and there appear to be two distinct triflate environments: one with a longer Sn-O distance of 2.741(6) Å and metrical parameters consistent with a "free" triflate anion and the other with a considerably shorter Sn-O distance of 2.331(6) Å and very slightly perturbed S-O distances. The Sn-O\textit{glyme} distances range from 2.378(3) to 2.725(3) Å of which three are roughly 2.5 Å or less and one is substantially longer – this is somewhat in contrast to \textit{5.1} in which there are two short, two intermediate and two long distances.

The tetragalyme complex \textit{5.5} crystallizes in the space group \textit{P2}_1/\textit{c} with one formula equivalent comprising the asymmetric unit (Figure 5.2). As in \textit{5.4}, the glyme ligand in \textit{5.5} binds the metal in a belt-like arrangement and the Sn-O\textit{glyme} distances range from 2.397(5) to 2.968(5) Å. The distribution of these ligand to metal contacts is more reminiscent of \textit{5.1} in that there are two at shorter distances, two somewhat further away and one with a considerably longer Sn-O distance. In contrast to \textit{5.1} and \textit{5.4}, there a much smaller range of distances between the tin atom and the triflate anions in complex \textit{5.5}: one triflate has a closest Sn-O distance of 2.408(5) Å and the other has a closest contact at 2.519(6) Å. The S-O distances within each of the triflate fragments in \textit{5.5} are consistent with those of a very slightly perturbed anion and suggest that the contact ion pair description is applicable to each triflate group.
Overall, the large variation in the coordination spheres around the tin atoms in complexes 5.1-5.5, including apparently very different levels of interactions between the tin atoms and both the anions and the ligands suggests that these systems should be excellent models to provide insight into the nature of the ligand-dependent reactivity differences outlined in the Introduction. Furthermore, we prepared the known salt [Sn([18]crown-6)Cl][SnCl$_3$], 5.6, which has a structure that is superficially similar to 5.1 – the solid state structure adopted by our samples of 5.6 was confirmed by pXRD to be consistent with that reported in the Cambridge Structural Database$^{81}$ – in an effort to rationalize the very different chemistry that is often observed for comparable low-valent halide and triflate analogues.

5.3.2 Mössbauer Spectroscopy

Samples of each of the complexes 5.1-5.6 were analyzed by $^{119}$Sn Mössbauer spectroscopy. Representative spectra are illustrated in Figure 5.3 and the isomer shifts (IS) and quadrupolar splittings (QS) at 90K extracted from each of the spectra are collected in Table 5.2.
Figure 5.3 $^{119}$Sn Mössbauer spectra for the triflate complexes 5.1-5.5 reported in this work. The peak at 0 mm·s$^{-1}$ is a Sn(IV) impurity.$^{44}$

Table 5.2 Summary of $^{119}$Sn Mössbauer spectroscopic results for the compounds reported in this work

<table>
<thead>
<tr>
<th>Complex</th>
<th>IS(90)$^\text{a}$ mm·s$^{-1}$</th>
<th>QS(90)$^\text{a}$ mm·s$^{-1}$</th>
<th>$-d\ln A/dT$ K$^{-1}$ x 10$^3$</th>
<th>Reference</th>
<th>QS(calcd)$^\text{b}$ mm·s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[18]Crown-6·Sn(OTf)$_2$ (5.1)</td>
<td>4.267(6)</td>
<td>0.924(6)</td>
<td>22.94</td>
<td>This work</td>
<td>-0.622</td>
</tr>
<tr>
<td>([15]Crown-5)$_2$·Sn(OTf)$_2$ (5.2)</td>
<td>4.504(6)</td>
<td>0.0(1)</td>
<td>19.36</td>
<td>This work; cf. $^{82,83}$</td>
<td>0.201</td>
</tr>
<tr>
<td>([12]Crown-4)$_2$·Sn(OTf)$_2$ (5.3)</td>
<td>4.480(6)</td>
<td>0.340(6)</td>
<td>16.85</td>
<td>This work</td>
<td>0.359</td>
</tr>
<tr>
<td>Triglyme·Sn(OTf)$_2$ (5.4)</td>
<td>4.056(6)</td>
<td>0.794(6)</td>
<td>22.09</td>
<td>This work</td>
<td>0.433</td>
</tr>
<tr>
<td>Tetragate·Sn(OTf)$_2$ (5.5)</td>
<td>4.062(6)</td>
<td>0.789(6)</td>
<td>18.07</td>
<td>This work</td>
<td>-0.757</td>
</tr>
<tr>
<td>Sn(OTf)$_2$</td>
<td>4.15</td>
<td>0.84</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>[SnCl([18]Crown-6)]$^+$ (5.6 cation)</td>
<td>3.83(2)</td>
<td>2.78(2)</td>
<td>-</td>
<td>This work and $^{30,31}$</td>
<td>-2.588</td>
</tr>
<tr>
<td>[SnCl$_3$] (5.6 anion)</td>
<td>3.45(2)</td>
<td>0.89(2)</td>
<td>-</td>
<td>This work and $^{30,31}$</td>
<td>-1.626</td>
</tr>
</tbody>
</table>
Isomer shift (IS) and quadrupole splitting (QS) at 90K for measurements obtained in this work. All of the spectra indicate anisotropic Sn motion, but this effect is not very large. The rapid decrease in the recoil-free fraction with increasing temperature (-dlnA/dT) precludes a more detailed analysis. QS calculated using the ADF method described in the experimental section for the complexes examined in this work.

As one would anticipate, in each of the spectra for the various complexes of Sn(OTf)$_2$, the major resonance is indicative of the presence of tin(II); however, there are several important observations that are apparent upon more detailed analysis. For example, it is clear that the magnitude of the isomer shift (IS) is directly correlated with the degree of spherical symmetry of the coordination sphere about each tin atom. The largest value of IS (4.504(6) mm·s$^{-1}$) is found for complex 5.2 in which the cation has almost $D_5$ point symmetry with an arrangement of oxygen atoms that is distributed approximately centrosymmetrically around the tin cation. Such a structure suggests that the two valence electrons on the Sn(II) atom occupy the 5s orbital almost exclusively, which is consistent with the large magnitude of the IS. The distorted crown-sandwich structure of the cation in 5.3 exhibits the next largest isomer shift whereas the IS magnitudes are the smallest for species 5.1, 5.4 and 5.5, which feature less symmetrical Sn bonding environments. The IS values for each of the triflate complexes are consistent with the Sn-ligand interaction being primarily ionic (rather than covalent) in nature. This assertion is supported by the effective mass calculation on each of the triflate complexes 5.1-5.5 which indicate a "vibrating mass" of close to 110 Da, that is, that of a "bare" Sn atom, in every instance. It is also worth noting that the ionic interpretation of the metal-ligand bonding in these complexes is in concordance with the results of XANES investigations of related Ge(II) complexes. In sharp contrast, the 3.83(2) mm·s$^{-1}$ value of IS for the crowned cation in the chlorine-containing complex 5.6, although still characteristic of a Sn(II) atom, is
considerably smaller than that (4.267(6) mm·s$^{-1}$) of the structurally-similar triflate complex 5.1.

The quadrupolar splitting (QS) magnitudes for each of the complexes provides insight into the symmetry of the electric field gradient (EFG) around the tin atoms in each of the complexes and the level of degeneracy of the 5p-type orbitals on Sn that comprise the LUMOs. As one might anticipate on the basis of the structure exhibited by the cation, it is found that the $^{119}$Sn Mössbauer spectrum of 5.2, which has the most spherically symmetrical distribution of oxygen atoms about the tin atom, consists of a single peak and is thus indicative of a negligible quadrupolar splitting. Although the complex does not conform to perfect cubic symmetry (which would require QS = 0), the arrangement of the ten oxygen atoms in two staggered pentagons provides a geometry that roughly emulates a centrosymmetric dodecahedron in which half of the vertices are occupied.$^{86}$ Provided that the charges at each vertex are identical, the EFG for such a polyhedron is predicted to be 0 at the center of symmetry.$^{87-89}$ Somewhat in spite of its appearance in Figure 5.3, analysis of the spectrum of 5.3 reveals that it is a doublet with a QS magnitude of 0.340(6) mm·s$^{-1}$. The relatively small size of the quadrupolar splitting is consistent with the bent-sandwich structure of the complex in which there is also a nearly spherically symmetrical arrangement of the oxygen atoms about the tin atom. The spectra of triflate complexes 5.1, 5.4 and 5.5 each feature obvious doublet signals with QS values consistent with less spherically symmetrical Sn coordination environments and significant Sn EFGs. The largest value of QS for any of the triflate complexes (0.924(6) mm·s$^{-1}$) is observed for compound 5.1, which features an asymmetrical arrangement of coordinating atoms around Sn, and, most importantly, possesses the shortest Sn-OTf
contact found in 5.1-5.5. Again, it should be emphasized that the QS magnitude observed for the cation of the chlorinated species 5.6 (2.78(2) mm·s⁻¹) is approximately three times as large as that of 5.1 and highlights the dramatically different properties of the two analogous salts in spite of the apparent similarity of their structures. Finally, it should be noted that the trends in the experimental magnitudes of the QS values are predicted with reasonable accuracy by DFT calculations using models derived from the solid state structures, as indicated in Table 5.2.

5.3.3 Solid-state NMR Spectroscopy

¹¹⁹Sn SSNMR spectroscopy can act as a powerful probe of the molecular and electronic structure of Sn complexes.⁹⁰,⁹¹ ¹¹⁹Sn chemical shift tensors are sensitive to both the symmetry and energies of occupied and virtual molecular orbitals with Sn character and are useful for confirming that single crystal X-ray structures are representative of the bulk material. Each of the tin triflate complexes 5.1-5.5, the chlorinated analogue 5.6, and the synthetic precursors, tin dichloride and tin ditriflate were examined using solid-state ¹¹⁹Sn NMR (Figures 5.4-5.6, S1 and S2). The ¹¹⁹Sn SSNMR spectra of 5.1-5.6 confirm that all samples are of high purity and do not indicate the presence of any tin-containing impurities.
Figure 5.4 Static $^{119}$Sn SSNMR spectra for the triflate complexes 5.1-5.4 reported in this work. The experimental spectra are depicted with black traces and the analytical simulations are drawn in red. The spectra of 5.2 indicate the presence of a second distinct Sn site, which is attributed to a secondary phase of 5.2 which contains an excess of free ligand in the crystal lattice; analytical simulations for each of the two overlapping sites are illustrated. MAS $^{119}$Sn SSNMR spectra of all complexes are shown in Figure S5.1.
Figure 5.5 (Left) Static $^{119}\text{Sn}$ SSNMR spectra for the triflate complexes 5.5 obtained at three different temperatures between 298 K and 313 K. The experimental spectra are depicted with black traces and the analytical simulations are drawn in red. All spectra were obtained with a spin echo pulse sequence. (Right) The CS tensor orientation obtained from DFT calculation on the low temperature structure of 5.5.
Figure 5.6 $^{119}$Sn MAS SSNMR spectra of 5.6. The simulation of the $v_{\text{rot}} = 12000$ Hz spectrum includes both the [SnCl([18]crown-6)] site (red trace) and the [SnCl$_3$] site (blue trace). Asterisks denote isotropic peaks. Inset: An expansion of the isotropic peak shows the fine structure of the [SnCl([18]crown-6)] resonances. The simulation illustrates that residual dipolar coupling and indirect spin-spin coupling to $^{35/37}$Cl are most likely responsible for the fine structure. Simulation parameters: $J_{\text{iso}}(^{119}\text{Sn}-^{35}\text{Cl}) = 380$ Hz, $D(^{119}\text{Sn}-^{35}\text{Cl}) = -307$ Hz, $\Delta J = 20$ Hz, $C_Q(^{35}\text{Cl}) = -45$ MHz, $\eta_Q(^{35}\text{Cl}) = 0.30$, $\alpha = 20^\circ$, $\beta = 50^\circ$. $D(^{119}\text{Sn}-^{35}\text{Cl})$ was calculated based upon the Sn-Cl bond length observed in the single crystal X-ray structure of 5.6 and the $^{35}$Cl EFG tensor parameters were based upon those obtained from DFT calculations. Note that there are large uncertainties (on the order of 20-50 %) associated with the values of $J_{\text{iso}}(^{119}\text{Sn}-^{35}\text{Cl})$, $\Delta J$, $C_Q(^{35}\text{Cl})$, $\eta_Q$, $\alpha$, and $\beta$ and employed in the simulations.
Table 5.3 Experimental and Calculated $^{119}$Sn Chemical Shielding Tensor Parameters$^{a}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>Geom.$^{b}$</th>
<th>$\sigma_{\text{iso}}$ (ppm)</th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$\delta_{11}$ (ppm)</th>
<th>$\delta_{22}$ (ppm)</th>
<th>$\delta_{33}$ (ppm)</th>
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</thead>
<tbody>
<tr>
<td>[SnOTf([18]crown-6)][OTf]</td>
<td>Expt.</td>
<td>-</td>
<td>-</td>
<td>-1578(2)</td>
<td>325(20)</td>
<td>0.15(5)</td>
<td>-1424</td>
<td>-1562</td>
<td>-1749</td>
</tr>
<tr>
<td></td>
<td>DFT/QZ4P</td>
<td>X</td>
<td>4353</td>
<td>-1799</td>
<td>589</td>
<td>0.30</td>
<td>-1534</td>
<td>-1741</td>
<td>-1799</td>
</tr>
<tr>
<td>[Sn([15]crown-5)$_2$][OTf]$_2$</td>
<td>Expt. (site 1)</td>
<td>-</td>
<td>-</td>
<td>-1721(2)</td>
<td>140(10)</td>
<td>0.85(10)</td>
<td>-1671</td>
<td>-1681</td>
<td>-1811</td>
</tr>
<tr>
<td>[Sn([15]crown-5)$_2$][OTf]$_2$</td>
<td>Expt. (site 2)</td>
<td>-</td>
<td>-</td>
<td>-1706(2)</td>
<td>143(10)</td>
<td>0.55(5)</td>
<td>-1647</td>
<td>-1680</td>
<td>-1791</td>
</tr>
<tr>
<td>[Sn([15]crown-5)$_2$]$_2$.$^{d}$</td>
<td>DFT/QZ4P</td>
<td>X</td>
<td>4472</td>
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<tr>
<td></td>
<td>DFT/QZ4P</td>
<td>O</td>
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<td>339</td>
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<td>-2100</td>
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<td>[Sn([12]crown-4)$_2$][OTf]$_2$</td>
<td>Expt.</td>
<td>-</td>
<td>-</td>
<td>-1405(2)</td>
<td>267(10)</td>
<td>0.09(5)</td>
<td>-1275</td>
<td>-1398</td>
<td>-1539</td>
</tr>
<tr>
<td>[Sn([12]crown-4)$_2$]$_2$.$^{d}$</td>
<td>DFT/QZ4P</td>
<td>X</td>
<td>4163</td>
<td>-1609</td>
<td>240</td>
<td>-0.09</td>
<td>-1486</td>
<td>-1616</td>
<td>-1725</td>
</tr>
<tr>
<td></td>
<td>DFT/QZ4P</td>
<td>O</td>
<td>4164</td>
<td>-1609</td>
<td>224</td>
<td>-0.38</td>
<td>-1483</td>
<td>-1638</td>
<td>-1707</td>
</tr>
<tr>
<td>[Sn(Triglyme)][OTf]$_2$</td>
<td>Expt. (high T)</td>
<td>-</td>
<td>-</td>
<td>-1436(1)</td>
<td>375(20)</td>
<td>0.27(4)</td>
<td>-1258</td>
<td>-1400</td>
<td>-1649</td>
</tr>
<tr>
<td></td>
<td>DFT/QZ4P</td>
<td>X</td>
<td>4079</td>
<td>-1524</td>
<td>644</td>
<td>0.29</td>
<td>-1233</td>
<td>-1462</td>
<td>-1877</td>
</tr>
<tr>
<td>[Sn(Tetraglyme)][OTf]$_2$</td>
<td>Expt. (low T)</td>
<td>-</td>
<td>-</td>
<td>-1457(1)</td>
<td>195(15)</td>
<td>0.96(4)</td>
<td>-1391</td>
<td>-1395</td>
<td>-1586</td>
</tr>
<tr>
<td></td>
<td>DFT/QZ4P</td>
<td>X</td>
<td>4249</td>
<td>-1694</td>
<td>427</td>
<td>0.17</td>
<td>-1493</td>
<td>-1671</td>
<td>-1920</td>
</tr>
<tr>
<td>[SnCl([18]crown-6)][SnCl]</td>
<td>Expt.</td>
<td>-</td>
<td>-</td>
<td>-840(5)</td>
<td>1700(150)</td>
<td>1.00(15)</td>
<td>-239</td>
<td>-341</td>
<td>-1939</td>
</tr>
<tr>
<td></td>
<td>DFT/QZ4P</td>
<td>X</td>
<td>3562</td>
<td>-1008</td>
<td>2269</td>
<td>0.99</td>
<td>-246</td>
<td>-262</td>
<td>-2515</td>
</tr>
<tr>
<td>[SnCl([18]crown-6)][SnCl]</td>
<td>Expt.</td>
<td>-</td>
<td>-</td>
<td>-58(2)</td>
<td>814(100)</td>
<td>1.00(15)</td>
<td>228</td>
<td>190</td>
<td>-588</td>
</tr>
<tr>
<td></td>
<td>DFT/QZ4P</td>
<td>X</td>
<td>2607</td>
<td>-53</td>
<td>821</td>
<td>0.83</td>
<td>244</td>
<td>173</td>
<td>-577</td>
</tr>
<tr>
<td>SnCl$_2$.$^{c}$</td>
<td>Expt.</td>
<td>-</td>
<td>-</td>
<td>-916(1)</td>
<td>347(10)</td>
<td>0.59(4)</td>
<td>-777</td>
<td>-848</td>
<td>-1124</td>
</tr>
<tr>
<td>SnOTf$_2$</td>
<td>Expt.</td>
<td>-</td>
<td>-</td>
<td>-1418(2)</td>
<td>517(10)</td>
<td>0.96(5)</td>
<td>-1242</td>
<td>-1253</td>
<td>-1759</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>Expt.</td>
<td>-</td>
<td>-</td>
<td>-208(7)</td>
<td>975(15)</td>
<td>1.00</td>
<td>117</td>
<td>117</td>
<td>-858</td>
</tr>
<tr>
<td>SnMe$_4$</td>
<td>Expt.</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>DFT/QZ4P</td>
<td>O</td>
<td>2554</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The CS tensor is defined by three principal components ordered such that $\delta_{11} \leq \delta_{22} \leq \delta_{33}$. $\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$. $\Omega = \delta_{11} - \delta_{33}$. $\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$. The uncertainties associated with the last digit of the experimental parameters are shown in brackets.

$^{b}$"X" refers to calculations using the X-ray structure derived the single point geometry and "O" refers to calculations employing geometry optimized structures.

$^{c}$An all electron quadruple-ζ doubly polarized (QZ4P) basis set was employed for Sn as indicated. An all electron triple-ζ doubly polarized (TZ2P) basis set was employed on all other atoms in all cases. Results using the TZ2P basis set on Sn are found in the supporting information (Appendix IV).
In cases where a tin containing ion is specified, the triflate groups were omitted from calculations.

Refer to the supporting information for details (Appendix IV).

The isotropic tin chemical shifts ($\delta_{iso}$) (Table 5.3) for all of the triflate complexes indicate that the $^{119}$Sn nuclei are highly shielded, which may arise from: 1) the ionic nature of the complexes, which feature no strongly covalent bonds to the tin atoms, and 2) the symmetry of the HOMO on the Sn atom (the "lone pair", which is best approximated as being a filled 5s orbital) and the low lying virtual orbitals on Sn (approximated by the vacant 5p-type orbitals). Either or both of these factors result in a situation in which the paramagnetic $\sigma_p$ component in Ramsey's treatment of shielding (93-95) ($\sigma_{tot} = \sigma_d + \sigma_p$) is likely to be small (this component normally is responsible for deshielding). In contrast, the $\delta_{iso}$ observed for both the cations and anions in the chlorinated analog 5.6 indicate that the $^{119}$Sn nuclei are considerably deshielded which is reflective of the existence of covalent Sn-Cl bonds. Moreover, the observation of fine structure in the MAS $^{119}$Sn SSNMR spectrum of 5.6 is attributed to indirect spin-spin coupling and residual dipolar coupling to quadrupolar $^{35/37}$Cl nuclei, which is also consistent with the presence of covalent Sn-Cl bonds (Figure 5.5).

The spans ($\Omega$) of the $^{119}$Sn SSNMR spectra are another feature that clearly differentiate the triflate complexes (5.1-5.5) from the chlorinated analogue (5.6), and appear to be related to the Mössbauer QS values. Within the triflate complexes, the salt with the most spherically symmetrical Sn environment, 5.2, exhibits the smallest $\Omega$ (and QS. Complexes 5.1, 5.3, 5.4 and 5.5 all have a larger $\Omega$ (and correspondingly larger QS values). The much larger $\Omega$ measured for the cation in 5.6 dwarfs those for all of the
triflate complexes, again demonstrating that there are fundamental differences between the seemingly analogous chloride and triflate complexes. In this regard, it is well known from $^{119}$Sn SSNMR studies of Sn(II) complexes$^{97-99}$ and $^{207}$Pb SSNMR studies of Pb(II) complexes,$^{100-102}$ that as the p-orbital character of the HOMO metal centered "lone pair" increases, $\Omega$ is usually observed to increase as well. Amongst the triflate complexes, 5.3-5.5 have the most positive values of $\delta_{\text{iso}}$, larger values of $\Omega$, and possess the least spherically symmetric Sn coordination environments. These observations imply that the HOMOs ("lone pair") in these complexes are of higher 5p character than in complexes 5.1 and 5.2.

Because of the unexpected appearance of the MAS spectrum of the tetraglyme complex (5.5) at room temperature, VT $^{119}$Sn NMR experiments were undertaken (Figure 5.5). The high temperature spectra (308 K and 315 K) exhibit a slightly reduced $\Omega$, and a skew ($\kappa$) of approximately +1, which indicates that the CS tensor is axially symmetric (i.e., $\delta_{11} = \delta_{22}$). The spectrum obtained at low temperature (298 K) has a larger $\Omega$ and non-axial $\kappa$ (-0.26), which is consistent with the theoretical CS tensor obtained from DFT calculations on a model derived from the low temperature single crystal X-ray structure. In both the high and low temperature spectra, the position of $\delta_{33}$ is the same, while $\delta_{22}$ and $\delta_{11}$ become equivalent at high temperature, which suggests that there may be a dynamic molecular motion which averages $\delta_{11}$ and $\delta_{22}$. The theoretical CS tensor orientation has $\delta_{11}$ and $\delta_{22}$ oriented in the O$_5$ plane of the tetraglyme ligand (Figure 5.5), hence there is a dynamic re-orientation of either the tetraglyme ligand, or the whole molecule, around the pseudo-axis formed by the triflates.$^{103}$
5.3.4 Cyclic Voltammetry

Cyclic voltammetry (CV) is used to assess the impact of ligands on the relative redox properties of transition metal complexes, in which the relevant electrons are located in d-orbitals and may not affect the overall structure. For the p-block metals, the population of p-orbitals (especially starting from a putative s²p⁰ valence electron configuration) usually has an obvious effect on the structure of the compound and CV is often not needed to assess the oxidation state or valence state of the metal. Regardless, we sought to determine the effect of the different poly-ether ligands on the oxidation potential of the tin atom with which they interact and to assess, in particular, if there is any obvious correlation between the oxidation potential of the tin atom and any of the spectral and/or structural data described above. Thus the CVs of CH₂Cl₂ solutions of complexes 5.1-5.5 were obtained in order to assess the relative stabilities of divalent tin atoms. Because we are most interested in the oxidation of the Sn²⁺ to Sn⁴⁺, all of the voltammograms were recorded using glassy carbon electrodes in order to observe the anodic peak for the couple, which is often not observed when platinum electrodes are employed.¹⁰⁴,¹⁰⁵
Figure 5.7 Representative cyclic voltammograms for solutions of triflate complexes 5.1-5.5 reported in this work and SnOTf$_2$.

Table 5.4 Summary of cyclic voltammetry data obtained for the ligand complexes of SnOTf$_2$.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Initial Sweep Positive</th>
<th>Initial Sweep Negative</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{A(2+\rightarrow 4+)}$ (mV)$^a$</td>
<td>$E_{C(4+\rightarrow 2+)}$ (mV)$^b$</td>
</tr>
<tr>
<td>5.1</td>
<td>1600</td>
<td>n/o</td>
</tr>
<tr>
<td>5.2</td>
<td>n/o</td>
<td>n/o</td>
</tr>
<tr>
<td>5.3</td>
<td>n/o</td>
<td>n/o</td>
</tr>
<tr>
<td>5.4</td>
<td>1380</td>
<td>n/o</td>
</tr>
<tr>
<td>5.5</td>
<td>1240</td>
<td>n/o</td>
</tr>
<tr>
<td>SnOTf$_2$</td>
<td>1320</td>
<td>n/o</td>
</tr>
</tbody>
</table>

$^a$Potentials were referenced using a Ag/AgNO$_3$ electrode. $^b$$E_A$ indicates the anodic potential and $E_C$ indicates the cathodic potential for the redox couple indicated in parentheses. "n/o" indicates not observed.

Every signal observed in the CVs of complexes 5.1-5.5 (Figure 5.7) are irreversible under all conditions investigated; therefore the potentials reported in Table 4 are those obtained by sweeping initially either toward more positive potentials (for Sn$^{+2}$ oxidation)
or negative potentials (for Sn$^{2+}$ reduction). Perhaps the most interesting observation is that compounds 5.2 and 5.3 do not feature any observable signal corresponding to the oxidation from Sn$^{2+}$ to Sn$^{4+}$. Given that the oxidation of tin(II) chloride was determined to occur through an inner sphere mechanism that requires the tin atom to be bridged to the anode, it is perhaps not surprising that the completely surrounded tin atoms in both complexes do not give rise to detectable oxidation currents under these conditions. Furthermore, compound 5.1 exhibits a significant oxidation current at roughly +1600 mV, which is considerably higher than the corresponding value for unligated SnOTf$_2$. In contrast, both of the glyme complexes 5.4 and 5.5 are considerably easier to oxidize than any of the crown ether complexes. These observations are somewhat counterintuitive, given that complex 5.2, which features a tin atom surrounded by ligands containing 10 oxygen donor sites, might be expected to be the most electron-rich complex investigated and the most easily oxidized. Furthermore, in spite of having 6 donor atoms in the ligand, the [18]crown-6 complex 5.1 is the least easily oxidized of any of the single-ligand complexes whereas oxidation of the two podand complexes require potentials similar to, or lower than, that of "free" SnOTf$_2$.

Overall, the CV data suggest that the observed (and unobserved) Sn$^{2+}$ to Sn$^{4+}$ oxidation potentials are attributable to the steric properties of the ligands about the tin atom rather than providing direct evidence about the relative energy of the valence electrons on tin. The most encapsulating coordination environments, such as in 5.2 and 5.3, preclude observation of an oxidation current. For the single-ligand complexes, in which the tin atom is not completely surrounded, the data are most consistent with there being a correlation between the percentages of s-character on the tin atoms and the
oxidation potentials of the complexes. Specifically, complexes in which the valence electrons on tin have a greater s-character require more energy to become oxidized. Therefore, it appears as if it is the nature of the interaction between the metal and the ligand and the manner in which the ligand perturbs the valence electrons on the metal, rather than simply the donor ability of the ligand, that determines the oxidation potential of the complex.\textsuperscript{107} The nature of these interactions and effects are investigated computationally in the following section.

5.3.5 Computational Investigations

As compiled in Table 5.5, we examined several different aspects of the electronic structures of models of the complexes 5.1-5.6 using MP2 and TD-DFT calculations in order to determine if there is any correlation to the experimentally observed properties. Most of the electronic properties were evaluated at the MP2 level of theory on model compounds in which the relative positions of the heavy atoms were fixed in the geometry observed by single-crystal X-ray diffraction, and in which the hydrogen atoms were placed in idealized positions using Gaussview.
Table 5.5 Summary electronic structure analyses for the single point MP2 and TD-DFT calculations on models of the compounds reported in this work (X = OTf, Cl).

<table>
<thead>
<tr>
<th>Model Complex</th>
<th>Q(Sn)</th>
<th>LP(Sn) %5s</th>
<th>$E_{LP(Sn)}$ (eV)</th>
<th>$\Delta E_{\text{H-L}}$ (eV)</th>
<th>WBI(^c) (M-O(_{\text{signal}})) range</th>
<th>WBI(^c) (M-X)</th>
<th>WBI(^c) (M) total</th>
<th>Trans(^c) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(^{2+}) models(^g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Sn(12cr4)(_2)]^{2+} (3')</td>
<td>1.64</td>
<td>97.1</td>
<td>-18.54</td>
<td>12.65</td>
<td>0.062-0.097</td>
<td>-</td>
<td>0.774</td>
<td>4.2666</td>
</tr>
<tr>
<td>[Sn(15cr5)(_2)]^{2+} (2')</td>
<td>1.61</td>
<td>99.7</td>
<td>-18.35</td>
<td>12.47</td>
<td>0.052-0.080</td>
<td>-</td>
<td>0.810</td>
<td>4.1432</td>
</tr>
<tr>
<td>SnX(^+) models</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(18cr6)Sn-OTf(_2)](^-) (1')</td>
<td>1.66</td>
<td>95.6</td>
<td>-16.58</td>
<td>12.41</td>
<td>0.047-0.090</td>
<td>0.170</td>
<td>0.687</td>
<td>4.1157</td>
</tr>
<tr>
<td>[(18cr6)Sn-Cl(_2)](^-) (6')</td>
<td>1.47</td>
<td>93.9</td>
<td>-15.59</td>
<td>12.47</td>
<td>0.057-0.080</td>
<td>0.536</td>
<td>1.018</td>
<td>4.4283</td>
</tr>
<tr>
<td>SnX(_2) models</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(18cr6):SnOTf(_2) (1&quot;)</td>
<td>1.63</td>
<td>97.8</td>
<td>-12.49</td>
<td>13.04</td>
<td>0.042-0.088</td>
<td>0.090; 0.133</td>
<td>0.781</td>
<td>4.4016</td>
</tr>
<tr>
<td>(trig):SnOTf(_2) (4&quot;)</td>
<td>1.67</td>
<td>95.9</td>
<td>-13.26</td>
<td>12.16</td>
<td>0.058-0.1015</td>
<td>0.090; 0.137</td>
<td>0.701</td>
<td>3.8524</td>
</tr>
<tr>
<td>(tetrag):SnOTf(_2) (5&quot;)</td>
<td>1.63</td>
<td>97.4</td>
<td>-12.55</td>
<td>12.72</td>
<td>0.041-0.095</td>
<td>0.110; 0.121</td>
<td>0.783</td>
<td>4.2286</td>
</tr>
</tbody>
</table>

\(^{a}\)NBO charge on the metal atom  \(^{b}\)NBO percentage of 5s character in the "lone pair" orbital on the metal atom  \(^{c}\)NBO energy of the "lone pair" on Sn  \(^{d}\)SCF HOMO-LUMO energy difference  \(^{e}\)NBO Wiberg Bond Index for the bonds indicated  \(^{f}\)TD-DFT lowest energy transition  \(^{g}\)the data are subdivided on the basis of the overall charge of the models employed.

Several important observations can be made on the basis of the computed data in Table 5.5 for the model tin(II) polyether complexes. The NBO charge on the Sn atom is almost always the same (+1.64 ± 0.03 au) for every complex of SnOTf\(_2\) regardless of the identity of the poly-ether ligand or the overall charge of the model in which it is located. These
values suggest that there is a relatively small (ca. -0.36 au) total transfer of charge from all of the ligands in the coordination spheres to the metals. The sums of the Wiberg Bond Indices (WBI) on the tin atoms are likewise remarkably similar and small (0.75 ± 0.06) for all of the triflate complexes. Taken together, these results are consistent with the conclusion from the Mössbauer investigations that the tin atom in each of the triflate complexes behaves like a free Sn^{2+} dication. In sharp contrast to the triflate complexes, the charge on tin is significantly less (+1.47 au) in 6', the model containing the chlorine substituent, and the sum of the WBIs for the tin atom in that complex (1.018) is markedly larger. More importantly, it is found that while no Sn-OTf bonds are identified by the NBO analysis for any of triflate model complexes, a Sn-Cl bond is identified for model complex 6'. The bond is quite polar, featuring ca. 89% contribution from orbitals on the chlorine atom, but its observation clearly illustrates that there is a fundamental difference between the superficially analogous complexes 1' and 6'.

Similarly, it is apparent that the calculated percentage of 5s character in the "lone pair" of electrons on Sn is very high (>90%) for each of the divalent tin model complexes; however, there are some notable differences. As one may anticipate, the percentage of 5s character for the "lone pair" is highest (99.7%) for the [15]crown-5 sandwich model complex 2', which most closely approximates spherical symmetry. The "lone pair" in the [12]crown-4 sandwich model complex 3' is found to be around 97.1% 5s and all of the other model triflate complexes have 5s percentages that exceed 95%. While the magnitude of the difference is not tremendous, it is again the chloride model complex 6' that is the outlier: this complex features the smallest percentage (93.9%) of s-character for the two non-bonding valence electrons. Although s-p mixing is not a
prerequisite for stereochemical activity of a "lone pair".\textsuperscript{108,109} Lower percentages of s character appear to correlate with higher reactivity for the systems herein.

The energies of the "lone pairs" of electrons on the tin atom in each model complex, as identified by the NBO analysis, were also examined in order to determine if there is any correlation between their energies and the tin coordination environments. The energies of these orbitals are found to be very similar to each other for triflate models of the same overall charge: e.g., the energies for the two dicationic models 2' and 3' are virtually identical. The only major difference observed is, again, between the triflate complex 1' and the chloride complex 6'. The energy of the lone pair in 6' is more than 1 eV higher than that of 1' which suggests that the chloride species should be more reactive as an electron donor; this result concurs with our observations of the related univalent indium systems.\textsuperscript{25} Furthermore, these data indicate that the complex with the highest charge on the tin atom is not necessarily the most reactive.

It must also be emphasized that the frontier orbitals in all of the models are almost exclusively based on tin. The molecular orbital that corresponds to the "lone pair" of valence electrons on the tin atom is the highest occupied molecular orbital (HOMO) for each of the model complexes examined. Furthermore, all of the lowest unoccupied molecular orbitals (LUMOs) on each of the complexes are primarily composed of the formally vacant 5p orbitals on tin – the relevant orbitals for model complexes 1' and 6' are illustrated in Figure 5.8.\textsuperscript{110} In spite of the different absolute energies found for the HOMOs described above, which suggest that the chlorinated compound is more basic, there does not appear to be any marked difference in the HOMO-LUMO gaps for any of
the complexes (as calculated using the MP2 method) nor in the lowest energy electronic transitions (as calculated with TD-DFT using the B3PW91 method).

One very important observation gleaned from the examination of the molecular orbitals in model complexes 1' and 6' is the presence of an obvious Cl-Sn bonding orbital in the latter (Figure 5.9). In contrast, no corresponding TfO-Sn bonding orbital is found in 1'; therefore, both the MP2 molecular orbitals and NBO analysis point to the conclusion that there really is a substantial difference between the bonding in the two superficially analogous ions. This observation provides a rationale for the considerable differences in the features observed in both the Mossbauer spectra and $^{119}$Sn SSNMR spectra. Moreover, the presence of the more covalent bond between the substituent and the tin

Figure 5.8 Depictions of selected MP2 frontier orbitals for model complexes 1' and 6'.

\[
\text{LUMO+1+2}
\]

\[
\text{LUMO}
\]

\[
\text{HOMO}
\]

\[
\text{[SnOTf([18]crown-6)] (1')}
\]

\[
\text{[SnCl([18]crown-6)] (6')}
\]
atom also explains the decreased stability of the "lone pair" of electrons on tin (Scheme 5.3).

![Figure 5.9 Depiction of the Sn-Cl "bonding" MP2 orbital for model complex 6'.](image)

Given the apparently different nature of the X-Sn bonding (X = OTf, Cl) between model complexes 1' and 6', we examined the Laplacian, $\nabla^2 \rho$, of the MP2 electron density for each of the complexes (Figure 5.10). It is clear that the electron density in 1' is consistent with the description of the complex as being a contact ion pair whereas the region between the tin atom and the chlorine atom in 6' has a region of electron density concentration between the two atoms that is consistent with the presence of a bond between tin and chlorine. Therefore, the conclusions obtained through analysis of the topology of the electron density are in accord with those derived from the various analyses of the molecular orbitals and the spectroscopic data: the nature of the interaction between the tin atom and the triflate substituent truly is different than the interaction with the chloride substituent.
Figure 5.10 Contour diagrams depicting the Laplacian, $\nabla^2 \rho$, of the MP2 electron density for model complexes $1'$ and $6'$. Contours depicted in red indicate regions of negative charge depletion (decreased electron density) and those in blue indicate regions of negative charge concentration (increased electron density).

Finally, in light of all of the preceding data, it is worth clarifying why the more covalent bond with chlorine destabilizes the "lone pair" on the tin atom. As illustrated in Scheme 5.3, the "lone pair" MO in $[\text{SnCl}]^+$ is formally the result of the anti-bonding interaction between the filled $5s^2$ orbital on a free Sn$^{2+}$ ion and a filled 3p orbital on a free Cl$^-$ anion. In this context, it is apparent that a stronger, more covalent interaction must result in a higher energy, more reactive "lone pair" on tin than is present in the free ion.
5.4 Conclusions

The structural, spectroscopic and computational results presented in this work clearly demonstrate that there are dramatic differences between the behavior of the non-bonding electrons in low-valent complexes. These differences can be rationalized on the basis of the nature of the multidentate ligand present and, more importantly, on the properties of the substituent that are bound to the low-valent metal. In particular, triflate substituents produce highly ionic contact ion pairs (featuring $\text{Sn}^{2+}$ dications) whereas chloride substituents generate species with covalently bonded $[\text{Sn-Cl}]^+$ cations: our investigations provide an explanation for the differing electrochemical behavior of solutions of $\text{SnCl}_2$ and $\text{SnOTf}_2$ in ionic liquids reported by Compton and co-workers, who proposed similar speciation. More generally, this observation provides insight as to how coordinating counter ions can destabilize electron-rich species and thus why very weakly coordinating counter ions are sometimes required to isolate particularly reactive low-valent species such as Ga(I).
In spite of the differences, all of the investigations also illustrate that the non-bonding electrons on the tin atom in each complex reside in orbitals that are almost exclusively of 5s character and the various poly-ether ligands appear to perturb those electrons only mildly. The properties of the sandwich-like complexes 5.2 and 5.3 are consistent with the least perturbation from an ideal 5s² electron configuration whereas the properties of the [18]crown-6 complexes 5.1, and to an even greater extent 5.6, appear to be the most perturbed. The increased perturbation caused by the [18]crown-6 ligand in comparison to either the free salt or the sandwich complexes provides a rationale for the observed differences in oxidative addition reactions of the related In¹ complexes.

Acyclic podand ligands also appear to be suitable for the stabilization and/or solubilization of low-valent p-block reagents and the properties of the resultant complexes are intermediate between those of the free salt and the [18]crown-6 complexes. We surmise that the more flexible nature of such ligands in comparison to their more constrained cyclic relatives may explain this observation.

Overall, this work provides a rationale for why ligands with multiple weak donors are useful for the stabilization, isolation or solubilization of electron-rich main group species. Consequently, these results also provide an explanation as to why stronger donors, such as tetramethylethylenediamine (TMEDA), which are often employed in an attempt to solubilize low-valent reagents, result in the decomposition of the species.¹¹³,¹¹⁴ Finally, the dramatically different bonding and properties of the chloride complexes with respect to their triflate analogues suggests that the relatively more stable triflate complexes may be conveniently rendered more reactive simply through the addition of better donors. Investigations to probe and exploit such behavior are currently underway.
References

(33) SMART2001, Bruker AXS Inc.
(34) SAINTPlus2001, Bruker AXS Inc.
(35) SADABS2001, Bruker AXS Inc.
(43) [http://www.megadaq.com](http://www.megadaq.com)
A spectrum of 1 taken after storing an o-ring closed sample at ambient temperature and in air suggests that most, if not all, of the Sn(IV) impurity arises from adventitious hydrolysis.


Frisch, M. J. e. a., *Gaussian 03, Revision D.012003*, Gaussian, Inc.

Frisch, M. J. e. a., *Gaussian09, Revision A12009*, Gaussian, Inc.


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(103) The existence of such dynamic behavior might also explain the poor predicted value of QS for compound 4 in Table 2.


(106) As inferred on the basis of the IS values observed in the Mössbauer experiments and the magnitudes of $\Omega$ observed in the Sn-119 SSNMR spectra.

(107) The nature of the polyether ligand present also affects the potentials required for metal deposition and "stripping" - some details are provided in the Supporting Information.


(110) Because all of the frontier orbitals are almost exclusively tin-based, the computational examination of the various electronic properties described above should indeed provide information that correlates with the experimental investigations that use the tin atom as a probe.


Chapter 6

Conclusion & Future Work

6.1 Deprotonation of \([([15]\text{crown-5Ge(H}_2\text{O})])(\text{OTf})_2\)

With the goal of generating compounds containing unsaturated germanium centers, we have treated the acidic complex \([\text{Ge([15]crown-5)-H}_2\text{O]}(\text{OTf})_2\] with a series of strong acids. In particular, we have tried to deprotonate the water complex by using \(^i\text{Pr-carbene}\) as illustrated in Scheme 6.1 with the aim of producing variants of GeO (the analogue of CO). Addition of \(^i\text{Pr-carbene}\) to \([\text{Ge([15]crown-5)-H}_2\text{O]}(\text{OTf})_2\] results in the deprotonation of the water complex and produces the triflate salt of the conjugate acid, which crystallizes as a colorless solid, and a yellow solid. The crystal structure of the resultant imidazolium salt is presented in Figure 6.1. This experiment is currently being repeated using 1:1 and 1:2 of \([\text{Ge([15]crown-5)-H}_2\text{O]}(\text{OTf})_2\] and carbene respectively. It is anticipated that the yellow precipitate is a form of germanium monoxide (GeO) or perhaps its crown ether complex but due to its limited solubility, this compound is difficult to analyze. Therefore, we intend to characterize this product by powder XRD and XPS. The structure of the imidazolium triflate has been characterized crystallographically, as illustrated in Figure 6.1.

![Scheme 6.1 Preparation of "GeO" using \(^i\text{Pr-carbene}\)
Several other bases were also employed in an attempt to de-protonate the water complex, including: proton sponge, DBU, DBN, and a phosphorus-based "Verkadesuperbase". While all of the bases seem to deprotonate the water complex, only the proton sponge produced a crystalline conjugate acid; the crystal structure of the protonated proton-sponge is illustrated in Figure 6.2. It is worth noting that an insoluble solid yellow residue identical in appearance to the one obtained from the reaction with the NHC was also generated.
In a similar vein, the treatment of a colourless solution of \([\text{Ge([15]crown-5)-H}_2\text{O}]\)[OTf]_2\) with sodium oxide to generate a yellow precipitate. The precipitate was filtered and the filtrate was subjected to evaporation. A white product was recovered after evaporation which was recrystallized and characterized as \([\text{Na([15]-crown-5)]OTf}\). This result is again consistent with the yellow precipitate being a form of "GeO". Overall, the preliminary results for the reaction of the water adduct with strong bases (Na_2O, proton sponge, NHC) indicate that deprotonation works but the resultant products remain to be identified conclusively.

6.2 Other novel Ge(II) adducts to try

Since we obtained other hydride adducts (e.g. NH_3) that have acidic protons, we wish to see if deprotonation can be used to generate unsaturated species such as GeN- (CN- analogue), and perhaps even compounds of the form GeC might be possible by the triple deprotonation of crown ether complexes of MeGe^{3+}, which might be accessible through the treatment of \([\text{Ge([15]crown-5)]OTf}\)_2\) with MeOTf.

6.3 Computational Investigation of the crowned Ge(II) complexes

We examined several different aspects of the electronic structure of several crowned Ge(II) complexes in order to determine if there is any correlation to the properties that we have observed experimentally. Most of the electronic properties were evaluated at the M062x/TZVP level of theory on model compounds in which the relative positions of the heavy atoms were fixed in the geometry observed in the solid state by single-crystal X-ray diffraction and in which the hydrogen atoms were placed in ideal positions using Gaussview. Geometry optimization of these complexes was performed using Gaussian09 implemented on Sharcnet. Preliminary studies show the NBO charge on the Ge atom for the crowned Ge(II) complexes with [GeCl]^+ cations
are all very similar to each other with a value of around 1.28 au. The charge on the triflates is comparatively higher ranging within 1.48 to 1.55 au.

Furthermore, it is observed that the percentage of 4s character in the "lone pair" of electrons on Ge is highest (>99%) for the most symmetrical Ge sandwich model complex of [12]-crown-4. This suggests that the germanium center in [12]crown-4 the triflate complex behaves like a free Ge$^{+2}$ dication the percentage of 4s character in the "lone pair" of electrons on Ge is highest (>99%) for the most symmetrical Ge sandwich model complex of [12]crown-4.

![Figure 6.3](image)

**Figure 6.3** [Ge[12]crown-4]$^{2+}$

Detailed studies on these molecules are still under investigation and the major focus lies on determination of the relative stability of the "bent"[GeCl([15]crown-5)]$^+$ ion with respect to a more conventional "planar" structure. Further studies on the electronic structures and bonding in these optimized models are underway.

### 6.4 Potential ligands for stabilizing Sn(II) complexes

Although stronger donors are predicted to unsuitable for In(I), for the more stable Sn(II) systems, ligands such as cyclen, BiPy, TMEDA, and PMDTA (Figure 6.4) were investigated as ligands for Sn(II).\(^1\) The products obtained were colourless but high-quality crystals were not
obtained from any of these systems. Each of these ligands have N-atoms as donors and it will be interesting to compare the coordination chemistry with the coronands and podands. It is anticipated that such systems should activate the lone pair on Sn(II) and generate more reactive species.

**Figure 6.4** Other potential ligands for activating Sn(II) centers: a.) cyclen; b.) bipyridyl; c.) TMEDA; d.) PMDTA

**References**

Appendix I : Supporting Information for Chapter 2.

1.1 X-ray Crystallography

Each crystal was covered in Nujol and placed rapidly into the cold N\textsubscript{2} stream of a Kryo-Flex low temperature device. The data were collected either by employing the SMART\textsuperscript{1} software on a Bruker APEX CCD diffractometer or by using the COLLECT\textsuperscript{2} software on a Nonius KAPPA CCD diffractometer, each being equipped with a graphite monochromator with MoK\textsubscript{\alpha} radiation ($\lambda = 0.71073$ Å). For each sample, a hemisphere of data was collected using counting times of 10-30 seconds per frame. The data were collected at either -100 or -123 °C. Details of crystal data, data collection and structure refinement are listed in Table S2.1. Data reductions were performed using the SAINT\textsuperscript{3} software and the data were corrected for absorption using SADABS\textsuperscript{4} or using the DENZO-Scalepack application.\textsuperscript{5} The structures were solved by direct methods using either the SHELX\textsuperscript{6} suite of programs or SIR97\textsuperscript{7} and refined by full-matrix least-squares on $F^2$ with anisotropic displacement parameters for the non-H atoms using SHELXL-97\textsuperscript{8} and the WinGX\textsuperscript{9} software package. Details of the final structure solutions were evaluated using PLATON\textsuperscript{10} and thermal ellipsoid plots were produced using SHELXTL\textsuperscript{11}.

As illustrated, figures S2.5 to S2.8, disorder of the crown ether ring positions (and sometimes in the orientation of the triflate ions) was observed in some instances. When necessary, the disorder was modeled using crown ethers fragments in two different orientations and appropriate restraints were employed, including: restraining the thermal parameters for the atoms in each part of the crown ether models to be similar; restraining the geometrical parameters of related crown ethers (or related triflate fragments) to be similar; or restraining related C-O and/or C-C bonds in a crown ether to be similar.
The supplementary crystallographic data for this paper has been deposited in the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/dataÅrequest/cif using the CCDC numbers in Table S2.1.

**Table S2.1** Summary of crystallographic data for the compounds in this work

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**Figure S2.5** Asymmetric unit of $2.2$[GeCl$_3$]$\cdot$([12]crown-4); the symmetry-related crown ethers on Ge(1), which sits on a site of -1 symmetry have been included for completeness. The
positions of the crown ethers on Ge(1) are disordered: the most occupied site is drawn with dark bonds and the position of lesser occupancy is drawn with open bonds.

Figure S2.6. Asymmetric unit of 2.2[OTf]₂; poor data quality preclude discussion of the metrical parameters but the connectivity is unambiguous.
**Figure S2.6.** Asymmetric unit of $2.3\text{[GeCl}_3\text{]}_2$. The positions of the crown ethers on Ge(1) and Ge(3) are partially-disordered: the most occupied site is drawn with dark bonds and the position lesser occupancy is drawn with open bonds.

**Figure S2.7** "Grown" asymmetric unit of $2.3\text{[OTf]}_2$: each of the component cations and anions lies on a mirror plane. The crown ether sits equally in each of the two arrangements that are depicted.
Figure S2.5. Asymmetric unit of 2.5[OTf]

Figure 2.8 Illustration of the cation from 2.6[OTf]; poor data quality preclude discussion of the metrical parameters but the connectivity and conformation adopted by the crown ether is unambiguous.
Figure 2.9 Asymmetric unit of 2.7[GeCl$_3$].

Figure 2.10 "Grown" asymmetric unit of 2.8; the molecule lies on a 2-axis.
References

Appendix II: Supporting Information for Chapter 3.

II.1 X-ray Crystallography

Each crystal was covered in Nujol and placed rapidly into the cold N\textsubscript{2} stream of a Kryo-Flex low temperature device. The data were collected either by employing the SMART\textsuperscript{1} software on a Bruker APEX CCD diffractometer or by using the software on a Nonius KAPPA CCD diffractometer equipped with a graphite monochromator with Mo K\textalpha{} radiation (\(\lambda = 0.71073\ \text{Å}\)). For each sample, a hemisphere of data was collected using counting times of 10-30 seconds per frame. The data were collected at -100 °C. Details of crystal data, data collection and structure refinement are listed in Table S3.1. Data reductions were performed using the SAINT\textsuperscript{2} software and the data were corrected for absorption using SADABS\textsuperscript{3} The structures were solved by direct methods using either the SHELX\textsuperscript{4} suite of programs or SIR97\textsuperscript{5} and refined by full-matrix least-squares on \(F^2\) with anisotropic displacement parameters for the non-H atoms using SHELXL-97\textsuperscript{6} and the WinGX\textsuperscript{7} software package. Details of the final structure solutions were evaluated using PLATON\textsuperscript{8} and thermal ellipsoid plots were produced using SHELXTL.\textsuperscript{9}
Table S1.1 Summary of crystallographic data for the compounds in this work

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<td>90</td>
<td>92.113(5)</td>
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<td>β (°)</td>
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<td>77.5850(10)</td>
<td>106.181(2)</td>
<td>106.438(5)</td>
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<tr>
<td>γ (°)</td>
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<td>73.0090(10)</td>
<td>90</td>
<td>94.088(5)</td>
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<tr>
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<td>1115.5(2)</td>
<td>1059.2(3)</td>
<td>1303.8(6)</td>
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<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
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<tr>
<td>Abs. coeff. (mm⁻¹)</td>
<td>2.796</td>
<td>1.666</td>
<td>7.130</td>
<td>1.437</td>
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<td>F(000)</td>
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<td>616</td>
<td>584</td>
<td>696</td>
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<tr>
<td>Colour</td>
<td>Colourless</td>
<td>Colourless</td>
<td>Colourless</td>
<td>Colourless</td>
</tr>
<tr>
<td>Crystal size (mm³)</td>
<td>0.25x0.20x0.10</td>
<td>0.20x0.10x0.10</td>
<td>0.30x0.30x0.60</td>
<td>0.20x0.20x0.40</td>
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<tr>
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<td>2.32 to 27.50</td>
<td>1.45-27.50</td>
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<td>2488 / 0 / 119</td>
<td>10237 / 0 / 357</td>
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<td>Goodness-of-fit F² (all data)</td>
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<td>1.283</td>
<td>1.068</td>
<td>1.0230</td>
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<td>Final R indices</td>
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<td>0.0275(2208)</td>
<td>0.0747(6456)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.2607</td>
<td>0.1240 (4886)</td>
<td>0.0736(2488)</td>
<td>0.2218(10237)</td>
</tr>
<tr>
<td>------------------</td>
<td>--------</td>
<td>--------------</td>
<td>--------------</td>
<td>--------------</td>
</tr>
<tr>
<td>Largest diff. peak and hole (eÅ⁻³)</td>
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<td>1.504</td>
<td>0.665</td>
<td>1.3710</td>
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<td>-0.590</td>
<td>-0.549</td>
<td>-0.858</td>
<td>-1.296</td>
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References

Appendix III: Supporting Information for Chapter 4.

III.1 X-ray Crystallography

The subject crystals were covered in Nujol® or Paratone-N®, mounted on a goniometer head and rapidly placed in the the dry N₂ cold-stream of the low-temperature apparatus (Kryoflex) attached to the diffractometer. The data were collected using the SMART¹ software on a Bruker APEX CCD diffractometer using a graphite monochromator with MoKα radiation (\(\lambda = 0.71073 \, \text{Å}\)). A hemisphere of data was collected for each crystal using a counting times ranging from 10 to 30 seconds per frame at -100 °C. Details of crystal data, collection and structure refinement are listed in Table S4.1. Data reduction was performed using the SAINT-Plus² software and the data were corrected for absorption using SADABS³. The structure was solved by direct methods using SIR97⁴ and refined by full-matrix least-squares on \(F^2\) with anisotropic displacement parameters for the non-disordered heavy atoms using SHELXL-97⁵ and the WinGX⁶ software package and thermal ellipsoid plots were produced using SHELXTL⁷. The space group assignments and structural solutions were evaluated using PLATON⁸. It must be noted that for [Sn([15]crown-5)₂][OTf]₂, we were never able to obtain crystals of high quality – the crystals are often twinned with a large number of different orientations and partial inclusion of CH₂Cl₂ – however the data for the crystal reported below, while of low quality (\(R_{int} = 0.1088\)), is clearly sufficient to establish the connectivity of the molecule without any ambiguity.

Thermal ellipsoid plots of each of the structures are depicted in the supporting information. The supplementary crystallographic data for this paper has been deposited in the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif using the CCDC numbers in Table 4.2.
Table S4.1 Summary of crystallographic data for the compounds in this work.

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<th>Compound number</th>
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<th>4.2[OTf]₂</th>
<th>4.3[OTf]₂</th>
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<td>749124</td>
<td>749123</td>
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<td>Empirical formula</td>
<td>C₁₄H₂₄F₆O₁₂S₂Sn</td>
<td>C₂₂H₄₀F₆O₁₆S₂Sn</td>
<td>C₁₈H₃₂F₆O₁₄S₂Sn</td>
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<tr>
<td>Formula weight</td>
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<td>173(2)</td>
<td>173(2)</td>
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<td>Wavelength (Å)</td>
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<td>0.71073</td>
<td>0.71073</td>
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<td>Crystal system</td>
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<td>Space group</td>
<td>P-1</td>
<td>P2₁/c</td>
<td>P2₁/c</td>
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<td>a (Å)</td>
<td>9.837(2)</td>
<td>12.6206(14)</td>
<td>11.7148(10)</td>
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<tr>
<td>b (Å)</td>
<td>9.896(2)</td>
<td>13.8047(16)</td>
<td>12.5654(11)</td>
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<tr>
<td>c (Å)</td>
<td>14.094(3)</td>
<td>20.390(2)</td>
<td>19.2307(17)</td>
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<tr>
<td>α (°)</td>
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<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
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<td>107.9810(10)</td>
<td>95.0820(10)</td>
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<tr>
<td>γ (°)</td>
<td>71.627(3)</td>
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<td>90</td>
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<tr>
<td>Volume (Å³)</td>
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<td>3378.9(7)</td>
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<tr>
<td>Z</td>
<td>2</td>
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<td>4</td>
</tr>
<tr>
<td>Abs. coeff. (mm⁻¹)</td>
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<td>0.980</td>
<td>1.158</td>
</tr>
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<td>F(000)</td>
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<td>1744</td>
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<tr>
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<td>Colorless</td>
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<tr>
<td>Crystal size (mm³)</td>
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<td>0.40x0.20x0.20</td>
<td>0.30x0.20x0.15</td>
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<tr>
<td>θ range for data collection (°)</td>
<td>1.55-25.00</td>
<td>1.70-27.50</td>
<td>1.75-27.50</td>
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<td>Data/restraints/parameters</td>
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<td>6373/0/370</td>
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<tr>
<td>Goodness-of-fit $F²$ (all data)</td>
<td>1.043</td>
<td>1.099</td>
<td>1.089</td>
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<tr>
<td>Final R indices $I &gt; 2σ(I)$</td>
<td>0.0832</td>
<td>0.1412</td>
<td>0.0457</td>
</tr>
<tr>
<td>wR2 indices (all data) a</td>
<td>0.1261</td>
<td>0.4130</td>
<td>0.1455</td>
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</table>
\begin{tabular}{|c|c|c|c|}
\hline
Largest diff. peak and & 1.319 and -0.874 & 5.845 and -1.210 & 1.173 and -0.680 \\
hole (e Å^{-3}) & & & \\
\hline
\end{tabular}

\( R1(F) = \Sigma |F_o| - |F_c|/\Sigma |F_o| \) for reflections with \( F_o > 4\sigma(Fo) \). \( wR2(F^2) = \{ \Sigma w(|F_o|^2 - |F_c|^2)/\Sigma w(|F_o|^2) \}^{1/2}, \) where \( w \) is the weight given each reflection. \( S = (\Sigma w(|F_o|^2 - |F_c|^2)^2)/\Sigma w(|F_o|^2)^2)/(n-p)^{1/2}, \) where \( n \) is the number of reflections and \( p \) is the number of parameters used.

### III.2 Theoretical Calculation.

All of the computational investigations were performed using the Gaussian03 suite of programs using the node of the Shared Hierarchical Academic Research Computing Network (SHARCNET) facilities located at the University of Windsor (tiger.sharcnet.ca). Calculations were performed with the Gaussian 03 suite of programs.\(^9\) Geometry optimizations have been calculated using density functional theory (DFT), specifically implementing the B3PW91 method [containing Becke’s three-parameter hybrid functional for exchange (B3, including ca. 20% Hartree-Fock exchange)\(^{10}\) combined with the generalized gradient approximation for correlation of Perdew and Wang (PW91)\(^{11}\)] in conjunction with Stuttgart/Dresden (SDD) relativistic effective core pseudopotential and basis set for Sn and In\(^{12}\) and the 6-31G(d) basis set for all other atoms. The geometry optimizations were not subjected to any symmetry restrictions and each stationary point was confirmed to be a minimum having zero imaginary vibrational frequencies unless otherwise indicated. Population analyses were conducted using the Natural Bond Orbital (NBO)\(^{13}\) implementation included with the Gaussian 03 package.
References

APPENDIX IV: Supporting Information for Chapter 5.

IV.1 X-ray crystallography

Crystallographic information files, summary of computational results and complete references for the Gaussian packages, solid state $^{13}$C NMR spectra, additional information regarding the solid state NMR experiments.

Additional SSNMR spectra

![SSNMR spectra images]

**Figure S5.1.** MAS $^{119}$Sn SSNMR spectra of complexes 5.1-5.5. The MAS spectra were utilized to determine $\delta_{\text{iso}}(^{119}\text{Sn})$ and obtain a rough measure of $\Omega$ and $\kappa$. For complex 5.5 both low and
high temperature spectra are shown. The low temperature spectra of 5.5 were acquired with sample temperatures of less than 300 K. Asterisks denote the isotropic chemical shifts.

**Figure S5.2.** Static and MAS $^{119}$Sn SSNMR spectra of SnCl$_2$ and Sn(OTf)$_2$. Experimental spectra are shown in black traces and analytical simulations are overlaid (red traces). A static $^{119}$Sn WURST-QCPMG spectrum of [SnCl([18]crown-6)][SnCl$_3$] (6) is shown at the bottom of the figure. Asterisks denote isotropic chemical shifts.
Figure S5.3. MAS $^{13}$C SSNMR spectra of complexes 5.1-5.6. All spectra were acquired with cross-polarization from $^1$H and $^1$H decoupling. The sample spinning rates ($\nu_{\text{rot}}$) are listed next to the individual spectra. Only the regions of the spectra containing $^{13}$C resonances are shown. Note that the spectra of 5.2 and 5.3 contain additional resonances which we have previously assigned to an excess of free ligand which has crystallized with the complexes.
IV.2 Cyclic Voltammetry

Although it is not a focus of the current investigation, it is worth noting that the potentials required for reduction of Sn$^{2+}$ to Sn$^{0}$ (and the reverse "stripping" process) are also found to be influenced by the nature of the ligand present. The use of ligands such as the poly-ether ligands examined in this work may thus be of some utility for those interested in the control of the electrochemical deposition of tin. It is also worth noting that the anomalous appearance of the regions corresponding to the Sn$^{2+}$/Sn$^{0}$ couple in the voltammograms of the sandwich compounds 5.2 and 5.3, in which the current profiles feature cross-over points, is consistent with previous observations on the electrochemical deposition of tin from some Sn$^{2+}$ species. These data suggest an overpotential-driven nucleation and growth process for the metal deposition; multi-cycle voltammograms that are consistent with this hypothesis are presented Figures S5.4 and S5.5.$^2$

![Multi-cycle CV of [Sn([15]crown-5)$_2$][OTf]$_2$.](image)

**Figure S5.4.** Multi-cycle CV of [Sn([15]crown-5)$_2$][OTf]$_2$. 
Figure S5.5. Multi-cycle CV of [Sn([12]crown-4)2][OTf]2.

IV.3 Computational Results

MP2 calculations

[Sn([12]crown-4)2]2+ from [Sn([12]crown-4)2][OTf]2

1\1\GINC-BUL85\SP\RMP2-FC\Gen\C16H32O8Sn1(2+)\CMACD\22-Oct-2010\0\# M P2/gen pseudo=read scf=tight pop=(full,nboread) test\Optimization and Frequency Calc on Sn(12-crown-4)2 dication\2,1\Sn,0,3.013,1.4743,4.0 718\O,0.4,7.177,0.764,2.4225\O,0.2,0.0517,0.1797,2.1682\O,0,1.1095,2.7342 ,2.554\O,0.3,7.968,3.3148,2.0942\C,0,4.2828,-0.2149,1.4613\C,0.2,8.858,0 ,0716,0.9961\C,0.6,8.42,0.524,1.8829\C,0.5,5335,1.9602,1.496\C,0,1.546 7.4,0.523,2.1569\C,0.2,8.068,4.0096,1.3447\C,0,4.8876,2.8725,1.757\C,0, 5.5892,1.8144,2.0017\O,0,3.5634,-0.8833,4.5869\O,0,1.0786,0.2312,4.983 6\O,0,2.6907,1.5028,6.6803\O,0,5,1.4381,1.1246,5.6527\C,0.2,7.104,-1.5166 ,5.5243\C,0,1.2757,-1.2038,5.1374\C,0,0.4922,0.9512,6.0971\C,0,1.4385, 1.0919,7.2464\C,0,3.7521,1.636,7.6027\C,0,5,0102,1.9816,6.8001\C,0,5.4 726,-0.2312,5.9994\C,0.5,0063,-1.0706,4.9075\H,0,2.9103402,-1.1419462 4.6,5.0642064\H,0.2,8.6911262,-2.574508915,5.50108268\H,0,1.04698067,-1.6 9098796,4.21261064\H,0,0.61880158,-1.56906044,5.89895714\H,0,0.2035386 2,1.926557,5.76505583\H,0,0.3,791213,0.4259678,6.42850661\H,0,1.571150 92,0,1.5344554,7.74791071\H,0,1.08135073,1.83453032,7.9289281\H,0,3.896 38372,0,7,1487434,8.12768545\H,0,3,5354458,2.42113389,8.29662055\H,0,5 86940656,1.8650417,7.42705952\H,0,4,9495273,2.99864954,6,47325285\H,0, 6.53171953,-0.33315178,6.11241177\H,0,4.97939157,-0.50609386,6.9082887
\[\text{Sn([15]\text{crown-5})_2^2}\] from \[\text{Sn([15]\text{crown-5})_2}[\text{OTf}_2]

1|\text{GINC-BUL13}\text{SP}\text{RMP2-FC/Gen}\text{C20H40O10Sn(2+)}|\text{CMACD23-Oct-2010}\text{00}#
\text{MP2/gen pseudo=\text{read scf=tight pop=(full,nboread) test}\text{\textbackslash Optimization an}
\text{d Frequency Calc on Sn(15-crown-5)2 dication\textbackslash 2,1\text{Sn,0.08638,1.81866}
\text{.22711C,0.3387,4.1221,5.7058C,0.38334,3.4656,6.7763C,0.37707,1.442}
\text{6.8,1281C,0.36807,0.0814,7.5579C,0.20571,-1.4964,6.817C,0.23101,
\text{-1.45365,6.3256C,0.16699,-0.2816,3.3707C,0.0658,0.6971,2.2927C,0.1
\text{2.87962,2.8258,2.84691C,0.08640,3.11751,0.36586499H,0.6,0.05800675,2.24021204,2.86418535H,0.0,5.55472813,3.6879437,1.08890698H,0
\text{.4,51375672,2.4900014,0.34869594\text{\textbackslash View}=\text{AM64L-G09RevB.01}}|\text{State=1-A\text{H}
\text{F\textasciitilde1226.1271052}\text{MP2\textasciitilde1229.6457967|RMSD=3.957e-09PG=C01 [X(C16H32O8Sn]}}}\text{\textbackslash @}

8\text{H,0,5.58236623,-0.84652967,4.03409277H,0.5,16770027,-2.09502175,5.1
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,2.7523923H,0.1,0.5272884,2.14898272,0.57966901H,0.0,-0.50280819,2.2032
1289.1,38686672H,0.2,86645289,0.9914361,0.44981505H,0.2,5.3882194,-0.7
7277862,0.37522326H,0.4,9.4416638,-0.20028407,6.2240007H,0.4,3.100078
7,-1.18469312,1.9146882H,0.1,1.79279984,6.3964993,3.03447405H,0.0,0.775
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,4.51375672,2.4900014,0.34869594\text{\textbackslash View}=\text{AM64L-G09RevB.01}\text{\textbackslash State=1-A\text{H}
\text{F\textasciitilde1226.1271052}\text{MP2\textasciitilde1229.6457967|RMSD=3.957e-09PG=C01 [X(C16H32O8Sn]}}}\text{\textbackslash @}
\[\text{SnOT}_2\text{[18]}\text{crown-6}]^+ \text{ from } \text{SnOT}_2\text{[18]}\text{crown-6}]\text{[OTf]}\]

I\[\text{\textbackslash GINCG-BUL23\textbackslashSP\textbackslashRMP2-FC\textbackslashGen\textbackslashC13H24F3O9S1Sn1(L+)}\text{\textbackslash CMACD\textbackslash23-Oct-2010\textbackslash0\textbackslash# MP2/\textbackslashgen pseudo=\textbackslashread scf=tight pop=(\textbackslashfull,\textbackslashnboared) test}\text{\textbackslashOptimization and Frequency Calc on Sn(18-crown-6)\textbackslashOTf complex\textbackslash1,1\textbackslashSn,0.437,3.2991,3.3469\textbackslashC,0.1,1.231,0.1,0.171,2.207\textbackslashC,0.4,0.632,5.3791,0.6583\textbackslashC,0.4,4.551,4.1637,-0.1338\textbackslashC,0.5,5.509,2.0768,0.0656\textbackslashC,0.6,5.334,1.3347,0.8917\textbackslashC,0.6,8\textbackslashO,0.3,094.2,9821\textbackslashC,0.6,8,079,-0.0585,4.22\textbackslashC,0.5,1512,0.8236,6.132\textbackslashC,0.4,6.266,2.0868,6.7273\textbackslashC,0.2,8.714,3.6373,6.4743\textbackslashC,0.1,1.9064,4.1457,5.4986\textbackslashC,0.1,8.063,5.4721,3.521\textbackslashC,0.2,6.4286,0.1332,3.4169\textbackslashO,0.3,2661,4.9099,1.7756\textbackslashO,0.5,2097,3.3015,0.7108\textbackslashO,0.5,9028,0.998,2.1166\textbackslashO,0.5,7.846,1.149\textbackslashO,4.9137\textbackslashO,0.3,6.172,2.6003,3.5866\textbackslashO,0.2,2.6595,4.7226,4.4049\textbackslashO,0.2,4.6468,2.1206,2.9126\textbackslashO,0.0,0.2489,2.4899,2.0864\textbackslashO,0.0,0.2123,1.8736,5.7047\textbackslashF,0.0,0.2.782,-0.3619,1.3035\textbackslashF,0.2,1.965,-0.6281,2.1611\textbackslashF,0.0,0.5801,-0.0858,3.3965\textbackslashS,0.1,1.4835,1.8428,1.8831\textbackslashH,0.3,3.38728862,6.67152231,2.81361497\textbackslashH,0.2,2.6684486,6.53963034,1.71813105\textbackslashH,0.1,1.3500374,6.2780757,4.0568429\textbackslashH,0.1,0.4951184,4.83086178,3.11977035\textbackslashH,0.1,1.29710205,3.34362289,5.13758988\textbackslashH,0.1,1.29117812,4.89476498,5.95169596\textbackslashH,0.3,5.2941456,4.42515537,6.7762946\textbackslashH,0.2,3.25370682,3.25146695,7.32754477\textbackslashH,0.5,4.1962848,2.79897569,6.821\textbackslashH,1.702\textbackslashH,0.4,2.05525135,1.88527014,7.6909722\textbackslashH,0.5,8.575714,0.37489723,6.7\textbackslashH,89787828\textbackslashH,0.4,3.4334076,0.14594043,5.95022831\textbackslashH,0.6,7.0847807,-0.6817172\textbackslashH,4.4,8.28941212\textbackslashH,0.5,1.8292491,-0.5742772,3.97526757\textbackslashH,0.7,6.3183221,0.947\textbackslash42358,3.2215082\textbackslashH,0.7,16.4995527,-0.5750228,2.49788518\textbackslashH,0.7,3.8712315,1.95133351,1.08096145\textbackslashH,0.6,6.83548079,0.44344248,0.38247782\textbackslashH,0.5,9.7779\textbackslash428,2.28626982,-0.89293204\textbackslashH,0.4,6.6981646,1.48265336,-0.05922614\textbackslashH,0.5,0.0500393,4.45703624,-0.97338387\textbackslashH,0.3,5.37654145,3.65651988,-0.4740987\textbackslashH,0.4,9.3798098,5.8798281,0.01736769\textbackslashH,0.3,4.8525987,6.04236121,0.0492271\textbackslash1\textbackslashVersion=AM64L-G09RevB.01\textbackslashState=1-A\textbackslashHF=-1.878.8254731\textbackslashMP2=-1.882.75604\textbackslash38\RMSD=5.022e-09\textbackslashPG=C01 \text{[X(C20H40O10Sn1)]}}\text{\textbackslash\textbackslash}]

\[\text{SnOT}_2\text{[18]}\text{crown-6}]\text{[OTf]} \text{ complete salt}\]

I\[\text{\textbackslash GINCG-BUL39\textbackslashSP\textbackslashRMP2-FC\textbackslashGen\textbackslashC14H24F6O12S2Sn1\textbackslash CMACD\textbackslash10-Nov-2010\textbackslash0\textbackslash# MP2/\textbackslashgen pseudo=\textbackslashread scf=tight pop=(\textbackslashfull,\textbackslashnboared) test}\text{\textbackslashSingle point Ca lc on Sn(18-crown-6)\textbackslashOTf2 x-ray geom complex\textbackslash0.1\textbackslashSn,0.4.37,3.2991,3.34\textbackslash69O,0.3,2.661,4.9099,1.7756\textbackslashO,0.5,2.097,3.3015,0.7108\textbackslashO,0.5,9.028,0.998,151}
[SnCl((18)crown-6)]^+ from [SnCl((18)crown-6)][SnCl_3]

\begin{align*}
\text{1|}^\text{\textbackslash GIN\textbackslash C12H24Cl1O6Sn1(1+)\textbackslash CMACD|24-Oct-2010|} \text{|# MP2\textbackslash gen\textbackslash pseudo=\textbackslash read\textbackslash scf=tight\textbackslash pop=(\textbackslash full\textbackslash nb\textbackslash read\textbackslash)\ test\textbackslash \textbackslash Single\textbackslash point\textbackslash calc\ on\ Sn-Cl(18\textbackslash crown-6)\ cation\ x-ray\ geom\}}\text{|1\textbackslash Sn,0.2,9784,0.1825,2,6708\textbackslash Cl,0.2,8255,0.4529,0.6073\textbackslash O,0.1,589,2,0023,3,8818\textbackslash C,0.2,1599,3.29,39,4,0345\textbackslash C,0.3,5399,3.1221,4.536\textbackslash O,0.4,2743,2.3902,3.5703\textbackslash C,0.5,6684,2.3139,3.8746\textbackslash C,0.6,364,1.5992,2.8091\textbackslash O,0.5,8,0.3081,2.6624\textbackslash C,0.6,6001,-0.5597,1.8447\textbackslash C,0.5,8954,-1.8321,1.7052\textbackslash O,0.4,6138,-1.6078,1.1148\textbackslash C,0.3,9646,-2.8208,0.6975\textbackslash C,0.2,5994,-2.4724,0.2249\textbackslash O,0.1,8583,-1.9555,1.3396\textbackslash C,0.0,463,-1.8315,1.0534\textbackslash C,0,-0.2145,-1.2696,2.2644\textbackslash O,0,0.3359,0.0076,2.4905\textbackslash C,0,-0.3634,0.7362,3.5138\textbackslash C,0,0.1933,2.111,3.5307\textbackslash H,0,0.9458303,2.5512148,2.56269699\textbackslash H,0,-0.32057982,2.70337717,4.25865386\textbackslash H,0,-0.2095423,0.26883892,4.46395863\textbackslash H,0,-1.40885683,0.76893127,3.283033\textbackslash H,0,-0.03308856,-1.90008656,3.10966717\textbackslash H,0,-1.26682886,-1.18771194,2.08890552\textbackslash H,0,0.3220188,-1.17245971,0.22232227\textbackslash H,0,0.0543699,-2.79361274,0.82479441\textbackslash H,0,0.2,66155047,-1.72989568,-0.54303532\textbackslash H,0,0.2,11506866,-3.34695749,-0.15650838\textbackslash H,0,0.4,51879444,-3.2722004,-0.09874506\textbackslash H,0,0.3,89964793,-3.49868717,1.52281825\textbackslash H,0,0.6,46521509,-2.48834514,1.08105813\textbackslash H,0,0.6,87436.57495.3189,0.884496,2.788.3,2784,0.8,1314,4.256,3.9066,0.14835,1.8428,1.8831,0.6,2418,5.8995,4.6265,0.3,38728682,6.67152231,2.81361497,0.2,0.26684486,6.5396303,4,1.71813105,0.1,3500374,6.2780757,4.0568429,0.1,0.4951184,4.830861,78,3,11977035,0.1,29711025,3.34362289,5.13758988,0.1,0.29117182,4.89,476498,5.95169596,0.3,52941456,4.42515537,6.77629462,0.2,3.5370682,3.25146695,7.3574477,5.41962848,2.79897569,6.8211702H,0,4.205521,35.1,88527014,7.69009722,0.5,8575714,0.37489723,6.79878728H,0,0.4,34334076,0.1,4594043,5.95022831H,0,6.70847807,-0.68171724,4.82941212H,0,5.18292491,-0.5747272,3.97526757H,0,7.63183221,0.94742358,3.22150082H,0,7.16499527,-0.57502285,2.49788518H,0,7,3.78172315,1.95133351,1.0809,6145H,0,6.83548079,0.44344248,0.38247782H,0,5,97779428,2.28626982,-0.89293240H,0,4.46981646,1.48265336,-0.05922614H,0,0.5,0500393,4.457036,24,-0.9733838H,0,3.57654145,3.65651988,-0.4740987H,0,0.4,93798098,5.8,798281,1.01736769H,0,3.48525987,6.04236121,0.04922711\textbackslash Version=AM64L-G09RevB.01\textbackslash State=1\textbackslash A\textbackslash HF=-2837.2302153\textbackslash MP2=-2842.4732767\textbackslash RMSD=3.978e-09\textbackslash PG=C01 [X(C14H24F6O12S2Sn1)]\textbackslash @
\end{align*}
NBO analysis of the Sn-Cl bond:

1. (1.99898) BD (1)Sn 1 -Cl 2

( 11.57%) 0.3402*Sn 1 s (6.63%) p 14.08 (93.37%)

-0.2463 -0.0750 0.0377 0.0028 0.0112
-0.0008 -0.9547 -0.1437

( 88.43%) 0.9404*Cl 2 s (25.85%) p 2.86 (73.99%) d 0.01 (0.16%)

0.0000 0.0000 -0.5083 -0.0087 0.0000
-0.0195 -0.0001 0.0000 0.0039 -0.0004
0.0000 0.8599 -0.0057 -0.0001 0.0010
-0.0005 0.0000 -0.0404

SnOTf$_2$ (triglyme) complete salt

\[ \text{SnOTf}_2 \text{(triglyme) complete salt} \]

1\%GINC-BUL54\SP\RMP2-FC\Gen\C10H18F6O10S2Sn1\CMACD\24-Oct-2010\0\#MP2/gap pseudo=read scf=tight pop=(full,nboread) test\Single point Ca lc on Sn(18-crown-6)OTf2 x-ray geom complex\0.1\Sn,0.4,2063,7.53565.1979\O,0.6,306,6.8411,6.7773\O,0.5,1512,5.4161,4.6781\O,0.3,2937,6.5519,3.1,4335\O,0.2,3622,9.0053,3.8294\C,0.5,982,7.2684,8.1497\C,0.6,3984,5.4671,6.677\C,0.6,4684,5.1332,5.2349\C,0.4,9988,4.9655,3.3305\C,0.3,5,702.5,1526,2.9773\C,0,1.9537,6.9427,2.7796\C,0,1.9675,8.4199,2.592\C,0,2.3102,10.4164,3.771\O,0,6,057,7.9651,3.8466\O,0.5,1818,9.9568,2.89\O,0,7,5735,9.7713,3.3087\S,0,3,1919,9.1476,3.0132\C,0,6,5391,8.4118,1.3854\F,0,6,7394,9.3472,0.4914\F,0,7,5743,7.5845,1.3723\F,0,5,4651,7.7216,1.0133\O,0,3,0991,5.9421,7.135\O,0,1,1731,5.5385,7.3655\O,0,0,9338,5.9573,8.1061\S,0,1,756,5.487,0.2979\C,0,1,8975,3.6995,7.3501\F,0,0,6851,3.1432,7.2891\F,0,2,3841,3.4431,8.5276\F,0,2,6213,3.1173,6.4154\H,0.3,304,10.8126,3.7895\H,0,1.7626,10.7874,4.6121\H,0,1.8229,10.7175,2.8672
SnOTf₂(tetraglyme) complete salt

Results for ADF calculated Mössbauer quadrupolar splittings

isotope = 119. Sn
nuclear spin = 0.5
\[ g_n = -2.0945600 \]
\[ Q = 0.00000 \text{ e } 10^{-24} \text{ cm}^2 \]

Sn bis(12-crown-4)(TZ2P Basis on Sn)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Sn</th>
<th>Input number</th>
<th>xyznuc(Angstrom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sn</td>
<td>1</td>
<td>3.0130 1.4743 4.0718</td>
</tr>
</tbody>
</table>

====== principal axes Q-tensor (EFG)

\[
\begin{array}{ccc}
11 & 22 & 33 \\
X & -0.021335 & 0.025656 & 0.999443 \\
Y & -0.803462 & 0.594473 & -0.032412 \\
Z & 0.594974 & 0.803706 & -0.007930 \\
\end{array}
\]

====== principal values EFG

Sn EFG: -0.295716E+00 -0.157374E+00 0.453090E+00 a.u.

====== principal values Q-tensor (have to be multiplied by Q (e 10^-24 cm^2) / 2I(2I-1))

\[
\begin{array}{ccc}
q_{11} & q_{22} & q_{33} \\
-0.694828E+02 & -0.369774E+02 & 0.106460E+03 \\
-0.231770E+02 & -0.123343E+02 & 0.355113E+02 \\
\end{array}
\]

Results for 119Sn, Q = 0.1280, Vzz = 0.440284E+01 10^21 V/m^2, NQCC = 0.136269E+02 MHz, eta = 0.30533

Mossbauer quadrupole splitting = 0.359 mm/s (unit conversion used 1 mm/s = 19.2601 MHz)

Sn bis(15-crown-5)^2+ (QZ4P Basis on Sn)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Sn</th>
<th>Input number</th>
<th>xyznuc(Angstrom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sn</td>
<td>1</td>
<td>0.0895 -0.0191 -0.0613</td>
</tr>
</tbody>
</table>

====== principal axes Q-tensor (EFG)

\[
\begin{array}{ccc}
11 & 22 & 33 \\
X & -0.054416 & 0.515209 & -0.855336 \\
Y & -0.284978 & -0.828990 & -0.481210 \\
Z & 0.956988 & -0.217567 & -0.191933 \\
\end{array}
\]

====== principal values EFG

Sn EFG: -0.195761E+00 -0.462952E+00 0.242056E+00 a.u.

====== principal values Q-tensor (have to be multiplied by Q (e 10^-24 cm^2) / 2I(2I-1))

\[
\begin{array}{ccc}
q_{11} & q_{22} & q_{33} \\
-0.459970E+02 & -0.108777E+02 & 0.568747E+02 \\
-0.153429E+02 & -0.362842E+01 & 0.189714E+02 \\
\end{array}
\]

Results for 119Sn, Q = 0.1280, Vzz = 0.235215E+01 10^21 V/m^2, NQCC = 0.727996E+01 MHz, eta = 0.61748
Mossbauer quadrupole splitting = 0.201 mm/s (unit conversion used 1 mm/s = 19.2601 MHz)

[SnOTf[18-crown-6)][OTf] (QZ4P Basis on Sn)
Atom 1  Sn Input number 1  xzynuc(Angstrom) = -4.4620  -0.4741  1.3756

===== principal axes Q-tensor (EFG)
11  22  33
X  0.867898  -0.475864  0.142500
Y -0.493984  -0.856994  0.146769
Z -0.052280  0.197773  0.978853

===== principal values EFG
Sn EFG -0.715314E+00  0.550366E-01  0.660278E+00  a.u.

===== principal values Q-tensor (have to be multiplied by Q (e 10^-24 cm^2) / 2I(2I-1))
q11  q22  q33
-0.168074E+03  0.129317E+02  0.155142E+03  MHz
-0.560633E+02  0.431354E+01  0.517498E+02  10^-4 cm^-1

Results for 119Sn, Q = 0.1280, Vzz = -0.695097E+01 10^21 V/m^2, NQCC = -0.215134E+02 MHz, eta = 0.84612
Mossbauer quadrupole splitting = -0.622 mm/s (unit conversion used 1 mm/s = 19.2601 MHz)

[Sn(triglyme)][OTf]_2 (QZ4P basis on Sn)
------------------------------------------
Atom 1  Sn Input number 1  xzynuc(Angstrom) = 4.2063  7.5356  5.1979

===== principal axes Q-tensor (EFG)
11  22  33
X  0.641661  0.261748  0.720944
Y -0.407337  -0.680155  0.609480
Z -0.649884  0.684746  0.329809

===== principal values EFG
Sn EFG -0.939394E+00  0.260162E+00  0.679231E+00  a.u.

===== principal values Q-tensor (have to be multiplied by Q (e 10^-24 cm^2) / 2I(2I-1))
q11  q22  q33
-0.220724E+03  0.611290E+02  0.159595E+03  MHz
-0.736257E+02  0.203904E+02  0.532353E+02  10^-4 cm^-1

Results for 119Sn, Q = 0.1280, Vzz = -0.912843E+01 10^21 V/m^2, NQCC = -0.282527E+02 MHz, eta = 0.44611
Mossbauer quadrupole splitting = -0.757 mm/s (unit conversion used 1 mm/s = 19.2601 MHz)

\([\text{Sn(tetraglyme)}][\text{OTf}]_2\) (QZ4P basis on Sn)

Atom 1  Sn  Input number 1  xyznuc(Angstrom) = -0.8900  0.2623  11.8567

===== principal axes Q-tensor (EFG)
    11     22     33
X  0.148119  0.319517  0.935933
Y -0.901480  0.432790  -0.005083
Z  0.406687  0.842972  -0.352142

===== principal values EFG
Sn EFG -0.452974E+00 -0.497444E-01  0.502718E+00 a.u.

===== principal values Q-tensor (have to be multiplied by Q (e 10^-24 cm^2) / 2I(2I-1))
q11  q22  q33
-0.106433E+03 -0.116882E+02  0.118121E+03 MHz
-0.355022E+02 -0.389876E+01  0.394010E+02 10^-4 cm^-1

Results for 119Sn, Q = 0.1280, Vzz = 0.488510E+01 10^21 V/m^2, NQCC = 0.151195E+02 MHz, eta = 0.80210
Mossbauer quadrupole splitting = 0.433 mm/s (unit conversion used 1 mm/s = 19.2601 MHz)

\([\text{SnCl(18c6)}]^+\) (QZ4P basis on Sn)

Atom 1  Sn  Input number 1  xyznuc(Angstrom) = 2.9784  0.1825  2.6709

===== principal axes Q-tensor (EFG)
    11     22     33
X  0.098933  0.462985  0.880827
Y -0.553630  -0.709916  0.435332
Z  0.826865   -0.530721  0.186088

===== principal values EFG
Sn EFG -0.331433E+01  0.160577E+01  0.170855E+01 a.u.

===== principal values Q-tensor (have to be multiplied by Q (e 10^-24 cm^2) / 2I(2I-1))
q11  q22  q33
-0.778750E+03  0.377300E+03  0.401450E+03 MHz
-0.259763E+03  0.125815E+03  0.133909E+03 10^-4 cm^-1

Results for 119Sn, Q = 0.1280, Vzz = -0.322065E+02 10^21 V/m^2, NQCC = -0.996800E+02 MHz, eta = 0.03101
Mossbauer quadrupole splitting = -2.588 mm/s (unit conversion used 1 mm/s = 19.2601 MHz)
[SnCl₃ site] (QZ4P basis on Sn)

Atom 2       Sn Input number 2 xzynuc(Angstrom) =  5.0221 -0.6745  6.6152

===== principal axes Q-tensor (EFG)

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<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>X</td>
<td>-0.441908</td>
<td>-0.086384</td>
</tr>
<tr>
<td>Y</td>
<td>-0.625059</td>
<td>0.734597</td>
</tr>
<tr>
<td>Z</td>
<td>0.643443</td>
<td>0.663024</td>
</tr>
</tbody>
</table>

===== principal values EFG
Sn EFG -0.206089E+01  0.773313E+00  0.128758E+01  a.u.

===== principal values Q-tensor (have to be multiplied by Q (e 10^-24 cm^2) / 2I(2I-1))

<p>| | | |</p>
<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>q11</td>
<td>-0.484237E+03</td>
<td>0.181701E+03</td>
</tr>
<tr>
<td>q22</td>
<td>0.161524E+03</td>
<td>0.606091E+02</td>
</tr>
<tr>
<td>q33</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Results for 119Sn, Q = 0.1280, Vzz = -0.200264E+02 10^21 V/m^2, NQCC = -0.619823E+02 MHz, eta = 0.24954
Mossbauer quadrupole splitting = -1.626 mm/s (unit conversion used 1 mm/s = 19.2601 MHz)

Complete References for Gaussian03³ and Gaussian09⁴

**Vita Auctoris**

**NAME:** Rajoshree Bandyopadhyay (née RoyChowdhury)

**Place of Birth:** Calcutta (Kolkata), West Bengal, India

**EDUCATION**

University of Windsor, Department of Chemistry and Biochemistry, Ph.D. 2007 – 2012

Memorial University of Newfoundland, Department of Chemistry, M.Sc. 2005 – 2007

University of Pune, India, Department of Chemistry and Biochemistry, M.Sc. 2002 – 2004

Fergusson College, University of Pune, India, Department of Chemistry, B.Sc.(Hons.) 1999 – 2002

**PUBLICATIONS**


Manuscript in progress – 1