Investigations into Cationic Polyether Complexes of Germanium(II) and Tin(II)

Jennifer Hien Nguyen

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Investigations into Cationic Polyether Complexes of Germanium(II) and Tin(II)

By

Jennifer Hien Nguyen

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

Windsor, Ontario, Canada

2014

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Investigations into Cationic Polyether Complexes of Germanium (II) and Tin(II)

by

Jennifer H. Nguyen

APPROVED BY:

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C. Macdonald, Advisor
Department of Chemistry & Biochemistry

September 29, 2014
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:

Sections of Chapter 2 of this thesis contain results published in a communication entitled “Water and Ammonia Complexes of Germanium(II) Dications” (Bandyopadhyay, R., Nguyen, J. H., Swidan, A.. Macdonald, C. L. B. Angew. Chem. Int. Ed. 2013, 52, 3469-3472). Rajoshree Bandyopadhyay and I are co-first authors. Rajoshree Bandyopadhyay obtained the initial crystal structure of the water adduct. I repeated these reactions for confirmation and further characterized the products through DOSY, VT-NMR, and pXRD experiments. Moreover, I was the principal investigator for the deprotonation of the water adduct and the NMR experiments with alcohols and amines. Crystal structure refinement and calculations were performed by Dr. Charles L. B. Macdonald. Ala’aeddeen Swidan performed $^{14}$N and $^{15}$N NMR studies. Dr. Macdonald and I had a major role in the preparation of the manuscript/chapter.

The work presented in Chapter 3 is unpublished and incorporates the outcome of joint research undertaken in collaboration with Jonathan W. Dube under the supervision of Dr. Paul J. Ragogna at Western University. I was the principal investigator, synthesizing starting materials, conducting reactions with $\text{H}_2\text{S}$, and characterizing the products through $^1\text{H}$ NMR, pXRD, and SEM/EDS. Jonathan W. Dube studied the reactivity of the polyether stabilized Ge(II) complexes towards $\text{PH}_3$ and also characterized the products through EDS. I, in addition to my supervisor, conducted DFT
calculations to obtain geometry optimized models of the adduct and insertion products. Moreover, I had a major role in the preparation of this chapter.

Chapter 4, whose results are also unpublished, details the stabilization of Ge(II) and Sn(II) salts by glyme ligands and was undertaken in collaboration with fellow Macdonald group members, Warren W. Friedl and Joanne Yu. Warren W. Friedl first synthesized and obtained the crystal structure of [Ge-tetraglyme][OTf]2. I supervised Joanne Yu who performed the reaction yielding [GeCl-triglyme][GeCl3]. I synthesized all other compounds and characterized them through multinuclear NMR studies and X-ray crystallography. Crystal structure refinement and calculations were conducted by Dr. Macdonald and EA was conducted by Dr. Janeen Auld. I also played a major role in the preparation of this chapter. Overall, I acknowledge my supervisor as a co-author in Chapters 1–5 as he made significant contribution to the editing of these manuscripts and chapters.

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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Abstract

Previously, crown ethers were demonstrated to be excellent ligands in the stabilization of “naked” Ge(II) dications. As an extension of this work, the reactivity of these complexes with small molecules was investigated. Herein, it is reported that the addition of one equivalent of water or ammonia to [Ge[15]crown-5][OTf]2 produces the stable complexes [Ge[15]crown-5⋅H2O][OTf]2 and [Ge[15]crown-5⋅NH3][OTf]2, respectively. The synthetic potential of these complexes is also described, investigating their deprotonated variants in pursuit of unsaturated Ge compounds, as well as their alcohol and amine analogues. The interaction of [Ge[15]crown-5][OTf]2 with heavier element hydrides was also studied. Unlike the aforementioned donor-acceptor complexes, the room temperature addition of H2S and PH3 results in the precipitation of GeS and GeP, respectively. Lastly, the suitability of glymes in the stabilization of Ge(II) and Sn(II) salts was confirmed. Both triglyme and tetraglyme complexes were isolated and structurally characterized, some with unexpected results.
Acknowledgements

First and foremost, I’d like to thank Chuck for all his patience, support, and guidance during these past five years of grad school and undergrad. It’s crazy how fast time flies. I still remember being nervous and unsure on my first day in lab back in second year and now I can’t even imagine working for anyone else. I’ve learned so much and I can’t say thank you enough!

Next, I would like to thank all the Macdonald group members, past and present. Lab would not nearly have been as enjoyable as it was without you all! Special thanks go to Raj for being my first friend in the lab and training me and to Ala, Steph, Justin, Fawzia, Martin, Joanne, Chris, Ben, and Greg. Also, this list would not be complete without the Johnson lab members including Meghan, Manar, Sha, Drake, and Matt. Although it got super cramped, I had such a good time sharing the office with you and leave with great memories! Nat and Gyll, thank you for always being there!

I would like to thank Dr. Steve Loeb and Dr. Chris Weisener for being in my committee. I would also like to thank Dr. Jon Dube and Dr. Paul Ragogna for their collaboration. Special thanks also go to all the staff in the department including Matt for NMR, Janeen for EA/MS, Sharon for SEM/EDS, Marlene for trying her hardest to keep me on track, and Una and Nedhal for being awesome lab coordinators.

Most importantly, I’d like to thank my family for all their love and support throughout the years. You are my inspiration and I wouldn’t be where I am today without all your encouragement. Lastly, I’d like to thank NSERC and the University of Windsor for their generous support.
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<tr>
<td>[12]crown-4</td>
<td>1,4,7,10-tetraoxacyclododecane</td>
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<td>doublet (NMR spectra)</td>
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<td>wavenumber or frequency</td>
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<td>Oak Ridge Thermal Ellipsoid Plot Program</td>
</tr>
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<td>OTf</td>
<td>triflate, CF$_3$SO$_3$</td>
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<td>pentet (NMR spectra)</td>
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<td>pnictogen</td>
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<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>$^{i}$Pr</td>
<td>isopropyl, –CH(CH$_3$)$_2$</td>
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PS          proton sponge
pXRD        powder X-ray diffraction
py          pyridine
q           quartet (NMR spectra)
R           alkyl group
σ           sigma-bonding
s           singlet (NMR spectra) or seconds
SEM         scanning electron microscope
SSNMR       solid state nuclear magnetic resonance
t           triplet (NMR spectra) or time
θ           theta diffraction angle
tetraglyme  2,5,8,11,14-pentaoxapentadecane
THF         tetrahydrofuran
Tip         2,4,6-triispropylphenyl
TMS         trimethylsilane
triglyme    2,5,8,11-tetraoxadodecane
VT-NMR      variable temperature nuclear magnetic resonance
WBI         Wiberg Bond Index
X           halogen
Chapter 1

An Introduction to the Chemistry of Low Oxidation State Germanium and Tin

1.1 General Information

Group 14 of the Periodic Table, collectively known as the “tetrels”, is comprised of the elements carbon, silicon, germanium, tin, and lead. This group spans a wide array of properties ranging from the non-metal, carbon; followed by the metalloids, silicon and germanium; to the metals, tin and lead. As inferred from the group name, these elements, with an electronic configuration of \([\text{core}]n^2np^2\), contain four valence electrons and are typically found in the +4 or +2 oxidation state. The former is more common for carbon, silicon, and germanium; whereas, the latter is more common for tin and lead. Compounds containing germanium and tin in the +2 oxidation state will be the primary focus of this thesis.

1.2 Oxidation States

The concept of an oxidation state, which is defined as the number of electrons that are formally missing from an atom, is fundamental in rationalizing and predicting key information such as bonding and reactivity of an atom within a molecule.\(^{1,2}\) In the simplest of models, oxidation states are assigned to atoms using established counting rules based on the relative electronegativities of the atoms within a molecule. For example, hydrogen and halogens are typically assigned oxidation states of +1 and -1, respectively. This method, while useful for balancing reduction-oxidation reactions, often fails to rationalize predicted and experimentally observed structures and reactivities for the main group p-block elements.
For example, consider the central carbon atoms in Me₂CCl₂ and :CCl₂. Based on conventional rules, both are assigned an oxidation state of -2. In spite of their common oxidation state, however, the aforementioned compounds differ vastly in their structural and chemical properties with the former being a stable liquid and the latter being a reactive intermediate. Moreover, when comparing Me₂CCl₂ with CH₂Cl₂ and :CCl₂ with :CHCl, the latter in each pair has carbon in the 0 oxidation state in spite of similar structures and reactivities with the former. It is apparent that there are shortcomings associated with the conventional model; consequently, results shouldn’t be overly interpreted.²

A similar, but distinct model from oxidation state is that of valence state, which describes the number of electrons an atom uses in bonding or charges.¹ More specifically, it is equal to the number of valence electrons in a free atom minus the number of non-bonding electrons on said atom within a molecule. Oftentimes, the terms "oxidation state" and "valence state" are incorrectly assumed to be synonymous. Generally, the confusion arises due to cases when both the oxidation and valence number (or their magnitudes) coincide, typically with simple element hydrides, but such instances are purely coincidental.¹ Unlike oxidation states, which can be assigned based on a molecular formula, knowledge of a molecule’s electronic distribution is required to determine an atom’s valence state.¹ Thus, when encountering an element in an unusual oxidation or valence state within a molecule, the valence state often provides more insight into the structure, bonding, and reactivity. However, valence states have deficiencies also: for example, there is a formal change in valence state when a donor (e.g. PMe₃) binds with an acceptor (e.g. AlCl₃) to make an adduct (Me₃P→AlCl₃). The change in valence state
of the donor (P$^{\text{III}}$ to P$^{\text{V}}$) suggests the presence of an electron transfer process but the valence state of the acceptor remains the same (Al$^{\text{III}}$) and is not consistent with any electron transfer having occurred.

As a result, an alternative method to assigning oxidation states is through the number of non-bonding electrons or "lone pairs" associated with an atom within a molecule.$^2$ Closely resembling the aforementioned concept of valence, this model highlights similarities in structure and reactivity between elements in a given oxidation state. As it pertains to Group 14, an atom with four, three, two, one and zero non-bonding electron(s) is assigned an oxidation number of 0, +1, +2, +3, and +4, respectively (Figure 1.1). It follows that the +1 and +3 oxidation states would be paramagnetic. Returning to the example of Me$_2$CCl$_2$ and CH$_2$Cl$_2$, the alternative model describes both central carbon atoms as having an oxidation state of +4. In the case of :CCl$_2$ and :CHCl, the oxidation state of carbon is +2. Here, the results are chemically intuitive and it is this model which will be considered for the remainder of this thesis, unless otherwise noted.

Generally, the most stable oxidation state for carbon, silicon, germanium, and tin is +4, while it is the +2 oxidation state for lead; though, Sn(II) is also very stable. The increasing stability of the lower oxidation state down the group is attributed to the inert pair effect$^3$ (the tendency of the $ns^2$ valence electrons to resist oxidation), weaker bond

![Figure 1.1: Oxidation states of Group 14 given the number of non-bonding electrons.](image)
energies\textsuperscript{4}, and relativistic effects\textsuperscript{5} (contraction of the s-orbital containing the $ns^2$ valence electrons).

When considering elements in lower oxidation states, they are necessarily more electron rich than their higher oxidation state counterparts. In contrast to the transition metals whose low oxidation state chemistry is much more established, the valence electrons for main group elements are found in VSEPR active s and p orbitals. Thus, for a low oxidation state main group element, the resulting atom is coordinatively unsaturated, which when coupled with its being electron rich, usually makes the centre highly reactive.\textsuperscript{6} These compounds often exhibit remarkably different structures and reactivities. They have been used to preform transition metal-like chemistry as catalysts and are also precursors for new materials.\textsuperscript{6,7}

For Group 14, the vast majority of study has been and remains dominated by the chemistry of carbon, most notably in the context of organic chemistry. However, the chemistry of the heavier Group 14 elements, particularly in lower oxidation states, has become a field of great interest these past few decades. Studies of these compounds have largely focused on comparisons to carbon chemistry. Yet, their structures and reactivities are oftentimes distinct from their carbon congeners\textsuperscript{8-10} or have no precedent in carbon chemistry.\textsuperscript{11} This thesis focuses on compounds containing Ge(II) and Sn(II) centres and the remainder of this chapter will briefly review chemistry involving these and other relevant low oxidation states species.
1.3 Syntheses, Structures, and Reactivities of Germanium(II) and Tin(II) Species

Due to the interest in comparative chemistry with carbon, much work involving heavier Group 14 elements in lower oxidation states has been with their carbene analogues, metallylenes. With a general form of ER₂, (E = Si-Pb) these species are divalent with an oxidation state of +2. Unlike carbenes, which can have a singlet or triplet ground state, the ground state electronic configuration of the metallylenes rests entirely in the singlet state (Figure 1.2).¹² This is commonly ascribed to the larger energy gap between the s- and p-orbitals of the heavier elements but is perhaps a consequence of greater differences in the spatial extent of those orbitals.¹³ The combination of their vacant p-orbital and lone pair of valence electrons makes the amphoteric metallylenes extremely reactive so kinetic and/or thermodynamic stabilization of the reactive vacant p-orbital is usually required to isolate these compounds. In the absence of such stabilization, these species will undergo rapid oligomerization, polymerization or reaction.

![Figure 1.2: Electronic configuration depictions of a singlet carbene (A), a triplet carbene (B), and a singlet metallylene (C) where E = Si-Pb and R = any group.](image)

Kinetic stability is afforded through the use of sterically demanding ligands which impede the ability to self-oligomerize/polymerize and/or prevent nucleophilic attack on
the vacant p-orbital. Thermodynamic or electronic stabilization involves the transfer of electron density from n or π donor ligands (where n is a non-bonding electron) to the empty π-orbital on the tetrel, reducing its electronic deficiency. This is accomplished in one of three ways: π-donation from an adjacent atom of an intramolecular donor (Figure 1.3A), σ-donation from an intramolecular donor (Figure 1.3B), or σ-donation from an intermolecular donor (Figure 1.3 C).

![Figure 1.3](image)

**Figure 1.3:** Electronic stabilization via π-donation from an adjacent atom (A), σ-donation from an intramolecular donor (B), and σ-donation from an intermolecular donor (C) where E = Si-Pb.

Consequently, simple molecules like EH₂ and ER₂ (R = small alkyl or aryl group) are not stable; however, many of the dihalometallylenes (EX₂, where X = F, Cl, Br, I) are stable under an inert atmosphere and are available as “bottleable” substances. Their stability is attributed to the halogens' π-donating abilities to the empty p-orbital, via either intra- or intermolecular interactions, and because of the σ-accepting properties of the halogens as a consequence of their greater electronegativities (which will stabilize the tetrel’s lone pair inductively).

Overall, despite being a relatively new field, germanium(II) chemistry (and much more well-established tin(II) chemistry) is rich and diverse. Multiple substituents/ligands
have been employed utilizing either kinetic or thermodynamic stabilization or both resulting in novel structures and reactivities, which have been the subject of recent reviews.\textsuperscript{10,12,14-16} Some of the various substituents/ligands used, the resulting compounds, and their reactivities will be discussed in the next few sections.

1.3.1 Dialkyl- and Diarylgermylenes (R\textsubscript{2}Ge) and Stannylenes (R\textsubscript{2}Sn)

Generally, the preparation of dialkyl- and diarylmetallylenes can be achieved through one of three methods: 1) the reduction of a dihalometallane species, R\textsubscript{2}EX\textsubscript{2} (X = Cl, Br); 2) photochemical or thermal elimination of ER\textsubscript{2} from a cyclotrismetallane; and 3) substitution of a pre-existing E(II) species with an organolithium or Grignard reagent which is by far the most common method used (Scheme 1.1).\textsuperscript{12}

![Scheme 1.1](image)

\textbf{Scheme 1.1:} General synthetic routes towards dialkyl- and diarylmetallylenes.

In solution, many of these compounds exist in equilibrium with their dimer, and it is usually the dimeric form that is isolated in the solid state. However, the judicial choice
of bulky substituents should favour formation of the metallylene. One such case is \( \text{Ge}[\text{CH}(	ext{SiMe}_3)_2]_2 \) which exists as a dimer in the solid state (Figure 1.4).\(^\text{17}\) By replacing only one of the \( \text{CH}(	ext{SiMe}_3)_2 \) groups with \( \text{C}(	ext{SiMe}_3)_3 \), to give \( \text{[(Me}_3\text{Si)}_3\text{C}][\text{(Me}_3\text{Si})_2\text{CH}]\text{Ge} \), Jutzi and co-workers were able to isolate the first monomer to be stable in both the solution and solid state.\(^\text{18}\) Of the many stable monomeric metallylenes reported, the majority feature bulky aryl substituents obtained from substitution reactions with the aforementioned E(II) compounds (Figure 1.5).\(^\text{19-21}\)

![Figure 1.4: Equilibrium between Lappert’s germylene monomer and its digermene dimer.](image)

![Figure 1.5: Examples of stable germylenes bearing bulky aryl substituents where Mes=2,4,6-Me_3C_6H_2, Ph=C_6H_5, Np=1-naphtyl.](image)

The chemistry involving metallylenes, while quite diverse and dependent on the substituents bonded to germanium or tin, can be categorized as insertion, cycloaddition, reduction, chalcogenation, or complexation (Scheme 1.2).\(^\text{12,14,22}\) Most of the chemistry is
driven by nucleophilic attack on the vacant p-orbital, resulting in two new bonds at the now E(IV) centre. Insertion of metallylenes into haloalkanes or alcohols to form R₂ER’X (X = halogen or OH) has been observed.¹⁰,²³⁻²⁵ In cycloaddition, interaction with alkenes or alkynes result in [2 + 2]-cycloadducts and interaction with butadienes give [2 + 4]-cycloadducts.²⁶⁻²⁸ Metallylenes may also undergo reduction by accepting an electron into the empty p-orbital to give radical anions.²⁹ Chalcogenation consists of reacting bulky metallylenes with elemental chalcogens (Ch = O, S, Se, Te) to form the corresponding “heavy ketone” analogues R₂E=Ch.³⁰,³¹ Lastly, these compounds can act as donors or acceptors to form donor-acceptor complexes.³²,³³

Scheme 1.2: Reactivity of germylenes and stannylenes (E = Ge, Sn).
1.3.2 Digermynes (RGeGeR) and Distannynes (RSnSnR)

A relatively new class of compounds are the dimetallynes which are the heavier analogues of alkynes. In the triply bonded form, the tetrel has a formal oxidation state of +1. However, the triply bonded species may also be viewed as a resonance form of the bis-metallylene, in which case the oxidation state would be +2 based on the number of lone pairs (Scheme 1.3). The general synthetic route involves reduction of a terphenylgermanium(II) or terphenyltin(II) chloride (which depending on the aryl group, may exist as a monomer or as a dimer) with an alkali metal.34 (Scheme 1.4).

Scheme 1.3: Resonance structures of dimetallynes (E = Ge, Sn).

Scheme 1.4: Synthesis of a dimetallyne (E = Ge, Sn).

The isolation of such compounds and other Group 14 analogues34-36 has been of great importance, allowing for comparison of bonding and reactivity to traditional organic chemistry. Unlike the linear alkynes, dimetallynes adopt a planar, trans-bent geometry which deviates from linearity. The difference in bonding between alkynes and the heavier Group 14 analogues can be explained by two models.
In the CGMT (Carter-Goddard-Malrieu-Trinquier) model,\(^9\) because the triplet state is accessible for carbon, the two putative triplet carbene fragments (with opposite spins) can combine following a least-motion pathway to form strong $\sigma$ and $\pi$ bonds resulting in a planar double bond (Scheme 1.5A). In contrast, the singlet state is the most stable for the remainder of Group 14. This is due to the large difference in S→T transition energy which increases with atomic number. When two of these putative singlet fragments combine, they must rotate so as to avoid repulsion (a non-least-motion pathway), allowing for delocalization of electron density from the filled $s$-orbital of one fragment to the vacant $p$-orbital of the other (Scheme 1.5B). The result is a trans-bent double bond with relatively weaker $\sigma$ and $\pi$ bonds.

**Scheme 1.5:** Multiple bond formation for carbon (A) and Si-Pb (B).

An alternative but equivalent explanation for the trans-bent geometry is a second order Jahn-Teller effect involving the $\pi$ and $\sigma^*$ (also $\sigma$ and $\pi^*$) orbitals of these fragments.\(^9\) Descending Group 14, these orbitals lie closer in energy due to weaker bond energies. Within the trans-bent geometry, they also have the appropriate symmetry allowing for orbital mixing. This results in non-bonding (i.e. lone-pair-like) electron density at the $\pi$-type orbital on the tetrel (Figure 1.6).
Given the low coordination number, weaker bond energies, and higher electron density at the tetrel centre, dimetallynes are anticipated to be highly reactive. Indeed, their unique bonding structure affords similar reactivity to organometallic compounds that was hitherto unseen in main group chemistry. In particular, their reactivity with hydrogen, olefins, azides, among other reagents, has recently been reviewed. Some of their important reactions are depicted on the following page (Scheme 1.6).
Scheme 1.6: Reactivity of digermynes and distannynes (E = Ge, Sn).

1.3.3 Diamidogermylenes (NR$_2$)$_2$Ge and Stannylenes (NR$_2$)$_2$Sn

Nitrogen-based substituents have long been used to stabilize Ge(II) and Sn(II) centres, with silylamides the first to be successfully utilized. In 1974, Lappert et al.\textsuperscript{41} reported the stable, acyclic diamidometallylenes, E[N(SiMe$_3$)$_2$]$_2$ and E[N(SiMe$_3$)(CMe$_3$)]$_2$ (E = Ge, Sn, Pb), launching a class of compounds that has since been widely investigated. The general synthetic route involves addition of two equivalents of a lithium amide salt, Li(NR$^1$R$^2$) to GeCl$_2$·dioxane or SnCl$_2$ to afford the diamidometallylenes, E(NR$^1$R$^2$)$_2$ and the LiCl by-product. The first compounds bore silyl
substituents on the nitrogen but alkyl, aryl, and germyl substituents have since been reported (Figure 1.7).\textsuperscript{12}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{example}
\caption{Examples of acyclic diamidometallallylenes (E = Ge, Sn).}
\end{figure}

In comparison to the dialkyl derivatives, the diamidometallallylenes exhibit greater stability.\textsuperscript{42} In addition to the steric protection afforded by bulky substituents on the nitrogen, the greater stability of the carbenoids is also attributed to the $\pi$-donating and $\sigma$-accepting ability of the amido groups. Their chemistry is varied where they can behave as neutral ligands in transition metal complexes, insert into alkyl/transition metal halide bonds and acid anhydrides, or act as precursors for other divalent species through substitution reactions with organolithium or Grignard reagents (Scheme 1.7).\textsuperscript{12,43,44}
1.3.4 *N*-Heterocyclic Germanynes (NHGe) and Stannylenes (NHSn)

Since Lappert’s initial report on acyclic diamidometallylenes\(^{41}\), a variety of cyclic variants have been isolated ranging in size from four to six membered rings. Of particular interest in this section are the imidazole based *N*-heterocyclic germanynes (NHGe) and stannylenes (NHSn). Resembling the analogous *N*-heterocyclic carbenes (NHC), they feature a divalent, diamino-stabilized E(II) centre contained within a five membered ring. Again, as with their acyclic analogues, electronic stabilization is afforded through the amino group, however, additional stability is gained from the effects associated with cyclization (e.g. chelate effect).
The first NHGe’s, featuring saturated species with methyl or phenyl substituents on nitrogen, were reported in 1985 by Meller and Gräbe\textsuperscript{45} and went largely unnoticed. Arduengo’s later discovery of stable NHCs (Figure 1.8A) in 1991\textsuperscript{46} sparked renewed interest in the heavier analogues, leading to the isolation of the first NHSn by Lappert \textit{et al.} in 1995.\textsuperscript{47} Since then, saturated (Figure 1.8C), unsaturated (Figure 1.8B), and benzannulated (Figure 1.8D) systems with diverse substituents have been reported for both Ge and Sn. Moreover, pyridine (Figure 1.8E), naphthalene (Figure 1.8F), and acenaphthene (Figure 1.8G) annulated derivatives have also been observed.\textsuperscript{15}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1_8.png}
\caption{NHC (A), the corresponding NHE (B) and derivatives (C-G).}
\end{figure}

Akin to the acyclic diamidometallylenes, the most widely used technique to synthesize the aforementioned NHGe’s and NHSn’s regardless of backbone involves the addition of equimolar quantities of a dilithiated diamine to GeCl\textsubscript{2}-dioxane or SnCl\textsubscript{2},
respectively (Scheme 1.8).\textsuperscript{48} The saturated NHGe’s are also accessible via reduction of a dichlorogermanium(IV) precursor with an alkali metal.

\textbf{Scheme 1.8:} General synthesis of unsaturated NHE (E = Ge or Sn, R = alkyl or aryl).

The chemistry of these compounds has been widely investigated with varying reactivities for the saturated, unsaturated and annulated systems. One of the more explored fields has been the coordination chemistry of the saturated systems to transition metals. For instance, the NHGe [(‘Bu)\text{-}N(CH\text{2})\text{2}N(‘Bu)Ge] was shown to coordinate terminally to Ni(CO)\text{4} by displacing CO to form Ni(CO)\text{n}NHGe (n = 2, 3) as reported by Herrmann \textit{et al.}\textsuperscript{48} NHSn’s display similar chemistry, however, it is worthwhile to note they may also adopt a bridging position across dinuclear metal units (Scheme 1.9).\textsuperscript{49}

\textbf{Scheme 1.9:} Coordination of NHSn to transition metal complexes (R = 2,6-‘Pr\text{2}C\text{6}H\text{3}).
The chemistry of the unsaturated systems is a bit more varied. Cowley and co-workers demonstrated that an unsaturated NHGe underwent metathesis with PCl₃ or AsCl₃ to afford the corresponding phosphenumium and arsenium cations, respectively (Scheme 1.10). The Ge(II) is oxidised to Ge(IV) forming the GeCl₅⁻ counter anion, though, no reduction product was reported. However, subsequent work suggests the reduction product is formally P(I), which is transient on the way to the cycloaddition that generates the P(III) species.

Scheme 1.10: The reaction of an NHGe with PCl₃ and AsCl₃.

In a separate reaction, transfer of tin from an NHSn to a diazabutadiene was observed, allowing for interconversion between different cyclic stannylene (Scheme 1.11). This reactivity was also predicted for the analogous germanium system. Stable paramagnetic stannylene have also been reported from the reaction of the NHSn [(Dipp)-N(CH₂)₂N(Dipp)Sn] with organic radicals, mercury(II), and silver(I) halides.
Regarding the annulated derivatives, the tetrel centre tends to be more electron deficient, resulting in an increase of their $\pi$-accepting abilities. Benzannulated NHGe's have been shown to react with trimethylsilylazide or triethylsilylazide to form tetraazagermoles. In addition, both a benzannulated NHGe and NHSn react with their carbene congener to form a stable donor-acceptor complex. In such complexes, the carbene acts as a neutral two electron donor to germanium or tin centre. Moreover, annulated NHGe's have been used as precursors in the synthesis of novel germanium-containing polymers. Reaction of Meller’s benzannulated NHGe with $p$-benzoquinones yields 2:1 copolymers (Ge:quinone). Other organic precursors have been used in polymerization and along with additional reactivities of these cyclic metallylenes can be found in recent reviews.

1.3.5 $\beta$-Diketiminate Complexes of Germanium(II) and Tin(II)

$\beta$-Diketiminates, commonly referred to as nacnac ligands, are monoanionic bidentate ligands which form six membered rings when coordinated to a metal centre (Figure 1.9B). While isolobal with the ubiquitous $\beta$-diketonate or acac ligands (Figure 1.9A), they are of particular interest due to the ease in tunability of steric or electronic
character by varying the substituents on the N atoms. As a result, they have been used to stabilize a variety of low oxidation state main group and transition metal elements.\textsuperscript{58}

![Diagram of β-Diketonate (A) and β-diketiminate (B) ligands.]

**Figure 1.9:** β-Diketonate (A) and β-diketiminate (B) ligands.

Dias et al. reported the first β-diketiminato chlorogermynes and stannylenes of the form ECl(Mes\textsubscript{2}nacnac) (E = Ge, Sn; Mes\textsubscript{2}nacnac = [{N(C\textsubscript{6}H\textsubscript{3}-2,4,6-Me\textsubscript{3})C(Me)}\textsubscript{2}CH].\textsuperscript{59} It features a three coordinate, E(II) centre. This was achieved through the reaction of GeCl\textsubscript{2}·dioxane or SnCl\textsubscript{2} with (Mes\textsubscript{2}nacnac)Li in a 1:1 molar ratio (Scheme 1.12). Since this initial report, additional compounds have been generated using this synthetic motif by varying the substituent at nitrogen. They range from the bulky 2,6-diisopropylphenyl\textsuperscript{60} or 2,6-dimethylphenyl\textsuperscript{61} to the relatively smaller isopropyl\textsuperscript{62} or phenyl\textsuperscript{63} groups, among others.
Scheme 1.12: Synthesis of the first Ge(II) and Sn(II) β-diketimimates.

Generally, the chemistry involving the chlorometallylenes can be grouped into three categories: 1) substitution of the chloride, 2) chalcogenation, and 3) coordination to transition metal complexes. In the case of germanium, broader reactivity has been reported, however, by far the most common reactivity for both Ge(II) and Sn(II) complexes is the substitution of the chloride by a wide range of substituents. The first example reported was that of NaN$_3$ with Dias’ complex to give the azidogermanium(II) and tin(II) derivatives.$^{59}$ Other species include alkyl,$^{64,65}$ amide,$^{63,66}$ hydride,$^{61,67}$ hydroxide,$^{68}$ fluoride,$^{61}$ and triflate$^{63}$ substituted derivatives, to name a few. Secondly, oxidation with elemental sulfur or selenium affords the respective thioacid chloride and selenoacid chloride; the tin complexes have yet to be crystallographically characterized, however.$^{63,69}$ Lastly, given the lone pair on the Group 14 centre, coordination chemistry has been observed for both germanium and tin complexes with transition metal complexes such as M(CO)$_5$(THF) (M = Cr, W) and Fe$_2$(CO)$_9$. Additional reactivity has been summarized in recent reviews.$^{15,54,70}$
**Scheme 1.13:** Reactivity of the $\beta$-diketiminate chlorogermynes and stannylenes.

The importance of these donor stabilized chlorometallylenes has been noted in their role as precursors for novel compounds, most notably the first structurally characterized Ge(II) hydride,\textsuperscript{61} hydroxide,\textsuperscript{68} and terminal Sn(II) hydride\textsuperscript{67}. Until recently, only +4 analogues were known. Both Ge(II) and Sn(II) hydrides have exhibited remarkable reactivity, inserting into various compounds containing C-C triple bonds, C-O double bonds, or C-N double bonds, among others (Scheme 1.14).\textsuperscript{71-74}
Scheme 1.14: Reactivity of E(II) hydrides (E = Ge, Sn; Dip = 2,6-‘Pr₂C₆H₃).

The reactivity of the Ge(II) hydroxide was also investigated (Scheme 1.15). Reactions with elemental sulfur and selenium resulted in the corresponding thioacid and selenoacid, respectively. Moreover, reactions with transition metal compounds afforded coordination complexes or oxo-bridged complexes.
Scheme 1.15: Reactivity of Ge(II) hydroxide (Dip = 2,6-Pr₂C₆H₃)

1.3.6 Cationic Crown Ether and Glyme Complexes of Germanium(II) and Tin(II)

Crown ethers are macrocyclic ligands with repeating ethyleneoxy -CH₂CH₂O-units and were first reported by Pedersen in 1967. Crown ethers have a general name of [m]crown-n where m is the number of atoms in the ring and n is the number oxygen atoms within that same ring. The term “crown” refers to their conformation and their ability to “crown” cations by complexation. The smallest value of n can be 2, as in [6]crown-2 or more commonly, 1,4-dioxane. Conversely, crown ethers with n as large as 24 have been reported. Moreover, replacement of oxygen with nitrogen or sulfur and the addition of aromatic and heterocyclic subunits have given rise to a multitude of crown ether derivatives. Below are common crown ethers which are of interest to this thesis (Figure 1.10).
Related compounds include glymes and cryptands (Figure 1.11). The former are acyclic variants of crown ethers. They exhibit similar properties and reactivity and are often used as solvents. The naming of glymes is also based on the number of oxygen atoms present. However, as dimethyl ethers of ethylene glycol, the parent glyme already has two oxygen atoms. As a result, there is one more oxygen atom present than implied by the name. The use of triglyme and tetraglyme as ligands will be discussed.

Cryptands, first synthesized by Lehn and co-workers\(^{81}\), are macropolycyclic ligands with a three-dimensional interior cavity (or crypt) which provides a binding site for guest ions. Bicyclic cryptands feature an additional third polyether strand in comparison to the monocyclic crown ethers of Pedersen’s. The most common example is
[2.2.2]cryptand where the numbers indicate the number of oxygen atoms in each of the three bridges (Figure 1.11).

The aforementioned ligands have been noted for their remarkable metal complexation properties. Chemical literature provides ample evidence of cryptands and crown ethers coordinating with s-block and to a lesser extent, d-block elements.\textsuperscript{78,82} In contrast, complexation of p-block elements is not as extensive. Reported examples of crown ether complexes of p-block elements include aluminum\textsuperscript{83}, gallium\textsuperscript{84}, indium\textsuperscript{84-87}, thallium\textsuperscript{88}, tin\textsuperscript{89}, lead\textsuperscript{90}, and bismuth\textsuperscript{91}. More specifically, the Macdonald group demonstrated that crown ethers, [18]crown-6 and [15]crown-5, can be used to isolate In(I) centres that are usually unstable.\textsuperscript{85} The resulting structures and reactivities were dependent on the size of the crown (Scheme 1.16) and the results suggested that ligation by polyether donors provides an alternative route to the stabilization of low valent species.
Scheme 1.16: Synthesis and reactivity of crowned InOTf (OTf = CF₃SO₃⁻).⁹²

For the group 14 elements, the stabilization of low oxidation state centres has almost universally required covalently bound substituents with the appropriate steric and electronic properties, as was the case for all compounds featured in previous sections. However, Baines and co-workers used the polyether ligation approach to successfully isolate and stabilize a “naked” germanium dication using the electron-rich [2.2.2]cryptand (Scheme 1.17).⁹³ In this salt, the Ge(II) centre is encapsulated within the cryptand – presumably stabilized by numerous weak donor-acceptor interactions – and shows minimal interaction with the triflate anions. Although metal complexation is well established, this was the first example of a cryptand encapsulated, cationic metalloid complex and illustrated that polyether ligation could also be used to isolate lighter p-block cations.
Scheme 1.17: Synthesis of [Ge[2.2.2]cryptand][OTf]$_2$ (OTf = CF$_3$SO$_3$). 

Given that Ge(II) is isolobal and isovalent with In(I) (Figure 1.12) and in light of previous work, it was reasoned that crown ethers would also be suitable ligands for the stabilization of Ge(II) centres. The Macdonald group, in collaboration with the Baines group and simultaneously with the Reid group, investigated the reactivity between GeCl$_2$·dioxane and "Ge(OTf)$_2$"$^{94}$ with the aforementioned crown ethers and their derivatives. The result was a series of unprecedented mono- and dicationic Ge$^{2+}$ complexes (Scheme 1.18).$^{95,96}$ As with the indium complexes, the structural properties are highly dependent on the size of crown ether used: Ge$^{2+}$ fits into the cavity of [15]crown-5 and [18]crown-6; whereas, it forms a sandwich complex with two [12]crown-4 ligands. The structural features are also dependent on the substituent on germanium as seen with [15]crown-5 adopting a folded structure with the [GeCl]$^+$ fragment and a planar conformation with [GeOTf]$^+$. 

Figure 1.12: Comparison of In(I) and Ge(II) centres.
Scheme 1.18: Synthesis of crowned Ge(II) halide and triflate salts.92

Sn(II) variants of the cryptand97 and crown ether98 complexes have been reported with similar structures and properties (Figure 1.13). Recently, the Macdonald group determined that the more flexible glyme ligands are also suitable in stabilizing low valent p-block elements, isolating the triglyme and tetruglyme complexes of Sn(OTf)2.92 In that same study, the properties of the crown and glyme stabilized Sn(II) triflate and chloride salts were studied using Mössbauer spectroscopy, solid state NMR spectroscopy, cyclic voltammetry, and DFT calculations in order to rationalize their stability and reactivity.92
In summary, the results of the Mössbauer studies showed that the Sn(II) valence electrons reside in orbitals that are almost exclusively of 5s character. Ligation by the poly-ether ligands only mildly perturbs the 5s^2 electron configuration with [15]crown-5 and [12]crown-4 having the smallest effect due to the almost symmetrical Sn bonding environment in the sandwich complexes. Conversely, [18]crown-6, triglyme, and tетraglyme, whose complexes feature less symmetrical Sn bonding environments, cause greater perturbation which can lead to increased reactivity (as seen for the [In[18]crown-6][OTf] complex). Furthermore, the Sn valence electrons in the triflate salts tend to have higher s-character as opposed to the chloride salts. This is attributed to the formation of highly ionic contact pairs between the tin, as a Sn^{2+} dication, and triflate. In the latter case, chloride is covalently bonded to tin, forming a [Sn-Cl]^+ cation which destabilizes the tin centre. $^{119}$Sn SSNMR data corroborate these results, highlighting the difference in chemical environments as the $^{199}$Sn nuclei are highly shielded in the triflate salt and are considerably deshielded in the chloride salt. The effect of the poly-ether
ligand and the substituent on Sn is also illustrated through cyclic voltammetry, where complexes in which the valence electrons on tin have greater s-character require more energy to become oxidized.

Although focused on Sn(II), overall, these findings explain why poly-ether ligands with multiple weak donors are suitable for the stabilization of low oxidation state main group elements: they do not overly destabilize the non-bonding valence electrons. Additionally, the reactivity of these species can be tuned through the substituent and/or donor ligand and will be discussed in subsequent chapters.

1.4 Syntheses, Structures, and Reactivities of Germanium(I) and Tin(I) Species

While the chemistry of Ge(II) and Sn(II) is much more established, it is worth noting that species with a formal +1 oxidation state have been observed. They come in the form of metastable E(I) halide salts (E = Ge, Sn) and are prepared in the gaseous phase by reacting Ge or Sn with HX (X = Br, I) at extremely high temperatures and pressures (Scheme 1.19).99-101 The gaseous products are then condensed at very low temperatures with donor solvents to form metastable solutions using a specially-designed apparatus.

Although the structures of the Group 14 monohalides have yet to be determined, they have been employed extensively to make novel clusters of the form EₓRᵧ (x > y; E = Ge, Sn; R = aryl, silyl, amido groups), where naked as well as ligand bound Ge or Sn atoms are present.102,103 As a result, the formal oxidation state of the tetrels averages between 0 and 1. The clusters are generated one of three ways (Scheme 1.19). The first involves a metathesis reaction between the E(I) monohalides and alkali metal reagents of
the aforementioned R groups. The second pathway consists of reductive coupling of
divalent Group 14 halides, R–E–X, with reducing agents such as potassium graphite.
Lastly, they can also be synthesized by reacting Group 14 zintl ion salts with ligand
halides, R–X. Unlike the monohalides, some of these clusters have been
crystallographically characterized. Their unique structures offer insight as bridges
between the molecular and bulk phases, much like nanoparticles.

\[ \text{E}(\text{g}) + \text{HX}(\text{g}) \xrightarrow{-1/2 \text{H}_2} \frac{1}{n} [\text{EX}]_n \xrightarrow{\text{KC}_8} \begin{array}{c} \text{M} \cdot \text{R} \\ -1/2(x-y) \text{R-R} \end{array} \xrightarrow{1/2(x-y) \text{R-R}} \begin{array}{c} \text{E}_x\text{R}_y \text{clusters} \\ \text{M' \cdot \text{R}} \\ -1/2(x-y) \text{R-R} \end{array} \xrightarrow{\text{M' \cdot \text{E}_x (zintl)}} \]

**Scheme 1.19:** Synthesis of the E(I) monohalides and E_xR_y clusters.

Based on the alternative oxidation state model, E(I) species would also include
radicals. To date, Jones and Driess have reported the only monomeric, neutral
germanium(I) radical.\textsuperscript{104} This was achieved through reduction of the β-diketiminato
chlorogermylene, GeCl(\textsuperscript{t}BuNacnac) (Nacnac = \{N(C_{6}H_{3}-2,6-\text{Pr}_{2})C(\text{t}Bu\}_2CH\}), with
either sodium naphthalenide or a Mg(I) dimer resulting in the neutral radical
[\{\textsuperscript{t}BuNacnac)Ge:]\textsuperscript{−} (Scheme 1.20). The identity of this radical complex has been
confirmed by X-ray crystallography, EPR spectroscopy and computational studies. It also
undergoes a reaction with \textsuperscript{t}Bu\textsubscript{3}SnH to form a mixture of products including a novel,
cyclic diamidogermylene and will revert to the chlorogermylene upon addition of
C_{2}Cl_{6}.\textsuperscript{104}
1.5 Syntheses, Structures, and Reactivities of Germanium(0) and Tin(0) Species

Compounds containing Group 14 elements in the 0 oxidation state feature either E-E bonds (for a formal oxidation state of 0) or a tetrel atom with two lone pairs. In general, these compounds are rare due to their tendency to disproportionate. However, careful selection of a donor ligand has resulted in a few isolable E(0) compounds. Jones and co-workers have reported dinuclear E=E cores (E = Ge, Sn) datively coordinated by two NHCs which were obtained through reduction of a NHC adduct of ECl₂ with a Mg(I) dimer (Figure 1.14A).¹⁰⁵,¹⁰⁶ Heavier Group 14 analogues of allenes have also been isolated from the reduction of E(II) or E(IV) precursors with alkali metal reagents affording products with a general form of R₂E=E=ER₂ where R is a silyl group or derivative (Figure 1.14B,C).¹⁰⁷,¹⁰⁸

A new class of E(0) compounds are the ylidones. These complexes are comprised of a tetrel atom with two lone pairs stabilized by two donor ligands through donor-acceptor interactions. Referring back to the heavier allene analogues, unlike allene, these complexes feature a non-linear E-E-E core. As such, it is better to consider them as ylidones with the two heavier metallylene fragments stabilizing the central E(0) atom which would account for the bent structure (Scheme 1.21A). The previously discussed
NHGe’s or NHSn’s may also be considered as ylidones, with diazabutadiene (DAB) as the donor ligand (Scheme 1.21B). The DAB ligands are redox active and can undergo one or two electron reduction, leading to ambiguity in oxidation states. As an ylidone, there is no significant π-delocalization from the tetrel to the ligand which supports the observation of germanium or tin exchanging from one DAB ligand to another neutral DAB ligand (Scheme 1.11). Other, more recent ligands successful in trapping E(0) centres include a biscarbene and DIMPY (2,6-diiminopyridine). Investigations into the reactivity of these complexes are currently underway. Given their unique electronic structure, these complexes are expected to possess unusual reactivity.

**Figure 1.14:** (A) NHC stabilized E=E (E = Ge, Sn, Ar = 2,6-Pr2C6H3, 2,4,6-Me3C6H2), (B) trigermallene, and (C) tristannaallene.

**Scheme 1.21:** Resonance structures of allene (A) and NHE (B) and their ylidones.
1.6 Outline of Thesis

Previously, the Macdonald group has demonstrated that crown ethers are suitable ligands for the stabilization of low-oxidation state main group elements. This thesis focuses on the reactivity of these compounds, in particular that of the crowned Ge(II) dications. It is believed that the less restrictive binding of [15]crown-5 and [18]crown-6 (as opposed to the [12]crown-4 sandwich complexes) should facilitate interaction between germanium and small molecules.

In Chapter 2, the reaction of [Ge[15]crown-5][OTf]2 with water and ammonia is explored. Unlike the insertion chemistry ubiquitous to Ge(II) compounds as described in Chapter 1, coordination chemistry is observed. The resultant products include the first crystallographically characterized water adduct of Ge(II). The synthesis and characterization of these stable complexes will be discussed.

Similarly, Chapter 3 describes the interaction between the crowned Ge(II) complex with the heavier element hydrides, hydrogen sulfide and phosphine. It was anticipated that the analogous donor-acceptor complexes would be isolated. However, the room temperature addition of H2S and PH3 results in the rapid formation of GeS and GeP, respectively. Characterization of these products will be discussed, in addition to preliminary computational investigations comparing the reactivity towards the light and heavy element hydrides.

Chapter 4 examines the ability of triglyme and tetraglyme to isolate and stabilize Ge(II) and Sn(II) triflate and chloride salts. Given the similar nature of glymes to crown ethers, it is anticipated that glymes may also stabilize low oxidation main group elements.
Indeed, several glyme stabilized Ge(II) and Sn(II) complexes have been isolated and are presented in this chapter. The structural and chemical properties will be compared and contrasted with the crown ether complexes. To conclude, a summary of this thesis including future work is given in Chapter 5.

1.7 References


Chapter 2

The Reactivity of Crowned Ge(II) Dications Towards Water, Ammonia, and Their Organic Analogues

2.1 Introduction

The chemistry of compounds containing heavier Group 14 elements in unusual bonding environments 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 Group 14 elements are often compared to and contrasted with appropriate carbon analogues; however, the structural and chemical properties of many of these compounds are often quite distinct from those of the carbon congeners.1-7 Recent investigations have focused on the preparation and chemistry of low-valent germanium complexes,8,9 multiple bonds,3 and radicals;2,10 some of these studies have yielded compounds that have no precedent in carbon chemistry (for example, Zintl ions11). In one of the most notable recent examples, Baines and co-workers discovered that a localized germanium dication can be stabilized by the [2.2.2]cryptand ligand.12 More recently, the Macdonald group, in collaboration with the Baines group and simultaneously with the Reid group, demonstrated that crown ethers are also appropriate ligands for the stabilization of unambiguous GeII dications.13-15 In that work, it was posited 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. To evaluate this postulate, an investigation into the reactivity of the GeII crown ether complexes with a variety of simple reagents
was undertaken. In this chapter, the first results of these studies regarding the simple coordination chemistry of the dication are presented, including the remarkable formation of the first crystallographically characterized water adduct of germanium(II).

2.2 Results and Discussion

2.2.1 Reactivity with Water

The addition of one molar equivalent of water or D₂O to a solution of [Ge[15]crown-5][OTf]₂ (2.1[OTf]₂) in CH₂Cl₂ generates the complexes [Ge[15]crown-5·H₂O][OTf]₂ (2.2[OTf]₂) and [Ge[15]crown-5·D₂O][OTf]₂ ([D₂]·2.2[OTf]₂), respectively (Scheme 2.1), as assessed by ¹H NMR spectroscopy in solution. Removal of all volatile components yields a colourless solid that was characterized as the water adduct by microanalysis and spectroscopic methods. Recrystallized material suitable for examinations by single-crystal X-ray diffraction was obtained through the slow evaporation of a dichloromethane solution of the crude product.


Complex 2.2[OTf]₂ crystallizes in the triclinic space group P-1 with one molecule in the asymmetric unit (Figure 2.1). The molecular structure of 2.2[OTf]₂ 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 oxygen atoms. The oxygen atom of the H₂O molecule (O1) 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-O1 distance of 2.003(4) Å is considerably longer than typical covalent Ge-O bonds (ca. 1.75–1.85 Å);¹⁶ the range of 1.70 to 1.90 Å covers the majority of such compounds reported in the Cambridge Structural Database.¹⁷ It must be noted that these distances mostly correspond to Ge⁴⁺ compounds, and it would be anticipated that the Ge⁴⁺-O distances should be somewhat longer because of the larger ionic radius (Ge²⁺ 87 pm; Ge⁴⁺ 67 pm).¹⁸ However, reported distances for the 11 neutral compounds with dicoordinate Ge atoms featuring a Ge-O bond also range from 1.765(6) Å¹⁹ to 1.888(4) Å.²⁰ The Ge-Oₐ₅ distances range from 2.265(4)–2.361(3) Å and are comparable to those observed in the starting material, [Ge[15]crown-5][OTf]₂.¹³ The O1-H bond lengths were restrained to be about 0.79 Å; the O1⋯Oₜriflâte 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.²¹ 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 (that is, O11 and O21) is somewhat longer than the remaining two. Together, these data clearly suggest that both of the triflate anions are hydrogen-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 357° for the angles at O1, as illustrated for the heavy water analogue (Figure 2.2).
Figure 2.1: Thermal ellipsoid plot (30% probability surface) of 2.2[OTf]₂. Ellipsoids set at 30% probability. Most hydrogens have been removed for clarity. Selected bond distances (Å) and angles (°): Ge–O1 2.003(4), O1–H11 0.79(4), O1–H12 0.79(4), O1⋯O11 2.631(7), O1⋯O21 2.681(5), Ge–O31 2.282(3), Ge–O32 2.265(3), Ge–O33 2.356(3), Ge–O34 2.276(3), Ge–O35 2.361(3); Σ<sub>O1</sub> 357.

Figure 2.2: Ball-and stick representation of [D₂]-2.2[OTf]₂. Most hydrogen atoms have been removed for clarity. Selected bond distances [Å] and angles [°]: Ge–O1 2.003(4), O1–H11 0.75(6), O1–H12 0.75(6), O1⋯O11 2.649(7), O1⋯O21 2.685(5), Ge–O31 2.278(3), Ge–O32 2.256(3), Ge–O33 2.354(3), Ge–O34 2.274(3), Ge–O35 2.363(3); Σ<sub>O1</sub> 355.
FT-IR spectra of the protio and deuterio (**Figure 2.3**) complexes clearly show the presence of H-bonded O–H and O–D stretches at 3458 and 1971 cm\(^{-1}\), respectively. Powder X-ray diffraction (pXRD) studies confirm that the only crystalline material present in the bulk samples is consistent with the single-crystal structures.

**Figure 2.3:** FT-IR spectrum of [Ge[15]crown-5•H\(_2\)O][OTf]\(_2\) (2.2[OTf]\(_2\)) (top) and [Ge[15]crown-5•D\(_2\)O][OTf]\(_2\) ([D\(_2\)]-2.2[OTf]\(_2\)) (bottom). * denotes peak of interest.

The \(^1\)H and \(^{13}\)C NMR spectra of 2.2[OTf]\(_2\) in CD\(_3\)CN contain resonances attributable to the crown ether at 4.02 ppm and 68.93 ppm, respectively. The resonance at 8.29 ppm in the proton NMR spectrum (which is D\(_2\)O-exchangeable) indicates that the protons of the water molecule have become considerably deshielded upon complexation given that the corresponding resonance for free water in the same solvent is 2.13 ppm. This change in chemical shift mirrors that observed for the complexation of H\(_2\)O to B(C\(_6\)F\(_5\))\(_3\) which increases the acidity of the water in both Brønsted and Lewis acid
The increased acidity of water upon complexation was confirmed through its deprotonation by the weak bases, N-methylimidazole, pyridine, and ammonia, which do not react (or react very weakly) with free water (see below).

The results of $^1$H diffusion ordered spectroscopy (DOSY) experiments in CD$_3$CN suggest that adduct 2.2[OTf]$_2$ is fluxional in solution given that the water and crown ether components diffuse at different rates. The measured diffusion constant of the water (Figure 2.4, peak H, ~8.3 ppm) is $10^{-8.3974}$ m$^2$s$^{-1}$ and that of the crown ether species (Figure 2.4, peak C, ~3.9 ppm) is $10^{-8.5521}$m$^2$s$^{-1}$, indicating that the water diffuses more rapidly than the Ge(II) crown ether fragment. Interestingly, the apparent diffusion constant of free water in CD$_3$CN is $10^{-8.4110}$ m$^2$s$^{-1}$, implying that the water in 2.2[OTf]$_2$ diffuses at essentially the same rate as free water.

![Figure 2.4](image.png)

**Figure 2.4**: 2D $^1$H DOSY spectrum of [Ge[15]crown-5•H$_2$O][OTf]$_2$ (2.2[OTf]$_2$) in CD$_3$CN at 20 °C where H = H$_2$O, C = crown ether.
Variable-temperature $^1$H NMR experiments of 2.2[OTf]$_2$ were also conducted. At the low temperature limit of -30 ºC, broad resonances corresponding to H$_2$O that range from 8.5-9.5 ppm are seen. With increasing temperature, the signals coalesce around -15 to -10 ºC and the broad peak sharpens, shifting upfield. These changes in the appearance and shift of the signal at 8.29 ppm corroborate the fluxional behaviour of the water complex. Furthermore, by varying the molar ratio of water to the crowned Ge(II) species, it was determined that the $^1$H NMR shift for the water resonates at the weighted average of the complexed and free values. This, too, is indicative of exchange that is rapid on the NMR timescale. While the addition of a small excess of water does not appear to degrade 2.2[OTf]$_2$, the addition of bulk amounts of water results in decomposition of the compound.

Figure 2.5: Variable-temperature $^1$H NMR spectrum of [Ge[15]crown-5•H$_2$O][OTf]$_2$ (2.2[OTf]$_2$) in CD$_3$CN where H = H$_2$O, C = crown ether. THF: 3.6 ppm (m); 1.8 ppm (m) is also present.
The isolation of a well-characterized water complex of Ge\textsuperscript{II} is remarkable and perhaps unexpected given the considerable reactivity exhibited by most divalent germanium compounds. As seen in Section 1.3, germynes have been noted for their tendency to undergo insertion into alkyl halide, alcohol, multiple bonds, among others. Of note is the hydrolysis of Roesky’s β-diketiminate chlorogermylene with a slight excess of water and one equivalent of NHC to generate the first fully characterized Ge(II) hydroxide (see Section 1.3.5).\textsuperscript{25} Similarly, Driess found that H\textsubscript{2}O and NH\textsubscript{3} undergo addition reactions with a related germylene to form analogous complexes.\textsuperscript{26} While, there are a handful of structurally authenticated Ge\textsuperscript{IV} water complexes, such species are very rare and all have GeO distances of less than 2 Å.\textsuperscript{27-31} Given the formation of this unique complex, the potential synthetic utility of 2.2[OTf]\textsubscript{2} is examined below.

2.2.2 Deprotonation of the Water Complex

The presence of potentially acidic hydrogen atoms on the water fragment in 2.2[OTf]\textsubscript{2} was confirmed through reactions with weak bases. Given that the dication 2.2 can be considered as a doubly protonated variant of “:Ge≡O:”,\textsuperscript{32} it is postulated that such deprotonation reactions may provide a new route for the preparation of new and potentially unsaturated main-group intermediates and compounds. In support of this conjecture, it is worth emphasizing that mass spectra of 2.2[OTf]\textsubscript{2} consistently reveal the presence of a major signal manifold corresponding to [Ge[15]crown-5-OH]\textsuperscript{+}, 2.3, which may be treated as a trapped singly-protonated germanium monoxide.\textsuperscript{33-38}

Although the preparation and characterization of the few germanium(II) hydroxides are well documented, germanium(II) oxide is not as well characterized.\textsuperscript{39} In
1930, Dennis and Hulse published a report wherein hydrous GeO was prepared by dissolving germanium dioxide in 5 M KOH, followed by addition of HCl, and then reduction by treatment with 30% H$_3$PO$_2$ at 95°C. for two hours. The anhydrous form was obtained by heating to 650 ºC, resulting in a black crystalline solid. Another synthetic method involves heating Ge and GeO$_2$ together at 1000 ºC to form a yellow sublimate. Given these harsh conditions, the deprotonation of the water adduct conducted at room temperature with milder reagents would provide a more convenient approach towards GeO and other unsaturated species.

Thus, in hopes of isolating the germanium hydroxide and monoxide, 2.2[OTf]$_2$ was treated with one and two molar equivalents of base, respectively. Both weak bases (NH$_3$, pyridine, and N-methylimidazole) and relatively strong bases (“proton sponge”, DBN, and N-heterocyclic carbenes) were used. For the majority of bases used, addition to the water adduct resulted in the immediate formation of a white precipitate which was subsequently collected through filtration. The precipitate proved difficult to characterize as an insoluble, amorphous material; however, SEM-EDS measurements indicated that Ge was present. Removal of solvent in vacuo of the colourless filtrate left a white residue which when characterized by $^1$H NMR showed resonances corresponding to the anticipated conjugate acid and conjugate base, confirming that deprotonation did occur. The residue was then washed with toluene, resulting in separation of the products as shown by $^1$H NMR (Figure 2.6, Figure 2.7). The conjugate acid, a white solid, was collected by filtration and work up of the filtrate resulted in a colourless oil containing the Ge crown ether product.
Figure 2.6: $^1$H NMR spectra of the reaction of $\text{2.2[OTf]}_2$ with one equivalent of $\text{N-methylimidazole (MeIm)}$ and subsequent separation of products in $\text{CD}_3\text{CN}$. DCM: 5.5 ppm (s) and toluene: 7.2 ppm (m); 2.3 ppm (s) are also present.

The $^1$H NMR spectra of the conjugate acids are as expected; resonances attributable to the acidic proton range from 8.5 to 19 ppm depending on the base used. From the mono-deprotonation reactions, the $^1$H NMR spectra of the conjugate base, $\text{2.3[OTf]}$, feature a broad resonance ranging from 8.5 to 11.5 ppm that corresponds to the OH proton. Given that the $\text{H}_2\text{O}$ peak (8.3 ppm) in $\text{2.2[OTf]}_2$ resonates at the weighted average between complexed and free values, this downfield shift suggests that the OH moiety is more strongly bound to the Ge centre. Also noted was the upfield shift of the
crown ether resonance to ~3.6 ppm which is close to free crown ether in CD$_3$CN. In the double deprotonation reactions, no peaks are observed in the water region which is expected.

![Diagram of the reaction](image)

**Figure 2.7:** $^1$H NMR spectra of the reaction of 2.2[OTf]$_2$ with two equivalents of proton sponge (base) and subsequent separation of products in CD$_3$CN. DCM: 5.5 ppm (s) and toluene: 7.2 ppm (m); 2.3 ppm (s) are also present.

Single crystals suitable for X-ray diffraction were obtained for the conjugate acids of proton sponge and \textit{iPrNHC}$^\text{Me}$. However, attempts to crystallize the germanium hydroxide and monoxide were unsuccessful. Instead, crystals of [Ge[15]crown-5][OTf]$_2$
were obtained, including a new polymorph (2.1*[OTf]₂) (Figure 2.8), or those of the water adduct. Trace amounts of the conjugate acid would be a plausible proton source.

**Figure 2.8**: Thermal ellipsoid plot (30% probability surface) of a polymorph of [Ge[15]crown-5][OTf]₂ (2.1*[OTf]₂) from a crystal with disordered refinement. Hydrogens have been removed for clarity.

### 2.2.3 Reactivity with Ammonia

Given the remarkable stability of the water complex, 2.2[OTf]₂, other simple element hydrides were investigated. Gratifyingly, the treatment of 2.1[OTf]₂ with a solution of NH₃ in dioxane results in the formation of a colorless compound for which there is evidence of complex formation (Scheme 2.2).

Although a single crystal structure for the compound has not yet been obtained, NMR, pXRD, FT-IR studies, and microanalysis confirm the formation of the proposed adduct. The FT-IR spectrum of the solid contains three broad peaks at 3250, 3200, and 3100 cm⁻¹ which correspond to N–H stretching modes (Figure 2.9). Additionally, the structure of the NH₃ adduct is anticipated to be isostructural to that of the H₂O adduct, as supported by their almost identical powder XRD patterns (Figure 2.10). Elemental analysis is consistent with a 1:1 adduct of [Ge[15]crown-5][OTf]₂ and NH₃.

Figure 2.9: FT-IR spectrum of [Ge[15]crown-5-NH₃][OTf]₂ (2.4[OTf]₂).
The $^1$H NMR spectrum of a CD$_2$Cl$_2$ solution of 2.4[OTf]$_2$ contains a signal at 8.54 ppm attributable to the protons of the coordinated amine; free NH$_3$ in the same solvent exhibits a singlet $^1$H NMR resonance at 0.43 ppm. The most intense signal in the $^{14}$N NMR spectrum in [D$_8$]-THF is a broad resonance at −72.2 ppm. It must be noted that the $^1$H NMR spectrum of the reaction mixture of [Ge[15]crown-5][OTf]$_2$ with a small excess of NH$_3$ in CD$_2$Cl$_2$ always features an additional minor 1:1:1 triplet signal at 6.15 ppm that is attributable to the coupling of the protons to the $^{14}$N ($I$=1; $^1J_{N-H}$=53.0 Hz) nucleus. The triplet resonance suggests the existence of [NH$_4^+$] cations in solution, and the additional minor pentet signals at about −361 ppm in the $^{14}$N and $^{15}$N NMR spectra confirm that assignment. The presence of [NH$_4^+$] indicates that the complexation (activation) of NH$_3$ by 2.1[OTf]$_2$ renders the protons sufficiently acidic to protonate other ammonia molecules.
In theory, removal of all three protons from 2.4 could produce the germanium analogue of cyanide. However, it should be noted that exposure of 2.1[OTf]₂ to a large excess of ammonia appears to result in the removal of the Ge from the crown ether and its replacement with an ammonium cation as evidenced by spectroscopy and the crystal structure of a related salt, [[18]crown-6-NH₄][GeBr₃]; alternative bases will be required in pursuit of salts of [:Ge≡N:]⁻.

![Figure 2.11: Thermal ellipsoid plot (30% probability surface) of [[18]crown-6-NH₄][GeBr₃].](image)

2.2.4 Computational Studies

Since the crystal structure for the adduct 2.4[OTf]₂ was not obtained, a series of density functional theory (DFT) calculations were performed to assess the likely structure of the complex. The computed structure of the water adduct 2.2' (where ' indicates the
geometry-optimized model structure of the indicated cation) (Figure 2.12a), reproduces the structure obtained experimentally quite accurately, so it is probable that the computed structure of the adduct 2.4’ (Figure 2.12b) is a reasonable model for the ammonia adduct. Furthermore, the calculated Ge–N bond of 2.0988 Å is consistent with that reported for the only structure with a Ge$^{II}$–NH$_3$ linkage (2.093(4)–2.107(4) Å), which was obtained unexpectedly from the decomposition of a Ge$^{II}$-N(SiMe$_3$)$_2$ precursor.$^{41,42}$ Geometry-optimized models were also calculated for the hydroxide (Figure 2.12c) and amine (Figure 2.12d) complexes for comparison.

**Figure 2.12**: Ball-and-stick representations of geometry-optimized model complexes, including: a) an overlay of the computed structure of [Ge[15]crown-5-H$_2$O]$^{2+}$ 2.2’ (—) and 2.2 (---) (most hydrogen atoms have been removed for clarity); b) the model complex [Ge[15]crown-5-NH$_3$]$^{2+}$ 2.4’; c) [Ge[15]crown-5-OH]$^+$ 2.3’; and d) [Ge[15]crown-5-NH$_2$]$^+$ 2.5’.
Table 2.1: Selected properties for model ions 2.2', 2.3', 2.4', and 2.5' calculated using the M062X/TZVP DFT method.

<table>
<thead>
<tr>
<th></th>
<th>2.2'</th>
<th>2.3'</th>
<th>2.4'</th>
<th>2.5'</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{\text{Ge-E}}$ [Å]</td>
<td>2.1057</td>
<td>1.8386</td>
<td>2.0988</td>
<td>1.8736</td>
</tr>
<tr>
<td>$Q_{\text{Ge}}$[a]</td>
<td>1.495</td>
<td>1.425</td>
<td>1.406</td>
<td>1.331</td>
</tr>
<tr>
<td>$Q_{\text{E}}$[a]</td>
<td>-0.974</td>
<td>-1.234</td>
<td>-1.099</td>
<td>-1.436</td>
</tr>
<tr>
<td>$Q_{\text{H(avg.)}}$[a]</td>
<td>0.541</td>
<td>0.492</td>
<td>0.424</td>
<td>0.387</td>
</tr>
<tr>
<td>WBI$_{\text{Ge-E}}$[b]</td>
<td>0.2178</td>
<td>0.4499</td>
<td>0.3465</td>
<td>0.5797</td>
</tr>
<tr>
<td>$\rho_{\text{crit(Ge-E)}}$[c]</td>
<td>0.0631</td>
<td>0.1222</td>
<td>0.0784</td>
<td>0.1257</td>
</tr>
<tr>
<td>$E_{\text{Ge-E, snap}}$[g]</td>
<td>129.46[e]</td>
<td>448.35[f]</td>
<td>182.94[e]</td>
<td>370.19[f]</td>
</tr>
<tr>
<td>$\Delta E_{\text{reaction}}$[h]</td>
<td>-106.99</td>
<td>-1141.44</td>
<td>-148.22</td>
<td>-1160.21</td>
</tr>
</tbody>
</table>


Having determined that the geometry optimized structures are reasonable models, calculations using these models were performed to ascertain the nature of bonding between the germanium and water, ammonia, and their deprotonated variants. The results of these calculations have been summarized in Table 2.1. In Natural Bond Orbital (NBO) analyses, molecular orbitals are transformed into the more intuitive, localised natural orbitals which reflect Lewis-like bonding structures (i.e. $\sigma$ and $\pi$ bonds, lone pairs). Doing so allows us to quantify where electron density resides in terms of atomic charges, orbital interactions, and bond orders, among other properties. Based on the calculated charges, the deprotonated variants 2.3' and 2.5' feature polar Ge–E single bonds;
whereas, the donor and acceptor fragments are regarded as separate in 2.2' and 2.4'. Moreover, in each model compound, the charges of the H-atoms in the complexed form are larger than those calculated for models of H₂O (0.457) and NH₃ (0.331). This is consistent with the observed deshielding of the ¹H NMR signals upon complexation for the water, ammonia, and hydroxide complexes. Also calculated were the Wiberg Bond Indices (WBI) to assess the degree of covalent bonding between Ge and E. Referring to Table 2.1, the relatively larger WBI values for 2.3' and 2.5' also suggest that their Ge–E bonds are more covalent in nature than in the dicationic complexes 2.2' and 2.4'.

This notion is further supported by Atoms in Molecules (AIM) analyses and bond cleavage/snapping energies. The former is concerned with bond critical points which represent a minimum in the electron density between two atoms. The electron density at this point, \( \rho_{\text{crit}} \), is also a very good indicator of bond order and strength. Examination of the \( \rho_{\text{crit}} \) values of these models shows that 2.2' and 2.4' have relatively little electron density in comparison to 2.3' and 2.5'. The increase in the electron density at the bond critical points going from the dications to the monocations and the nature of the BCPs are consistent with increased covalent bonding between the elements.

In bond cleavage, the energy required to break the Ge–E bond both homolytically and heterolytically is calculated to determine which is more favourable. Using Haaland’s approach, a covalent bond is one in which the energy of homolytic bond cleavage is lower than that of heterolytic bond cleavage and a dative bond is indicated by a more favorable heterolytic cleavage. Again, results are consistent with dative bonding in 2.2' and 2.4' and covalent bonding in 2.3' and 2.5'. A related concept to bond cleavage is that of bond snapping energy, which is the negative energy difference between a compound
and the non-relaxed fragments obtained by the cleavage of the bond in question.\textsuperscript{46} Simply put, the fragments after bond cleavage have the exact same geometries as they had in the bonded compound. This quantity thus provides an estimate of how much energy is required to actually break the bond. Covalent bonds are stronger than dative bonds and will have larger bond snapping energies; this is reflected in the data for these model complexes.

Lastly, gas phase reaction energies for the combining of a donor and acceptor to a form a complex were calculated. These energies were obtained by comparing the energies of the optimized donor and acceptor fragments with that of the resulting complex. Formation of all four complexes is exergonic with formation of the deprotonated models \(2.3'\) and \(2.5'\) much more energetically favourable.

Interestingly, it is worth noting that calculated energies for the putative oxidative addition products \([\text{H–Ge–OH}·[15]\text{crown-5}]^{2+}\) \((2.6')\) and \([\text{H–Ge–NH}_2·[15]\text{crown-5}]^{2+}\) \((2.7')\) are found to be less stable than \(2.2'\) and \(2.4'\) by about 13 kJ mol\(^{-1}\) and 57 kJ mol\(^{-1}\), respectively. The uncrowned system favours Ge\(^{II}\) over Ge\(^{IV}\) to a greater extent and illustrates the effect of crown ether ligation. The relative favourability of the \([\text{GeOH}_2]^{2+}\) tautomer over the \([\text{HGeOH}]^{2+}\) form can be rationalized in terms of the Ge–H versus O–H bond strengths and the proton affinities of \([\text{GeOH}]^+\) for protonation at the Ge and O atoms. In the former case, the O–H bond is stronger and in the latter case, protonation is more favourable at O, all of which contribute to the greater stability of \([\text{GeOH}_2]^{2+}\), especially in the absence of an auxiliary ligand (e.g. crown ether) to destabilize the Ge “lone pair”.\textsuperscript{47} Finally, the relatively small energy difference between
2.2′ and 2.6′ suggests that variants of the ligated Ge´ tautomer might be accessible experimentally.

Overall, the computational data indicate that the dicationic adducts 2.2′ and 2.4′ are best described as donor-acceptor complexes held together by longer and weaker dative bonds, while the deprotonated model complexes 2.3′ and 2.5′ feature considerably shorter and stronger covalent Ge–E bonds. Moreover, comparison of the model water adduct with the ammonia adduct reveals that the latter is expected to have a much stronger Ge–E bond as is anticipated on the basis of relative basicities of NH₃ and OH₂. These calculations also suggest that deprotonation of these readily made element hydride adducts is a viable approach to new covalently bonded species.

2.2.5 Reactivity with Alcohols and Amines

Given the relative ease with which crowned Ge(II) systems form adducts with water and ammonia, their reactivity towards the organic analogues, alcohols and amines, were investigated. Of interest are primary or secondary alcohols and amines for ease of characterization. Preliminary studies show that complexation does occur as assessed by ¹H NMR experiments where one molar equivalent of alcohol or amine was added to a NMR sample of 2.1[OTf]₂ in CD₃CN.

In summary, much like the water and ammonia adducts, the hydroxyl and amine proton resonances exhibit a downfield shift in the presence of 2.1[OTf]₂ compared to the free alcohol and amine in the same solvent (Table 2.2). Moreover, it is expected that this downfield shift also corresponds to an increase in the acidity of the alcohol or amine as it does for water and ammonia. In regard to the amine complexes, the presence of a 1:1:1
triplet signal at ~6.6 ppm – corresponding to the appropriate alkylammonium species – confirms this. It should be noted that all the major $^1$H NMR resonances are assigned to the soluble alkylammonium salt; the addition of amine results in a yellow or off-white product precipitating from solution which is anticipated to be the desired amine complex.

**Table 2.2: $^1$H NMR (500 MHz, CD$_3$CN) Chemical Shifts of Hydroxyl and Amine Protons**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Free substrate (ppm)</th>
<th>Complexed substrate (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>2.16</td>
<td>5.36</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2.47</td>
<td>5.68</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>2.83</td>
<td>7.24</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>3.27</td>
<td>7.42</td>
</tr>
<tr>
<td>1-Hexanol</td>
<td>2.81</td>
<td>7.42</td>
</tr>
<tr>
<td>Isopropylamine</td>
<td>1.08</td>
<td>8.74</td>
</tr>
<tr>
<td>tert-Butylamine</td>
<td>1.24</td>
<td>8.80</td>
</tr>
<tr>
<td>Diethylamine</td>
<td>0.88</td>
<td>8.03</td>
</tr>
<tr>
<td>Diisopropylamine</td>
<td>0.65</td>
<td>7.89</td>
</tr>
</tbody>
</table>

Additionally, fluxional behaviour is also expected for these complexes as assessed by $^1$H DOSY and VT-NMR experiments. In the $^1$H DOSY spectrum for the addition of one equivalent of ethanol to 2.1[OTf]$_2$ in CD$_3$CN, the measured diffusion constants of ethanol and the crown ether fragment are $10^{-8.6253}$ m$^2$s$^{-1}$ and $10^{-8.8974}$ m$^2$s$^{-1}$, respectively, indicating that ethanol diffuses more rapidly. Additionally, the behaviour in the $^1$H VT-NMR experiment mirrors that of the water adduct where the OH resonance sharpens and shifts upfield as the temperature increases. Given the similar deshielding of the hydroxyl
and amine proton resonances of the other substrates in the presence of 2.1[OTf]₂, it suggests that the fluxional behaviour is a feature of these complexes as well.

Unfortunately, attempts to isolate both the alcohol and amine complexes by increasing the scale of the reaction were unsuccessful. In the case of the former, removal of solvent in vacuo also resulted in the removal of alcohol as determined by the ¹H NMR, suggesting that the alcohol was not strongly bound to the Ge centre. In the latter case, removal of solvent yielded an insoluble oily residue which was difficult to characterize. Further work is required to optimize the synthesis and isolation of these adducts but preliminary results are promising.

2.3 Conclusions

Overall, it was discovered that crown ether stabilized germanium(II) triflate can be used to produce remarkably stable complexes of water and ammonia which have been characterized by multinuclear NMR, FT-IR, microanalysis, X-ray diffraction, and DFT calculations. It was observed that the acidity of the water and ammonia increased upon complexation. The synthetic potential of these complexes is currently being pursued, including further studies with the organic analogues and deprotonated variants, and new studies involving catalysis by O–H and N–H activation, and their role as material precursors.
2.4 Experimental

2.4.1 Reagents and General Methods

All manipulations were carried out under an anhydrous N₂ atmosphere using standard Schlenk line, glovebox and glovebag techniques at room temperature. Solvents were dried by passing through Grubbs'-type alumina columns and then stored over 4 Å molecular sieves. CD₃CN and C₆D₆ were distilled over CaH₂ and then stored over 4 Å molecular sieves. H₂O and D₂O were stored under oxygen-free conditions. Alcohols were distilled over CaO and stored over 4 Å molecular sieves. [Ge[15]crown-5][OTf]₂ (2.1[OTf]₂) was synthesized according to literature procedures. All other chemicals were purchased from commercial sources and used without further purification. Yields were not recorded for NMR reactions or for reactions where the product was an oily residue.

All NMR spectra were collected at room temperature (unless otherwise stated) using Bruker Avance 300 MHz and 500 MHz spectrometers and chemical shifts are reported in ppm. The resonances in the ¹H and ¹³C NMR spectra were referenced to SiMe₄ using appropriate solvent resonances as internal standards. The ¹⁹F NMR spectra were referenced externally to CFCl₃ (0 ppm) and ¹⁴N and ¹⁵N NMR spectra were referenced externally to MeNO₂ (0 ppm). ¹H DOSY experiments were carried out using the longitudinal eddy current delay with bipolar gradient pulse pair and two spoil gradients (ledbpgp2s) pulse program. Gradient strength was varied from 5 to 95% in 32 linear increments with 16 scans per increment. The diffusion time (Δ) and diffusion
gradient length (δ) were held constant at 25 ms and 4.4 ms, respectively. The data was processed using Topspin 2.1.

Elemental analysis was performed at University of Windsor, Ontario, Canada and Atlantic Microlab Inc., Atlanta, USA. Mass Spectra were recorded at the McMaster Regional Mass Spectrometry Facility. FT-IR spectra of the bulk material are reported in \( \text{cm}^{-1} \) and were collected as Nujol mulls between KBr plates using a Bruker Vector22 spectrometer. Melting points were determined under a \( \text{N}_2 \) atmosphere and are uncorrected.

2.4.2 Synthetic Procedures

2.4.2.1 General Synthetic Procedure of \([\text{Ge}[15]\text{crown}-5][\text{OTf}]_2\) with Element Hydrides and Deuterides

The element hydride or deuteride was added via micropipette to a colourless solution of \(\text{2.1[OTf]}_2\) in \(\text{CH}_2\text{Cl}_2\) (30 mL). The reaction mixture was stirred overnight at room temperature after which a white precipitate was formed. All volatile components were removed under reduced pressure. The resultant white solid was dissolved in \(\text{CH}_2\text{Cl}_2\) and slow evaporation of the solvent afforded a colorless crystalline material.

**Synthesis of \([\text{Ge}[15]\text{crown}-5\cdot\text{H}_2\text{O}][\text{OTf}]_2, \text{2.2[OTf]}_2\)**

Water (4.0 \(\mu\text{L}, 0.222 \text{ mmol}) and \(\text{2.1[OTf]}_2\) (131 mg, 0.222 mmol) yielded a white solid. Recrystallization from \(\text{CH}_2\text{Cl}_2\) afforded single crystals suitable for X-ray diffraction. Yield: 80\% (108 mg, 0.177 mmol). \(^1\text{H NMR (CD}_3\text{CN)}: 8.29 \text{ (s, 2H, OH)}; 3.99 \text{ (s, 20H, CH}_2\text{).} \(^{13}\text{C}\{^1\text{H}\} \text{ NMR (CD}_3\text{CN)}: 121.8 \text{ (q, 2C, CF}_3\text{SO}_3\text{, }^{1}J_{\text{CF}} = 320.5 \text{ Hz;}}\)
69.9 (s, 10C, CH₂). ¹⁹F{¹H} NMR (CD₃CN): -78.8 (s, 6F, CF₃SO₃). M.P.: 140 – 145 °C. FT-IR (Nujol): O-H = 3456 cm⁻¹. Anal. Calcd. for C₁₂H₂₀O₁₂GeF₆S₂: C, 23.66; H, 3.64; Found: C, 22.46; H, 4.22. LRMS: [Ge(C₁₀H₂₀O₅)OH(H₂O)]⁺ = m/z 325-332 and [Ge(C₁₀H₂₀O₅)OH]⁺ = m/z 307-314


D₂O (4.0 µL, 0.224 mmol) and 2.1[OTf]₂ (132 mg, 0.224 mmol) yielded a white solid. Recrystallization from CH₂Cl₂ afforded single crystals suitable for X-ray diffraction. Yield: 80% (109 mg, 0.178 mmol). ¹H NMR (CD₃CN): 4.01 (s, 20 H CH₂).


Ammonia (0.5 M) in dioxane (338 µL, 0.169 mmol) and 2.1[OTf]₂ (100 mg, 0.169 mmol) yielded a white solid that was modestly soluble in CH₂Cl₂ or CH₃CN but soluble in THF. The product was characterized by pXRD. Yield: 77% (79 mg, 0.129 mmol). ¹H NMR (THF-d₈): 12.91 (s(br), 3H, NH₃); 3.60 (s, 20H, CH₂). ¹H NMR (CD₂Cl₂): 8.54 (s(br), 3H, NH₃); 3.89 (s, 20H, CH₂). ¹H NMR (CD₃CN): 9.48 (s(br), 3H, NH₃); 3.99 (s, 20H, CH₂). ¹³C{¹H} NMR (THF-d₈): 121.4 (q, 2C, CF₃SO₃, ¹JC-F = 319.4 Hz); 71.6 (s, 10C, CH₂). ¹³C{¹H} NMR (CD₃CN): 121.4 (q, 2C, CF₃SO₃, ¹JC-F = 319.4 Hz); 68.9 (s, 10H, CH₂). ¹⁴N NMR (THF-d₈): -72.2 (s(br), 1N, NH₃, w₁/₂ 22.8 Hz). ¹⁹F{¹H} NMR (THF-d₈): -79.5 (s, 6F, CF₃SO₃) (¹³C satellites: d, ¹JC-F = 318.1 Hz). ¹⁹F NMR (CD₃CN): -80.0 (s, 6F, CF₃SO₃). M.P.: 180 – 185 °C. FT-IR (Nujol): N-H = 3250,
3200, 3100 cm\(^{-1}\). Anal. Calcd. for C\(_{12}\)H\(_{23}\)O\(_{11}\)GeF\(_6\)S\(_2\)N: C, 23.70; H, 3.81, N, 2.30. Found: C, 22.72; H, 3.16; N, 1.97.

2.4.2.2 Synthetic Procedures for the Deprotonation of [Ge[15]crown-5·H\(_2\)O][OTf]\(_2\)

**Mono-deprotonation of 2.2[OTf]\(_2\) by N-methylimidazole**

N-Methylimidazole (13.1 µL, 0.164 mmol) was added to a colourless solution of 2.2[OTf]\(_2\) (100 mg, 0.164 mmol) in CH\(_2\)Cl\(_2\) (50 mL) by micropipette. A white precipitate formed immediately. The reaction was stirred at room temperature for 2 hours, after which the precipitate was collected by filtration. Removal of all volatiles from the filtrate under reduced pressure left a white residue which was then washed with toluene (40 mL). A second white precipitated was collected and characterized as the conjugate acid by \(^1\)H NMR. Removal of all volatiles from the filtrate under reduced pressure yielded a colourless oil which contained the crown ether fragment as assessed by \(^1\)H NMR.

[MeImH][OTf]: \(^1\)H NMR (CD\(_3\)CN): 11.72 (t(br), 1H, N(3)H, \(^1\)J\(_{NH}\) 66.51 Hz); 8.47 (s, 1H, N(1)-CH-N(3)); 7.40 (s, 1H, CH); 7.35 (s, 1H, CH); 3.83 (s, 3H, N(1)-CH\(_3\)). \(^1\)N NMR (THF): -206 (s(br), 1N, NH\(_3\)).

[GeOH[15]crown-5][OTf]: \(^1\)H NMR (CD\(_3\)CN): 11.46 (s(br), 1H, OH); 3.64 (s, 20H, CH\(_2\)).

**Mono-deprotonation of 2.2[OTf]\(_2\) by pyridine**

Pyridine (13.3 µL, 0.164 mmol) was added to a colourless solution of 2.2[OTf]\(_2\) (100 mg, 0.164 mmol) in CH\(_2\)Cl\(_2\) (50 mL) by micropipette. A white precipitate formed immediately. The reaction was stirred at room temperature for 2 hours, after which the
precipitate was collected by filtration. Removal of all volatiles from the filtrate under reduced pressure left a white residue which was then washed with toluene (40 mL). A second white precipitate was collected and characterized as the conjugate acid by $^1$H NMR. Removal of all volatiles from the filtrate under reduced pressure yielded a colourless oil which contained the crown ether fragment as assessed by $^1$H NMR.

[PyH][OTf]: $^1$H NMR (CD$_3$CN): 13.53 (t, 1H, NH, $^1$J$_{NH}$ = 67.12 Hz); 8.74 (m, 2H, C(2,6)-H); 8.62 (m, 1H, C(4)-H); 8.06 (m, 2H, C(3,5)-H).

[GeOH[15]crown-5][OTf]: $^1$H NMR (CD$_3$CN): 11.13 (s(br), 1H, OH); 3.64 (s, 20H, CH$_2$).

**Mono-deprotonation of 2.2[OTf]$_2$ by proton sponge**

A colourless solution of proton sponge (44 mg, 0.205 mmol) in CH$_2$Cl$_2$ (25 mL) was added to a colourless solution of 2.2[OTf]$_2$ (125 mg, 0.205 mmol) in CH$_2$Cl$_2$ (25 mL). A white precipitate formed immediately. The reaction was stirred overnight at room temperature, after which the precipitate was collected by filtration. Removal of all volatiles from the filtrate under reduced pressure left a white residue which was then washed with toluene (40 mL). A second white precipitate was collected and characterized as the conjugate acid by $^1$H NMR. Removal of all volatiles from the filtrate under reduced pressure yielded a colourless oil which contained the crown ether fragment as assessed by $^1$H NMR. Recrystallization by slow evaporation of a solution of [BaseH][OTf] in CH$_2$Cl$_2$ afforded crystals suitable for X-ray diffraction.
Mono-deprotonation of 2.2[OTf]$_2$ by $i$Pr$_2$NHC$^\text{Me}$

A very pale yellow solution of $i$Pr$_2$NHC$^\text{Me}$ (30 mg, 0.164 mmol) in THF (25 mL) was added to a colourless solution of 2.2[OTf]$_2$ (100 mg, 0.164 mmol) in THF (25 mL). The resulting pale yellow solution was stirred overnight at room temperature. No change was observed. Removal of all volatiles under reduced pressure afforded a yellow oily residue which contained both conjugate acid and base. Recrystallization by slow evaporation of the oil in THF afforded crystals of the conjugate acid suitable for X-ray diffraction.

$[i$Pr$_2$NHC$^\text{Me}$H][OTf]: $^1$H NMR (CD$_3$CN): 8.45 (s, 1H, CH$^+$); 4.50 (sept, 2H, N(1,3)CH(CH$_3$)$_2$, $^3J_{CH} = 6.67$ Hz); 2.24 (s, 6H, C(4,5)-CH$_3$); 1.50 (d, 12H, N(1,3)CH(CH$_3$)$_2$, $^3J_{CH} = 6.67$ Hz).

[GeOH[15]crown-5][OTf]: $^1$H NMR (CD$_3$CN): 8.55 (s(br), 1H, OH); 3.76 (s, 20H, CH$_2$).

Double-deprotonation of 2.2[OTf]$_2$ by N-methylimidazole

N-Methylimidazole (26.2 μL, 0.328 mmol) and 2.2[OTf]$_2$ (100 mg, 0.164 mmol) in CH$_2$Cl$_2$ (50 mL) yielded a white solid, [MeImH][OTf], and colourless oil, “GeO[15]crown-5”, using the same procedure as in the mono-deprotonation reaction.
[MeImH][OTf]: $^1$H NMR (CD$_3$CN): 11.62 (t(br), 1H, N(3)-H, $^1$J$_{NH}$ = 66.51 Hz); 8.41 (s, 1H, N(1)-CH-N(3)); 7.35 (s, 1H, CH); 7.33 (s, 1H, CH); 3.85 (s, 3H, N(1)-CH$_3$).


**Double-deprotonation of 2.2[OTf]$_2$ by pyridine**

Pyridine (26.6 μL, 0.328 mmol) and 2.2[OTf]$_2$ (100 mg, 0.164 mmol) in CH$_2$Cl$_2$ (50 mL) yielded a white solid, [PyH][OTf], and colourless oil, “GeO[15]crown-5”, using the same procedure as in the mono-deprotonation reaction.

[PyH][OTf]: $^1$H NMR (CD$_3$CN): 13.56 (t, 1H, NH, $^1$J$_{NH}$ = 67.12 Hz); 8.76 (m, 2H, C(2,6)-H); 8.58 (m, 1H, C(4)-H); 8.03 (m, 2H, C(3,5)-H).


**Double-deprotonation of 2.2[OTf]$_2$ by proton sponge**

Proton sponge (70 mg, 0.328 mmol) and 2.2[OTf]$_2$ (100 mg, 0.164 mmol) in THF (50 mL) yielded a white solid, [BaseH][OTf], and colourless oil, “GeO[15]crown-5”, using the same procedure as in the mono-deprotonation reaction.

[BaseH][OTf]: $^1$H NMR (CD$_3$CN): 18.70 (s, 1H. NH); 8.05 (m, 2H, H$_{ar}$); 7.90 (m, 2H, H$_{ar}$); 7.72 (m, 2H, H$_{ar}$); 3.11 (s, 12H, N-CH$_3$)

2.4.2.3 General Procedure for NMR Experiments of [Ge[15]crown-5][OTf]2 with Alcohols and Amines

One equivalent of alcohol or amine was added via micropipette to an NMR sample of 2.1[OTf]2 in CD3CN. The reaction mixture was sonicated at room temperature for 30 minutes after which the NMR experiments were run.

**NMR data for the reaction of 2.1[OTf]2 with methanol**

Methanol (3.4 μL, 0.085 mmol) and 2.1[OTf]2 (50 mg, 0.085 mmol) yielded a colourless solution. $^1$H NMR (CD3CN): 5.36 (s(br), 1 H, OH); 4.03 (s, 20H, CH2); 3.41 (s, 3H, CH3OH). $^{13}$C{$^1$H} NMR (CD3CN): 121.53 (q, 2C, CF3SO3, $^1$JCF = 319.5 Hz); 70.3 (s, 10C, CH2); 51.27 (s, 1C, CH3OH). $^{19}$F{$^1$H} NMR (CD3CN): -79.6 (s, 6F, CF3SO3).

**NMR data for the reaction of 2.1[OTf]2 with ethanol**

Ethanol (4.9 μL, 0.085 mmol) and 2.1[OTf]2 (50 mg, 0.085 mmol) yielded a colourless solution. $^1$H NMR (CD3CN): 5.68 (s(br), 1H, OH); 4.01 (s, 20H, CH2); 3.69 (q, 2H, C(1)-H, $^3$JHH = 7 Hz); 1.18 (t, 3H, C(2)-H, $^3$JHH = 7 Hz). $^{13}$C{$^1$H} NMR (CD3CN): 121.54 (q, 2C, CF3SO3, $^1$JCF = 319.5 Hz); 70.3 (s, 10C, CH2); 59.52 (s, 1C, C(1)); 17.93 (s, 1C, C(2)). $^{19}$F{$^1$H} NMR (CD3CN): -79.5 (s, 6F, CF3SO3).

**NMR data for the reaction of 2.1[OTf]2 with 1-propanol**

1-Propanol (6.3 μL, 0.085 mmol) and 2.1[OTf]2 (50 mg, 0.085 mmol) yielded a colourless solution. $^1$H NMR (CD3CN): 7.24 (s(br), 1H, OH); 3.99 (s, 20H, CH2); 3.63 (t, 2H, C(1)-H, $^3$JHH = 6.5 Hz); 1.57 (qt, 2H, C(2)-H, $^3$JHH = 7.5 Hz, 6.5 Hz); 0.91 (t, 3H, C(3)-H, $^3$JHH = 7.5 Hz). $^{13}$C{$^1$H} NMR (CD3CN): 121.52 (q, 2C, CF3SO3, $^1$JCF = 319.5 Hz).
Hz); 70.3 (s, 10C, CH₂); 65.87 (s, 1C, C(1)); 25.65 (s, 1C, C(2)); 10.39 (s, 1C, C(3)).

\(^{19}\text{F}\{^1\text{H}\} \text{NMR (CD}_3\text{CN): -79.9 (s, 6F, CF}_3\text{SO}_3\}.

**NMR data for the reaction of 2.1[OTf]₂ with 1-pentanol**

1-Pentanol (9.2 μL, 0.085 mmol) and 2.1[OTf]₂ (50 mg, 0.085 mmol) yielded a colourless solution. \(^1\text{H NMR (CD}_3\text{CN): 7.42 (s(br),1H, OH); 3.99 (s, 20H, CH}_2\); 3.68 (t, 2H, C(1)-H, \(^3\text{J}_\text{HH} = 6.75 \text{ Hz}); 1.56 (p, 2H, C(2)-H, \(^3\text{J}_\text{HH} = 7.5 \text{ Hz}); 1.33 (m, 4H, C(3,4)-H); 0.91 (t, 3H, C(5)-H, \(^3\text{J}_\text{HH} = 7.5 \text{ Hz}). \(^{13}\text{C}\{^1\text{H}\} \text{NMR (CD}_3\text{CN): 121.53 (q, 2C, CF}_3\text{SO}_3\), \(^1\text{J}_{\text{CF}} = 319.6 \text{ Hz}); 70.08 (s, 10C, CH₂); 64.26 (s, 1C, C(1)); 32.21 (s, 1C, C(2)); 28.58 (s, 1C, C(3)-H); 23.12 (s, 1C, C(4)); 14.32 (s, 1C, C(5)). \(^{19}\text{F}\{^1\text{H}\} \text{NMR (CD}_3\text{CN): -79.5 (s, 6F, CF}_3\text{SO}_3\}.

**NMR data for the reaction of 2.1[OTf]₂ with 1-hexanol**

1-Hexanol (10.6 μL, 0.085 mmol) and 2.1[OTf]₂ (50 mg, 0.085 mmol) yielded a colourless solution. \(^1\text{H NMR (CD}_3\text{CN): 7.42 (s(br),1H, OH); 3.99 (s, 20H, CH}_2\); 3.68 (t, 2H, C(1)-H, \(^3\text{J}_\text{HH} = 6.5 \text{ Hz}); 1.55 (p, 2H, C(2)-H, \(^3\text{J}_\text{HH} = 7 \text{ Hz}); 1.31 (m, 6H, C(3,4,5)-H); 0.91 (t, 3H, C(6)H, \(^3\text{J}_\text{HH} = 7 \text{ Hz}). \(^{13}\text{C}\{^1\text{H}\} \text{NMR (CD}_3\text{CN): 121.52 (q, 2C, CF}_3\text{SO}_3\), \(^1\text{J}_{\text{CF}} = 319.2 \text{ Hz}); 70.08 (s, 10C, CH₂); 64.22 (s, 1C, C(1)); 32.38 (s, 1C, C(2)); 32.28 (s, 1C, C(3)); 26.05 (s, 1C, C(4)); 23.33 (s, 1C, C(5)); 14.33 (s, 1C, C(6)). \(^{19}\text{F}\{^1\text{H}\} \text{NMR (CD}_3\text{CN): -79.7 (s, 6F, CF}_3\text{SO}_3\).
NMR data for the reaction of 2.1[OTf]2 with isopropylamine

Isopropylamine (7.2 μL, 0.085 mmol) and 2.1[OTf]2 (50 mg, 0.085 mmol) yielded a yellow mixture. 1H NMR (CD3CN): 8.74 (s(br), 2H, NH2; 6.62 (t, 3H, RNH3+, 1JNH = 51.5 Hz); 3.85 (s, 20H, CH2); 3.44 (septet, 1H, CH, 3JHH = 6.5 Hz); 1.30 (d, 6H, CH3, 3JHH = 6.5 Hz). 13C{1H} NMR (CD3CN): 121.72 (q, 2C, CF3SO3, 1JCF = 319.6 Hz); 69.8 (s, 10C, CH2); 46.01 (s, 1C, CH); 20.67 (s, 2C, CH3). 19F{1H} NMR (CD3CN): -79.5 (s, 6F, CF3SO3).

NMR data for the reaction of 2.1[OTf]2 with t-butyramine

t-Butoxyamine (8.9 μL, 0.085 mmol) and 2.1[OTf]2 (50 mg, 0.085 mmol) yielded a yellow mixture. 1H NMR (CD3CN): 8.80 (s(br), 2H, NH2; 6.74 (t, 3H, RNH3+, 1JNH = 50.5 Hz); 3.89 (s, 20H, CH2); 1.35 (s, 9H, CH3). 13C{1H} NMR (CD3CN): 121.69 (q, 2C, CF3SO3, 1JCF = 319.3 Hz); 70.08 (s, 10C, CH2); 48.45 (s, 1C, C), 28.93 (s, 3C, CH3). 19F{1H} NMR (CD3CN): -79.8 (s, 6F, CF3SO3).

NMR data for the reaction of 2.1[OTf]2 with diethylamine

Diethylamine (8.8 μL, 0.085 mmol) and 2.1[OTf]2 (50 mg, 0.085 mmol) yielded a white mixture. 1H NMR (CD3CN): 8.03 (s(br), 1H, NH(CH2CH3)2); 6.82 (t, 2H, NH2(CH2CH3)2+, 1JNH = 50 Hz); 3.73 (s, 20H, CH2); 3.06 (sextet, 4H, CH2, 3JHH = 7 Hz); 1.24 (t, 6H, CH3), 3JHH = 7 Hz). 13C{1H} NMR (CD3CN): 121.83 (q, 2C, CF3SO3, 1JCF = 319.2 Hz); 70.17 (s, 10C, CH2); 42.82 (s, 2C, CH2); 11.03 (s, 2C, CH3). 19F{1H} NMR (CD3CN): -79.7 (s, 6F, CF3SO3).
**NMR data for the reaction of 2.1[OTf]2 with diisopropylamine**

Diisopropylamine (12 μL, 0.085 mmol) and 2.1[OTf]2 (50 mg, 0.085 mmol) yielded a yellow mixture. \(^1\)H NMR (CD\(_3\)CN): 7.89 (s(br), 1H, NH); 6.62 (t, 2H, NH\(_2\)R\(_2^+\), \(^1\)J\(_{\text{NH}}\) = 49 Hz); 3.80 (s, 20H, CH\(_2\)); 3.47 (septet, 2H, CH, \(^3\)J\(_{\text{HH}}\) = 6.5 Hz); 1.30 (d, 12H, CH\(_3\), \(^3\)J\(_{\text{HH}}\) = 6.5 Hz). \(^1\)C\(^{\text{\text{1}}}\)H NMR (CD\(_3\)CN): 121.89 (q, 2C, CF\(_3\)SO\(_3\), \(^1\)J\(_{\text{CF}}\) = 330 Hz); 70.03 (s, 10C, CH\(_2\)); 49.12 (s, 2C, CH); 19.10 (s, 4C, CH\(_3\)). \(^19\)F\(^{\text{\text{1}}}\)H NMR (CD\(_3\)CN): -79.7 (s, 6F, CF\(_3\)SO\(_3\)).

**2.4.3 SEM/EDS**

SEM/EDS analysis was conducted at the Great Lakes Institute for Environmental Research at the University of Windsor. Samples were observed under a FEI Quanta 200 FEG microscope and analyzed with an EDAX SDD detector using TEAM software. Samples were mounted on carbon tape and positioned at a working distance of 10 mm. EDS spot analysis of the white residue was conducted with an accelerating voltage of 12 kV and a collection time of 30 s.

![SEM micrograph of the residue obtained from the addition of one equivalent of MeIm to 2.2[OTf]2.](image)

**Figure 2.13:** SEM micrograph of the residue obtained from the addition of one equivalent of MeIm to 2.2[OTf]2.
Table 2.3: Atomic Percentages from EDS Spot Analysis

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<th>Spot</th>
<th>C</th>
<th>O</th>
<th>F</th>
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<th>S</th>
<th>Ge</th>
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<td>21.67</td>
<td>16.96</td>
<td>1.25</td>
<td>3.4</td>
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<td>3</td>
<td>31.09</td>
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<td>4</td>
<td>38.39</td>
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<td>38.48</td>
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<td>29.12</td>
<td>1.02</td>
<td>1.74</td>
<td>13.03</td>
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</table>

The high percentage of carbon is due to the carbon tape on which the sample was placed, although crown ether may be present. Examining spots 1, 4, and 6, Ge and O exist approximately in a 1:1 ratio, which suggests that the white residue may be GeO. Spots 3 and 5 deviate from this ratio; however, these spots also feature rather high percentages of Si in the form of silica, which appears white on the SEM micrograph. The source of this impurity is the fritted glass filter used to collect the sample. Taking into account the amount of O present as SiO₂, the ratio of Ge to O is now closer to 1:1. The presence of S and F is indicative of triflate which is found in the starting material.

2.4.4 X-ray Crystallography

Each subject crystal was covered in Nujol®, mounted on a goniometer head and rapidly placed in the dry N₂ cold-stream of the low-temperature apparatus (Kryoflex) attached to the diffractometer. The data were collected using the SMART software⁵⁰ on a Bruker APEX CCD diffractometer using a graphite monochromator with MoKα radiation (\(\lambda = 0.71073 \text{ Å}\)). For each crystal, a hemisphere of data was collected using a counting time of 10 seconds per frame at -100 °C. Data reductions were performed using the SAINT-Plus software⁵¹ and the data were corrected for absorption using SADABS.⁵² Each structure was solved by direct methods using SIR97⁵³ and refined by full-matrix
least-squares on $F^2$ with anisotropic displacement parameters for the heavy atoms using SHELXL-97$^{54}$ and the WinGX$^{55}$ software package, the solution were assessed using tools in PLATON,$^{56}$ and thermal ellipsoid plots were produced using SHELXTL.$^{57}$ For compound [Ge[15]crown-5•H$_2$O][OTf]$_2$, the hydrogen atoms on the water fragment were restrained to have similar thermal parameters and the O–H distances were restrained to be similar. CIF files can be found in the enclosed CD.

Powder X-ray diffraction (pXRD) experiments were conducted with a Bruker D8 Discover diffractometer equipped with a Hi-Star area detector using CuKα radiation ($\lambda = 1.54186$ Å). Powder XRD pattern simulations were performed using Mercury CSD 2.2.$^{58}$ For comparison and analysis, the patterns of possible known compounds were simulated on the basis of relevant data contained in the Cambridge Structural Database (CSD).$^{59}$

\textbf{Table 2.4: Summary of Crystallographic Data}

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<td>900517</td>
<td>900518</td>
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<td>b (Å)</td>
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<td>616</td>
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<td>2488 [R(int) = 0.0402]</td>
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<td>Completenss to theta max</td>
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### Table 2.5: Summary of Crystallographic Data continued

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<td>C_{12}H_{20}F_{6}GeO_{11}S_{2}</td>
<td>C_{12}H_{21}F_{3}N_{2}O_{3}S</td>
<td>C_{15}H_{19}F_{3}N_{2}O_{3}S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>590.99</td>
<td>330.37</td>
<td>364.38</td>
</tr>
<tr>
<td>Temperature</td>
<td>150(2) K</td>
<td>173(2) K</td>
<td>173(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
<td>0.71073 Å</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 21/n</td>
<td>P2(1)</td>
<td>Pnma</td>
</tr>
<tr>
<td>a (Å)</td>
<td>8.4650(4)</td>
<td>7.9946(18)</td>
<td>21.818(5)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.5520(6)</td>
<td>8.3929(19)</td>
<td>12.782(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>13.3353(8)</td>
<td>12.236(3)</td>
<td>6.0730(14)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>101.210(2)</td>
<td>93.900</td>
<td>90</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1057.69(10)</td>
<td>819.1(3)</td>
<td>1693.6(7)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated) g·cm⁻³</td>
<td>1.856</td>
<td>1.339</td>
<td>1.429</td>
</tr>
<tr>
<td>Absorption coefficient mm⁻¹</td>
<td>1.751</td>
<td>0.238</td>
<td>0.238</td>
</tr>
<tr>
<td>F(000)</td>
<td>596</td>
<td>348</td>
<td>760</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.280 x 0.250 x 0.100</td>
<td>0.20 x 0.10 x 0.10</td>
<td>0.40 x 0.20 x 0.20</td>
</tr>
<tr>
<td>Theta range for data collection (°)</td>
<td>3.115 to 27.495</td>
<td>2.55 to 27.47</td>
<td>1.87 to 27.50</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-10 ≤ h ≤ 10</td>
<td>-10 ≤ h ≤ 10</td>
<td>-27 ≤ h ≤ 28</td>
</tr>
<tr>
<td></td>
<td>-12 ≤ k ≤ 12</td>
<td>-10 ≤ k ≤ 10</td>
<td>-16 ≤ k ≤ 16</td>
</tr>
<tr>
<td></td>
<td>-17 ≤ l ≤ 17</td>
<td>-15 ≤ l ≤ 15</td>
<td>-7 ≤ l ≤ 7</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>37983</td>
<td>8662</td>
<td>15463</td>
</tr>
</tbody>
</table>
2.4.5 Computational Methods

All of the computational investigations were performed by Dr. Macdonald using the Compute Canada Shared Hierarchical Academic Research Computing Network (SHARCNET) facilities (www.sharcnet.ca) with the Gaussian09 program suite. For the crown ether complexes, geometry optimizations have been calculated using density functional theory (DFT), specifically implementing the M062X method in conjunction with the TZVP basis set for all atoms. The base-free GeOH₂ tautomer investigations were done using the B3PW91/6-31+G(d) method. 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. Population analyses were conducted using the Natural Bond Orbital (NBO) implementation included with the
Gaussian package and the Atoms In Molecules (AIM) analyses were conducted using AIM2000. Plots of molecular orbitals and electron densities were generated and examined using MOLDEN or Gaussview 3.0. Summaries of the optimized structures, including electronic energies and Cartesian components for each of the atoms, are detailed in Appendix A2 on the enclosed CD.

2.5 References


Chapter 3

The Reactivity of Polyether Germanium(II) Dications Towards Hydrogen Sulfide and Phosphine

3.1 Introduction

In the previous chapter, it was demonstrated that both water and ammonia coordinate to [Ge[15]crown-5][OTf]$_2$ to form remarkably stable donor-acceptor complexes. In light of this, the reactivity of polyether stabilized Ge(II) centres towards the heavier element hydrides, hydrogen sulfide and phosphine, was also investigated. The results are presented in this chapter. Although there are no prior reports of Ge(II) adducts of H$_2$S nor PH$_3$, treatment of other Ge(II) precursors with these reagents have afforded a variety of materials, including thin films and nanoparticles of GeS, GeP, and related compounds. These compounds have recently become of interest with applications in photovoltaics, batteries, and optical electronics.

3.2 Results and Discussion

3.2.1 Reactivity with H$_2$S

In pursuit of the H$_2$S variant of [Ge[15]crown-5•H$_2$O][OTf]$_2$ ($3.2[OTf]_2$), H$_2$S generated from the reaction between FeS and 1M HCl in diethyl ether was bubbled through a solution of [Ge[15]crown-5][OTf]$_2$ ($3.1[OTf]_2$) in CH$_2$Cl$_2$. Removal of all volatile components yielded a colourless residue which was characterized by $^1$H NMR, FT-IR and X-ray crystallography. However, instead of the desired H$_2$S adduct, the water adduct $3.2[OTf]_2$ was obtained. Repeated attempts to isolate the H$_2$S adduct through this approach were also unsuccessful, as were reactions where H$_2$S was generated in even
greater excess than \(3.1\)[OTf]_2\). In all instances, the water adduct was isolated. Perhaps, the small scale of these reactions caused the generated \(\text{H}_2\text{S}\) to dissipate before it could be bubbled through, leaving water available to enter the system.

As a result, a second series of reactions were conducted with pressurized \(\text{H}_2\text{S}\) gas. An excess of \(\text{H}_2\text{S}\) was bubbled through a colourless solution of \(3.1\)[OTf]_2\) in \(\text{CH}_2\text{Cl}_2\) at room temperature. Immediately, a dark red-orange solid precipitated from solution and was collected by filtration. The precipitate was found to be air stable but amorphous and insoluble in common laboratory solvents, making characterization rather difficult. The remaining colourless filtrate was dried \textit{in vacuo}, yielding an off-white oily residue. Characterization by \(^1\)H NMR revealed a resonance consistent with crown ether and a second, broad resonance near 11.5 ppm, likely excess \(\text{H}_2\text{S}\). Unfortunately, attempts to recrystallize and identify this residue were unsuccessful; instead, a colourless, gelatinous material formed.

This description of an amorphous, dark red-orange solid is consistent with that of GeS as reported by Dennis and Hulse.\(^{11}\) In their report, GeS was generated by the passing of \(\text{H}_2\text{S}\) through a hot solution of \(\text{GeCl}_2\) until it had cooled to room temperature. Other reported methods include heating GeS\(_2\) to extreme temperatures in the presence of metallic Ge or \(\text{H}_2\).\(^{12,13}\)

Consequently, SEM/EDS (Scanning Electron Microscope/Energy Dispersive X-ray Spectroscopy) analysis was conducted to determine and confirm the composition of the solid. Examination of the SEM micrograph (\textbf{Figure 3.1}) reveals a granular morphology. Comparison of the atomic percentages of Ge and S shows an approximate
A 1:1 ratio, confirming the presence of GeS (Table 3.1). In addition, the brighter regions on the micrograph were found to contain Si, likely silica from the frit used to collect the sample. The high percentage of C is attributed to the carbon tape and residual crown ether.

![Figure 3.1: SEM micrograph (top view) of Sample A obtained from the passing of excess H$_2$S$_{(g)}$ through a solution of 3.1[OTf]$_2$ in CH$_2$Cl$_2$.](image)

### Table 3.1: Atomic Percentages from EDS Spot Analysis of Sample A.

<table>
<thead>
<tr>
<th>Spot</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>S</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>76.99</td>
<td>14.35</td>
<td>3.82</td>
<td>2.41</td>
<td>2.43</td>
</tr>
<tr>
<td>2</td>
<td>50.85</td>
<td>6.36</td>
<td>1.69</td>
<td>6.65</td>
<td>6.63</td>
</tr>
<tr>
<td>3</td>
<td>86.85</td>
<td>-</td>
<td>-</td>
<td>6.54</td>
<td>6.61</td>
</tr>
<tr>
<td>4</td>
<td>84.07</td>
<td>10</td>
<td>-</td>
<td>2.62</td>
<td>3.31</td>
</tr>
</tbody>
</table>

A third series of reactions was conducted where one equivalent of 0.8 M H$_2$S in THF was added to a solution of 3.1[OTf]$_2$ in CH$_2$Cl$_2$ at room temperature. As was the case in the previous set of reactions, both a dark red-orange precipitate and off-white residue (after removal of all volatiles from the filtrate) were obtained as products. Again, SEM/EDS analysis was used to determine the composition of the solid. The SEM
micrograph (Figure 3.2) reveals larger sized, angular particles. The composition as determined by EDS shows a 1:0.65 ratio of Ge:S (Table 3.2). Of note is the absence of C, O, and Si. In the case of C and O, the sample was washed with CH₂Cl₂ to remove any residual crown ether; in the last case, the solid was collected by centrifugation to avoid contamination by Si.

![SEM micrograph](image)

**Figure 3.2:** SEM micrograph (top view) of Sample B obtained from the addition of one equivalent of 0.8 M solution of H₂S in THF to a solution of 3.1[OTf]₂ in CH₂Cl₂.

<table>
<thead>
<tr>
<th>Spot</th>
<th>S</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>34.76</td>
<td>65.24</td>
</tr>
<tr>
<td>2</td>
<td>42.34</td>
<td>57.66</td>
</tr>
<tr>
<td>3</td>
<td>41.58</td>
<td>58.41</td>
</tr>
</tbody>
</table>

**Table 3.2:** Atomic Percentages from EDS Spot Analysis of Sample B.

According to Dennis and Hulse’s report,¹¹ GeS is readily soluble in solutions of alkali hydroxides or sulfides. The precipitates from both reactions were dissolved in a NaOH solution, forming red-orange solutions. However, both solutions turned colourless overnight. For the solution containing Sample B, slow evaporation of the solvent yielded
colourless crystals suitable for X-ray diffraction. The crystals were characterized as [Na[15]crown-5][OTf] which was unsurprising given the presence of residual crown ether and their affinity for binding Group I and II metals (Figure 3.3). Slow evaporation of the solvent from the solution of Sample C did not yield a crystalline material.

**Figure 3.3:** Thermal ellipsoid plot (30% probability surface) of [Na[15]crown-5][OTf] from a crystal with disordered refinement. Hydrogens have been removed for clarity.

It is worth noting that when the same reactions are conducted in THF, a dark orange precipitate still forms, but the reaction mixture is noticeably thicker. This may be attributed to the polymerization of THF. As a result, separation of the solid by centrifugation is much slower, however, the formation of a film along the base of the centrifuge tube was observed, as opposed to the solid powders described in the reactions with CH₂Cl₂. The film, as seen on the SEM micrograph, features a rough/pitted surface with prominent cracks (Figure 3.4). EDS analysis indicates that Ge and S are present in a
1:0.80 ratio (Table 3.3). Excess crown ether is also present; however, this can be removed through washings.

Figure 3.4: SEM micrograph (top view) of Sample C, a film obtained from the addition of one equivalent of 0.8 M solution of H₂S in THF to a solution of 3.1[OTf]₂ in THF.

Table 3.3: Atomic Percentages from EDS Spot Analysis of Sample C.

<table>
<thead>
<tr>
<th>Spot</th>
<th>C</th>
<th>O</th>
<th>S</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45.45</td>
<td>7.19</td>
<td>20.55</td>
<td>26.8</td>
</tr>
<tr>
<td>2</td>
<td>48.86</td>
<td>5.91</td>
<td>20.75</td>
<td>24.87</td>
</tr>
</tbody>
</table>

The treatment of other Ge(II) precursors with H₂S has also resulted in thin film formation. In one study, Gordon and co-workers treated a N-heterocyclic germylene and stannylene with H₂S yielding uniformly thick GeS and SnS thin films that were deposited by atomic layer deposition (ALD) into holes with high aspect ratios.⁹ The GeS films were smooth and amorphous with a Ge/S atomic ratio was 1:0.85. The SnS films were polycrystalline and granular with a Sn/S atomic ratio of 1:1.
In summary, the addition of $\text{H}_2\text{S}$ to $[\text{Ge}[15]\text{crown-5}][\text{OTf}]_2$ results in the precipitation of GeS as a solid or film whose compositions were confirmed by EDS. The crown ether dissociates from Ge and remains in solution, coordinated to what is likely excess $\text{H}_2\text{S}$ or HOTf as assessed by $^1\text{H}$ NMR. This room temperature generation of GeS presents a more convenient approach in comparison to methods previously reported.$^{11-13}$ Consequently, further work will investigate the potential of the crown ether stabilized Ge(II) centres as materials precursors towards thin films and nanoparticles which continue to receive considerable attention for their electrical and optical properties.$^5-8,10,14$

3.2.2 Reactivity with PH$_3$

Note: The reactions/results presented in this section were performed by Jonathan W. Dube under the supervision of Dr. Paul J. Ragogna at Western University.

Unlike the reactivity displayed with NH$_3$, the treatment of $[\text{Ge}[15]\text{crown-5}][\text{OTf}]_2$ ($3.1[\text{OTf}]_2$) and $[\text{Ge-tetraglyme}][\text{OTf}]_2$ ($3.3[\text{OTf}]_2$) with PH$_3$ results in the isolation of germanium phosphide. Vials containing the polyether Ge(II) complexes in a solution of THF or toluene were placed in a stainless steel manifold and excess PH$_3$ was added at room temperature. The extent of the reaction is dependent on the exposure time to PH$_3$: GeP begins to form along the walls of the vial after three hours of exposure. After 24 hours, the entire vial is coated in a thin film of GeP.

It was found that the tetraglyme stabilized complex formed better films than the analogous crown ether complexes. As a result, the reaction was repeated with a small glass slide placed within the reaction vial on which the brown GeP film deposited (Figure 3.5). EDS measurements were taken both before and after a gold coating was
applied to the film to prevent charge build-up. In each case, both Ge and P were present, along with other elements consistent with glass. The measurements with the Au coating reveal that the Ge/P atomic ratio is approximately 1:0.85 (Table 3.4). Also of note is the absence of carbon. It appears that the formation of GeP results in the dissociation of crown ether from the Ge centre, as it does with the H₂S reactions.

![Image](image.jpg)

**Figure 3.5:** GeP deposited on a glass slide (Sample D) from the addition of PH₃ to 3.3[OTf]₂.

**Table 3.4:** Atomic Percentages from EDS Analysis of Sample D.

<table>
<thead>
<tr>
<th>Spot</th>
<th>O</th>
<th>Na</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>53.02</td>
<td>8.56</td>
<td>0.91</td>
<td>24.79</td>
<td>3.94</td>
<td>1.06</td>
<td>0.36</td>
<td>2.71</td>
<td>4.66</td>
</tr>
</tbody>
</table>

Germanium phosphide has been known for some time and has applications as a semiconductor. However, only recently have there been investigations into GeP thin films and their photovoltaic properties. One such study was conducted by Parkin and co-workers³ where GeX₄ (X = Cl, Br) was treated with PCyH₂ (Cy = cyclohexyl) at 600 °C. The thin films were then deposited on glass substrates through chemical vapour deposition (CVD). EDS measurements revealed varying compositions from Ge₃P to GeP₂.
with the composition more dependent on the Ge concentration. The band gap of the thin film was found to be 1.1 eV.

Thus, this room temperature approach would be an improvement over this protocol. Further study is needed but initial work confirms that the addition of PH₃ to [Ge[15]crown-5][OTf]₂ and [Ge-tetraglyme][OTf]₂ results in the formation of GeP with a Ge/P atomic ratio of 1:0.85.

3.2.3 Computational Studies

To rationalize the difference in reactivity exhibited by [Ge[15]crown-5][OTf]₂ (3.1[OTf]₂) towards the lighter element hydrides (H₂O and NH₃) and their heavier analogues (H₂S and PH₃), preliminary DFT calculations were performed to assess the relative stabilities of the adduct and insertion products. The computed structure of the water adduct 3.2' (where ' indicates the geometry-optimized model structure of the indicated cation) reproduces the structure obtained experimentally quite accurately, so it is probable that the computed structures of 3.5', 3.7', and 3.9' are reasonable models for the ammonia, hydrogen sulfide and phosphine adduct, respectively (Figure 3.6). Using these adduct models, geometry-optimized models were also calculated for the corresponding insertion products, 3.6', 3.8', and 3.10'. The sum of the electronic and zero point energies were calculated for each complex. These were then used to calculate the difference in energy between the insertion and adduct products (Table 3.5).
Figure 3.6: Ball-and-stick representations of geometry-optimized models of
Table 3.5: Relative energies of the adduct and insertion products of [Ge[15]crown-5]$^{2+}$ calculated using the M062X/TZVP DFT method.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>$\Delta E$ (kJ/mol) (inserted-adduct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>+13.1</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>-29.5</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>+57.3</td>
</tr>
<tr>
<td>PH$_3$</td>
<td>-3.7</td>
</tr>
</tbody>
</table>

The general trend ascertained from these calculations is that the lighter element hydrides, H$_2$O and NH$_3$, favour the formation of the adduct complex, whereas, H$_2$S and PH$_3$ favour the formation of the insertion product. In the case of the former group, this is in agreement with what is observed experimentally. For the latter group, the relative favourability of the oxidative addition products can be rationalized in terms of Ge–H versus S–H and P–H bond strengths and the relative proton affinities of Ge, S, and P. All three bond strengths are comparable as are the electronegativities of Ge, S, and P, unlike O and N which are much more electronegative than Ge. While insertion products may be accessible for the heavier hydrides, perhaps they are too reactive which leads to the formation of GeS and GeP. Although, another possible explanation for the difference in products is that H$_2$S and PH$_3$ are generally added to [Ge[15]crown-5][OTf]$_2$ in excess. Further investigation will be needed to determine the mechanism behind the formation of GeS and GeP.
3.3 Conclusions

In summary, the room temperature addition of the heavier element hydrides, H$_2$S and PH$_3$, to [Ge[15]crown-5][OTf]$_2$ (3.1[OTf]$_2$) yields GeS and GeP, respectively. In the case of GeS, products in the form of solid powder and film were obtained, whereas, GeP was obtained as a thin film. The elemental compositions of these products were confirmed by EDS analysis. While these results are unexpected given the formation of the water and ammonia adducts, the rapid and room temperature formation of GeS and GeP is exciting. Typically, these products are generated at extreme temperatures. Owing to the electrical and optical properties of GeS and GeP, future work will involve optimizing the formation of these materials, as well as investigating their properties.

3.4 Experimental

3.4.1 Reagents and General Methods

All manipulations were carried out under an anhydrous N$_2$ atmosphere using standard Schlenk line, glovebox and glovebag techniques at room temperature. Solvents were dried by passing through Grubbs'-type alumina columns and then stored over 4 Å molecular sieves. CD$_3$CN was distilled over CaH$_2$ and then stored over 4 Å molecular sieves. [Ge[15]crown-5][OTf]$_2$ (3.1[OTf]$_2$) was synthesized according to literature procedures. [Ge-tetraglyme][OTf]$_2$ was synthesized as outlined in Chapter 4 of this thesis. FeS, 1 M HCl solution in diethyl ether, H$_2$S (pressurized cylinder), and 0.8 M H$_2$S solution in THF were purchased from Sigma Aldrich and used without further purification.
The PH\textsubscript{3} reactions were conducted by Dr. Jonathan Dube, of the Ragogna Lab at Western University. PH\textsubscript{3} (pressurized cylinder) was obtained from Cytec Corporation and used as received. The reactions were performed in a stainless steel manifold and excess PH\textsubscript{3} was burned and converted into H\textsubscript{3}PO\textsubscript{4} with water.

All NMR spectra were collected at room temperature using Bruker Avance 500 MHz spectrometers and chemical shifts are reported in ppm. The resonances in the \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were referenced to SiMe\textsubscript{4} using appropriate solvent resonances as internal standards. The \textsuperscript{19}F NMR spectra were referenced externally to CFCl\textsubscript{3} (0 ppm).

3.4.2 Synthetic Procedures

**Reaction of 3.1[OTf]_2 with H\textsubscript{2}S generated by FeS + 2 HCl**

An excess of H\textsubscript{2}S generated from the neat reaction of FeS (30 mg, 0.338 mmol) and 1 M HCl solution in diethyl ether (1.35 mL, 0.677 mmol) was bubbled through a colourless solution of 3.1[OTf]_2 (100 mg, 0.169 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (50 mL) at room temperature while vigorously stirring for one minute. The resultant colourless solution was stirred overnight at room temperature after which small amount of white precipitate formed. Removal of all volatile components under reduced pressure yielded a white residue. Recrystallization from CH\textsubscript{2}Cl\textsubscript{2} afforded single crystals suitable for X-ray diffraction but were characterized as [Ge[15]crown-5·H\textsubscript{2}O][OTf]_2, \textbf{2.2}[OTf]_2. Multinuclear NMR spectroscopy also confirms this. \textsuperscript{1}H NMR (CD\textsubscript{3}CN): 8.70 (s, 2H, OH); 3.94 (s, 20H, CH\textsubscript{2}). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (CD\textsubscript{3}CN): 121.8 (q, 2C, CF\textsubscript{3}SO\textsubscript{3}), \textit{J}_{CF} = 320.5 Hz); 69.8 (s, 10C, CH\textsubscript{2}). \textsuperscript{19}F\{\textsuperscript{1}H\} NMR (CD\textsubscript{3}CN): -78.9 (s, 6F, CF\textsubscript{3}SO\textsubscript{3}).

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**Reaction of 3.1[OTf]₂ with H₂S(g)**

An excess of H₂S from a pressurized cylinder was bubbled through a colourless solution of 3.1[OTf]₂ (100 mg, 0.169 mmol) in CH₂Cl₂ (50 mL) at room temperature while vigorously stirring for 20 seconds. A rust coloured precipitate immediately formed and the reaction was stirred overnight at room temperature. The precipitate was collected through a frit or centrifugation and pumped to dryness. The rust coloured solid (Yield: 11 mg) was found to be insoluble in all common solvents and amorphous. Characterization by SEM/EDS shows an approximate 1:1 ratio of Ge to S.

Removal of all volatile components of the pale yellow filtrate under reduced pressure afforded an off-white oily residue which was characterized by ¹H NMR. ¹H NMR (CD₃CN): 11.67 (s(br)); 3.74 (s, 20H, CH₂). Integration of the resonances shows a relative ratio of 1:4 of the signal at 11.67 ppm to the signal at 3.74 ppm.

**Reaction of 3.1[OTf]₂ in CH₂Cl₂ with 0.8 M H₂S in THF**

0.8 M H₂S solution in THF (0.42 mL, 0.338 mmol) was added to a colourless solution of 3.1[OTf]₂ (200 mg, 0.338 mmol) in CH₂Cl₂ (50 mL). The solution immediately turned orange followed by the precipitation of dark orange solid after a few minutes of stirring. The reaction was stirred overnight at room temperature after which the solid was collected through a frit or centrifugation. The rust coloured solid (Yield: 30 mg) was found to be insoluble in all common solvents and amorphous. Characterization by SEM/EDS shows an approximate 1:0.65 ratio of Ge to S.
Removal of all volatile components of the almost colourless filtrate under reduced pressure afforded a pale orange solid residue which was characterized by $^1$H NMR.

$^1$H NMR (CD$_3$CN): 11.27 (s(br)); 3.85 (s, 20H, CH$_2$). Integration of the resonances shows a relative ratio of 1:5.5 of the signal at 11.27 ppm to the signal at 3.85 ppm.

**Reaction of 3.1[OTf]$_2$ in THF with 0.8 M H$_2$S in THF**

0.8 M H$_2$S solution in THF (0.63 mL, 0.508 mmol) was added to a colourless solution of 3.1[OTf]$_2$ (300 mg, 0.508 mmol) in THF (50 mL). The solution immediately turned orange followed by the precipitation of dark orange solid after a few minutes of stirring. The reaction was stirred overnight at room temperature after which it was noted that the consistency of the mixture had become very thick. Attempts to separate the solid through centrifugation were somewhat difficult, owing to the thick mixture, however, some precipitate was obtained as a film. The rust coloured solid was found to be insoluble in all common solvents and amorphous. Characterization by SEM/EDS shows an approximate 1:0.80 ratio of Ge to S. Removal of all volatiles from the remaining orange supernatant was unsuccessful due to its thickness.

**Reaction of 3.1[OTf]$_2$ and 3.2[OTf]$_2$ with PH$_3$**

[Ge[15]crown-5][OTf]$_2$ and [Ge-tetraglyme][OTf]$_2$ were dissolved in THF or toluene. Vials containing the solution and a glass slide were placed in a stainless steel manifold and excess PH$_3$ was added at room temperature. After 24 hours, a brown thin film had deposited on the glass slide. Excess PH$_3$ was removed by careful and continuous purging with N$_2$ and incineration of PH$_3$ residues in a burn-box. The thin film was characterized by EDS and had a Ge/P atomic ratio of 1:0.85.
3.4.3 SEM/EDS

SEM/EDS analysis was conducted at the Great Lakes Institute for Environmental Research at the University of Windsor. Samples were observed under a FEI Quanta 200 FEG microscope and analyzed with an EDAX SDD detector using TEAM software. Samples were mounted on carbon tape and positioned at a working distance of 10 mm. EDS spot analysis was conducted for each sample with an accelerating voltage of 21 kV and a collection time of 30 s.

3.4.4 X-ray Crystallography

The subject crystal was covered in Nujol®, mounted on a goniometer head and rapidly placed in the dry N₂ cold-stream of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were collected using the APEX2 software suite on a Bruker D8 Venture with PHOTON 100 diffractometer using a graphite monochromator with CuKα radiation (λ = 1.54178 Å). A hemisphere of data was collected using a counting time of 30 seconds per frame at −100 °C. Data reductions were performed using the using the APEX2 software suite and the data were corrected for absorption using SADABS. Each structure was solved by direct methods using SHELXS-2013 and refined by full-matrix least-squares on \( F^2 \) with anisotropic displacement parameters for the heavy atoms using SHELXL-2013 and the WinGX software package. The solutions were assessed using tools in PLATON, and thermal ellipsoid plots were produced using SHELXTL. CIF files can be found in the enclosed CD.
**Table 3.6: Summary of Crystallographic Data**

<table>
<thead>
<tr>
<th>Compound</th>
<th>[Na[15]crown-5][OTf]</th>
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<tr>
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<td>C(<em>{11})H(</em>{16})F(_3)NaO(_8)S</td>
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<td>(P2_1/m)</td>
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<tr>
<td>c (Å)</td>
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<tr>
<td>(\beta) (°)</td>
<td>105.771(2)</td>
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<tr>
<td>(\gamma) (°)</td>
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<tr>
<td>(V) (Å(^3))</td>
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</tr>
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<td>(Z)</td>
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<td>Density (calculated) g·cm(^{-3})</td>
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<td>Data / restraints / parameters</td>
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Goodness-of-fit on $F^2$ 1.043
Final R indices [I>2sigma(I)] R1 = 0.0419, wR2 = 0.1156
R indices (all data) R1 = 0.0499, wR2 = 0.1226
Largest diff. peak and hole (e-Å³) 0.752 and -0.265

3.4.5 Computational Methods

All of the computational investigations were performed by Dr. Macdonald using the Compute Canada Shared Hierarchical Academic Research Computing Network (SHARCNET) facilities (www.sharcnet.ca) with the Gaussian09 program suite. For the crown ether complexes, geometry optimizations have been calculated using density functional theory (DFT), specifically implementing the M062X method in conjunction with the TZVP basis set for all 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. Summaries of the optimized structures, including electronic energies and Cartesian components for each of the atoms, are detailed in Appendix A2 on the enclosed CD.

3.5 References


Chapter 4

Glyme Complexes of Germanium(II) and Tin(II)

4.1 Introduction

Investigations into the preparation and chemistry of low-oxidation state germanium and tin complexes continue to be of considerable interest.\textsuperscript{1-6} Notable examples are the conductive organic tin halide perovskites of the form $[\text{NR}_4][\text{SnX}_3]$ and binary metal perovskites, which have recently been identified as promising photovoltaic materials.\textsuperscript{7,8} Typically, stabilization of these low oxidation state centres almost always requires covalently bound substituents with the appropriate steric and electronic properties. However, the polyether ligation approach is also a viable method towards stabilization as seen with the $[2.2.2]$cryptand stabilized Ge(II) complex reported by Baines and co-workers.\textsuperscript{9} Previously, the Macdonald group demonstrated that the related crown ether ligands are also suitable for the stabilization of Ge(II) and Sn(II) centres.\textsuperscript{10-12} Moreover, glymes, which are acyclic variants of crown ethers, can also isolate low oxidation state p-block elements as seen in the synthesis and characterization of triglyme and tetruglyme complexes of Sn(OTf)$_2$.\textsuperscript{13} As a result, germanium and other tin variants were pursued. To this end, GeCl$_2$·dioxane, "Ge(OTf)$_2"$,\textsuperscript{14} and SnCl$_2$ were treated with triglyme and tetruglyme. The resultant products are presented in this chapter.
4.2 Results and Discussion

4.2.1 Triglyme Complexes of Ge(II)

The addition of one equivalent of triglyme and two equivalents of Me₃SiOTf to GeCl₂•dioxane in CH₂Cl₂ afforded a colourless oil after removal of all volatile components (Scheme 4.1). Slow evaporation of a solution in toluene afforded a colourless crystalline material characterized as [Ge-triglyme][OTf]₂ (4.1[OTf]₂) by multinuclear NMR spectroscopy, elemental analysis and X-ray crystallography.

![Scheme 4.1: Synthesis of [Ge-triglyme][OTf]₂ (4.1[OTf]₂).](image)

Complex 4.1[OTf]₂ crystallizes in the monoclinic space group P2₁/c with one formula equivalent in the asymmetric unit (Figure 4.1). The triglyme adopts a planar conformation, binding to germanium in a belt-like manner. The germanium is situated closest to O31, O32, and O33 while O4 is substantially farther away: Ge–Oglyme distances range from 2.092(2) to 2.781(2) Å. Two distinct triflate environments are seen. One triflate anion lies closer in proximity to the germanium centre, in a position that is essentially perpendicular to the glyme. Although, the Ge–O triflate (Ge–O11) separation of 2.027(3) Å is longer than typical covalent Ge–O bonds (ca. 1.75–1.85 Å)¹⁵, it is comparable to other known Ge–O triflate distances.¹⁰,¹⁶ Furthermore, examination of the
triflate's three S–O bonds lengths reveals that the S–O11 bond length of 1.475(3) Å is longer than those of S–O12 (1.410(3) Å) and S–O13 (1.412(3) Å) which is indicative of a slightly perturbed anion. This suggests that this Ge-triflate interaction can be best described as a contact ion pair, based on a previously related study involving polyether complexes of Sn(II) triflate and chloride. The second triflate anion is distinctly separate from the glyme-Ge moiety and the closest Ge–O_{triflate} separation (Ge–O22) is 2.674(3) Å.

Figure 4.1: Thermal ellipsoid plot (30% probability surface) of 4.1[OTf]₂. All hydrogens have been removed for clarity. Selected bond distances [Å]: Ge–O11, 2.027(3); Ge–O31, 2.315(2); Ge–O32, 2.092(2); Ge–O33, 2.212(2); Ge–O34, 2.781(2); S1–O11, 1.475(3); S1–O12, 1.410(3); S1–O13, 1.412(3); S2–O21, 1.437(3); S2–O22, 1.422(3); S–O23, 1.422(3).
The direct reaction of triglyme and GeCl$_2$•dioxane was also investigated to determine the effect of changing the substituent at the Ge centre. Half an equivalent of triglyme was added to GeCl$_2$•dioxane in CH$_2$Cl$_2$ (Scheme 4.2). A colourless oil was obtained and slow evaporation of a solution in toluene afforded crystals suitable for X-ray crystallography. The product was confirmed to be [GeCl-triglyme][GeCl$_3$] (4.2[GeCl$_3$]), however, the solid state structure revealed that the complex had dimerized in a manner that was quite unexpected.

**Scheme 4.2:** Synthesis of [GeCl-triglyme][GeCl$_3$] (4.2[GeCl$_3$]).

Complex 4.2[GeCl$_3$] crystallizes in the space group $P2_1/c$. The asymmetric unit contains one formula equivalent where the cation is comprised of a triglyme bound $^+$GeCl fragment and the anion consists of a distinctly separate GeCl$_3$. Examining the cation, the Ge–Cl distance of 2.320(2) Å is somewhat longer than typical Ge–Cl bond lengths of 2.09-2.21 Å. However, the Ge-Cl interaction is still expected to be covalent in nature as was described in a previous study. Unlike in 4.1[OTf]$_2$, the triglyme adopts a folded conformation where Ge1, O1, O2, O3 and Cl1 are coplanar with O4 and its adjacent methyl group almost perpendicular to the plane. The relatively larger size of the $^+$Ge–Cl fragment and the likely presence of a stereochemically active lone pair contributes to this folded arrangement much like in [GeCl[15]crown-5][GeCl$_3$] in which the crown ether
also adopts a bent geometry. Additionally, the \(^{+}\text{GeCl}\) fragment is situated near the centroid of the four oxygen atoms with Ge–O distances ranging from 2.107(5) to 2.175(5) Å. This is a much smaller range than what is observed in 4.1[OTf]₂. Examining the GeCl₃ anion bond lengths shows that the Ge2–Cl22 bond length of 2.368(2) Å is considerably longer than those of Ge2–Cl21 (2.203(2) Å) and Ge2–Cl23 (2.213(2) Å). In general, the average bond length in GeCl₃ is approximately 2.30 Å and ranges from 2.213 to 2.365 Å as reported in the Cambridge Structural Database.

The full structure reveals that both the cation and anion have dimerized about inversion centres (Figure 4.2). In the former, the two Ge(II) atoms, separated by a distance of 3.390(1) Å, are bridged by two chlorine atoms. The chloro-bridges feature Ge–Cl bonds lengths of 2.320(2) and 2.427(2) Å and a Ge–Cl–Ge bond angle of 91.10(6)°. Due to the folded nature of the glyme, Ge1, Cl1, O2, and O4 define one plane, while Ge1, O1, and O3 define an essentially orthogonal plane. The remarkable Ge₂Cl₆²⁻-dianion features the same core: two Ge(II) atoms, separated by 3.197(1) Å, are joined through two \(\mu^2\)-bridging chlorine atoms. The chloro-bridges are essentially symmetrical with Ge–Cl bonds lengths of 2.345(2) and 2.368(2) Å and a Ge–Cl–Ge bond angle of 85.42(6)°.
Figure 4.2: Thermal ellipsoid plot (30% probability surface) of \( \text{4.2}[\text{GeCl}_3] \) showing dimerization of the cation and anion. All hydrogens have been removed for clarity. Selected bond distances (Å) and angles (°): Ge1–Cl1, 2.320(2), 2.427(2); Ge1–O1, 2.111(5); Ge1–O2, 2.107(5); Ge1–O3, 2.141(5); Ge1–O4, 2.175(5); Ge2–Cl21, 2.213(2); Ge2–Cl22, 2.345(2), 2.368(2); Ge2–Cl23, 2.03(2). Ge1–Cl1–Ge1, 91.10(6); C11–Ge–Cl1, 88.91(6); Ge2–Cl22–Ge2, 85.42(6), Cl22–Ge2–Cl22, 94.58(6).

The isolation of such a complex is quite unexpected. While there are several examples of \( \text{E}_2\text{Cl}_2 \) dimers (\( \text{E} = \text{Group 13, Sn, Pb} \)) as seen in the Cambridge Structural Database,\(^{17}\) there are no reports of a Ge(II) variant. However, there is one example of a chloride-bridged Ge(IV) dimer reported by Alcarazo and co-workers which is obtained through treatment of a carbodiphosphorane stabilized \( ^+\text{GeCl} \) salt with elemental sulfur.\(^{18}\) The bridging Ge–Cl bond lengths of 2.216(1) and 2.227(2) Å are shorter than those in \( \text{4.2}[\text{GeCl}_3] \), as is the Ge–Cl–Ge bond angle of 83.61(5)°; however, this is anticipated due to the larger ionic radius of Ge\(^{2+} \) (87 pm) in comparison to Ge\(^{4+} \) (67 pm).\(^{19}\) It is perhaps worth noting that the Sn(II) analogue of Alcarazo's compound does indeed adopt a dimeric dicationic form in the salt \( \text{[LSn(μ-Cl)]}_2\text{SnL}][\text{AlCl}_4]_2 \). So while dimerization of \( \text{4.2} \)
is conceivable, that of GeCl$_3$ remains perplexing. Whereas a simple qualitative MO treatment of the fragment orbitals involved suggests that bonding may indeed be possible for such a dimeric dianion, in practice, attempted geometry-optimization calculations of Ge$_2$Cl$_6^{2-}$ did not converge; identical calculations on the cation dimer did indeed yield a geometry-optimized structure consistent with that observed experimentally. The presence of twinning in the crystal structure is possible, however, no indications of twinning have yet been found. Further investigations will be needed.

In contrast to all of the crown ether stabilized Ge(II) and Sn(II) complexes previously reported,$^{10-12}$ 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. More specifically, the $^1$H NMR resonances of 4.1[OTf]$_2$ and 4.2[GeCl$_3$] in CD$_3$CN (ca. 3 to 4 ppm) are considerably deshielded in comparison to free triglyme in the same solvent. However, the glyme protons in 4.2[GeCl$_3$] are deshielded to a smaller extent. All $^{13}$C NMR resonances ca. 60 to 75 ppm are assigned to triglyme. The exception is a quartet at 120.1 ppm which is assigned to the triflate group in 4.1[OTf]$_2$. The corresponding $^{19}$F NMR chemical shift of the triflate is a singlet at -79.08 ppm. The single resonance suggests that, in solution, 4.1 may exist as a dication rather than the monocation seen in the solid state structure. The rapid exchange of bound and free triflate fragments is another possible explanation for this observation.
4.2.2 Tetraglyme Complexes of Ge(II)

To observe what effect ligand size would have on these systems, tetraglyme variants of the aforementioned complexes were pursued. The synthetic procedures previously outlined were repeated, but with tetraglyme instead (Scheme 4.3). Products were characterized by multinuclear NMR spectroscopy, elemental analysis, and X-ray crystallography and were confirmed to be [Ge-tetraglyme][OTf]$_2$ (4.3[OTf]$_2$) and [GeCl-tetraglyme][GeCl$_3$] (4.4[GeCl$_3$]).

![Scheme 4.3: Synthesis of [Ge-tetraglyme][OTf]$_2$ (4.3[OTf]$_2$) and [GeCl-tetraglyme][GeCl$_3$] (4.4[GeCl$_3$]).](image)

[Ge-tetraglyme][OTf]$_2$ (4.3[OTf]$_2$) crystallizes in the space group $P2_1/c$ with one formula equivalent comprising the asymmetric unit (Figure 4.3). As in 4.1[OTf]$_2$, the glyme binds the Ge in a belt-like manner with Ge situated along the line of symmetry of the glyme. Ge–O$_{\text{glyme}}$ distances are therefore fairly symmetric with Ge closest to O33 at a distance of 2.281(2) Å, followed by O32 at 2.355(2) Å and O34 at 2.393(2) Å, and farthest away are O31 at 2.499(2) Å and O35 at 2.562(2) Å. Again similar to 4.1[OTf]$_2$, two distinct triflate environments are seen. The cation features a Ge–O$_{\text{triflate}}$ separation of 1.9962(17) Å, which is shorter than observed in 4.1[OTf]$_2$, but still comparable to other reported Ge–O$_{\text{triflate}}$ distances.$^{10,15}$ The S–O bond distances in this particular triflate are
also slightly perturbed. Overall, these parameters are consistent with a contact ion pair interaction. Conversely, the second triflate is distanced 2.969(2) Å from the Ge and combined with other metrical parameters, can be characterized as a “free” triflate anion.

**Figure 4.3:** Thermal ellipsoid plot (30% probability surface) of 4.3[OTf]2. All hydrogens have been removed for clarity. Selected bond distances (Å): Ge–O11, 1.996(2); Ge–O31, 2.499(2); Ge–O32, 2.355(2); Ge–O33, 2.281(2); Ge–O34, 2.393(2); Ge–O35, 2.562(2); S1–O11, 1.473(2); S1–O12, 1.422(2); S1–O13, 1.420(2); S2–O21, 1.436(2); S2–O22, 1.439(2); S2–O23, 1.420(3).

Given the unexpected dimerization of 4.2[GeCl3], the change to tetrathyline was investigated to determine the effect, if any, it would have on the structure. The solid state structure reveals the tetrathyline stabilized +GeCl cation remains a monomer while the GeCl3 anion dimerizes. Complex 4.4[GeCl3] crystallizes in the space group P-1 with one formula equivalent in the asymmetric unit and is described as a discrete cation-anion system. The cation is comprised of the +GeCl cation bound by tetrathyline in a belt-like manner and the GeCl3 anion has a closest Ge\textsubscript{cation}–Cl\textsubscript{anion} separation of 3.641(2) Å. Analyzing the cation, the Ge–O\textsubscript{glyme} separations range from 2.333(4) to 2.611(5) Å with
two short, two intermediate, and one long contact(s). Moreover, the Ge–Cl bond length of the cation is 2.248(1) Å, which is shorter than observed in 4.2[GeCl₃] and more closely agrees with typical covalent Ge–Cl bonds lengths of 2.09-2.21 Å.¹⁵ The longer Ge–Cl bond in 4.2 is attributed to the bridging chloride, whereas, 4.4 is monomeric. On the other hand, the GeCl₃ anion, much like in 4.2[GeCl₃], contains one longer Ge–Cl bond at 2.359(1) Å and two shorter bonds of similar length (∼2.21 Å). Viewing the full structure shows dimerization of GeCl₃ with the two Ge centres bridged by two chlorides (Figure 4.4).

Figure 4.4: Thermal ellipsoid plot (30% probability surface) of 4.4[GeCl₃] showing dimerization of the anion. Only one of the cations is shown. All hydrogens have been removed for clarity. Selected bond distances (Å) and angles (°): Ge1–Cl1, 2.248(1); Ge1–O1, 2.611(5); Ge1–O2, 2.481(4); Ge1–O3, 2.353(4); Ge1–O4, 2.333(4); Ge1–O5, 2.520(4); Ge2–Cl21, 2.208(2); Ge2–Cl22, 2.359(1), 2.358(2); Ge2–Cl23, 2.209(2). Ge2–Cl22–Ge2, 85.41(6), Cl22–Ge2–Cl22, 94.59(5).
Closer examination of the Ge₂Cl₆²⁻ moiety shows the two Ge(II) atoms separated by 3.199(1) Å. The chloro-bridges are essentially identical with Ge–Cl bonds lengths of 2.358(2) and 2.359(1) Å and a Ge–Cl–Ge bond angle of 85.41(5)°. These parameters are consistent with the anion dimer in 4.2[GeCl₃].

The \(^1\)H and \(^{13}\)C NMR chemical shifts for both 4.3[OTf]₂ and 4.4[GeCl₃] also confirm complexation by tetrاغyme. The \(^1\)H NMR resonances range from 3.4 to 4 ppm and the \(^{13}\)C NMR resonances range from 58 to 72 ppm. The glyme protons have become noticeably deshielded in comparison to free ligand. Complexation also results in some loss of symmetry for the glyme, as illustrated by the presence of four proton environments in comparison to three for the free ligand. Lastly, the \(^{19}\)F NMR spectrum of 4.3[OTf]₂ contains a single resonance for the triflate at -78.7 ppm.

**4.2.3 Triglyme and Tetrاغyme Complexes of SnCl₂**

Having previously determined that glymes are suitable ligands for the stabilization of Sn(OTf)₂,\(^{13}\) the triglyme and tetrاغyme stabilized SnCl₂ salts were investigated. Half an equivalent of glyme was added to SnCl₂ in CH₂Cl₂ and removal of all volatile components yielded a colourless oil (Scheme 4.4). Colourless crystals were obtained from slow evaporation of a THF or CH₂Cl₂ solution and characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. The structures obtained were of the expected complexes [SnCl-triglyme][SnCl₃] (4.5[SnCl₃]) and [SnCl-tetrاغyme][SnCl₃] (4.6[SnCl₃]).
Scheme 4.4: Synthesis of [SnCl-triglyme][SnCl₃] (4.5[SnCl₃]) and [SnCl-tetraglyme][SnCl₃] (4.6[SnCl₃]).

[SnCl-triglyme][SnCl₃] crystallizes in the space group $P2_1/c$ with one formula equivalent in the asymmetric unit (Figure 4.5). The triglyme is in a planar conformation and binds to SnCl in a belt-like manner. The Sn–Oglyme distances range from 2.459(2) to 2.587(2) Å and are generally longer than those observed for Ge–Oglyme which is expected due to the larger ionic radius.¹⁹ The Sn–Cl bond is perpendicular to the plane defined by the triglyme and the bond length of 2.5106(7) Å is comparable with other polyether stabilized $^+\text{SnCl}$ cations.²⁰-²² The SnCl₃ is present as a distinctly separate anion; the closest Sn$\text{cation}$–Cl$\text{anion}$ separation is 3.900(1) Å. All three Sn–Cl bond lengths are approximately 2.51 Å and are consistent with previously reported structures listed on the Cambridge Structural Database.¹⁷
Figure 4.5: Thermal ellipsoid plot (30% probability surface) of 4.5[SnCl₃]. All hydrogens have been removed for clarity. Selected bond distances (Å): Sn1–Cl1, 2.511(1); Sn1–O1, 2.548(2); Sn1–O2, 2.459(2); Sn1–O3, 2.482(2); Sn1–O4, 2.587(2); Sn2–Cl21, 2.514(1); Sn2–Cl22, 2.505(1); Sn2–Cl23, 2.507(1).

[SnCl-tetraglyme][SnCl₃] (4.6[SnCl₃]) crystallizes in the space group $P2_1/n$, also with one formula equivalent in the asymmetric unit (Figure 4.6). It is structurally similar to 4.5[SnCl₃] upon comparison of bonding motif and metrical parameters. Sn–Oglyme distances range from 2.454(2) to 2.776(3) Å, with one close, two intermediate, and one long contact(s). The cationic SnCl bond length of 2.4514(9) Å is shorter than in 4.5[SnCl₃], but is still comparable with other polyether stabilized $^+$SnCl cations whose bond lengths range from 2.428 to 2.533 Å.²⁰-²² Regarding the SnCl₃ anion, the closest Sn_{cation}–Cl_{anion} distance is 3.676(1) Å and the three bond lengths are all approximately
2.49 Å. ¹H and ¹³C NMR resonances for both 4.5[SnCl₃] and 4.6[SnCl₃] are similar to those observed for the glyme stabilized Ge(II) centres previously described.

Figure 4.6: Thermal ellipsoid plot (30% probability surface) of 4.6[SnCl₃]. All hydrogens have been removed for clarity. Selected bond distances (Å): Sn1–Cl1, 2.451(1); Sn1–O1, 2.776(3); Sn1–O2, 2.517(2); Sn1–O3, 2.454(2); Sn1–O4, 2.513(3); Sn1–O5, 2.663(2); Sn2–Cl21, 2.482(1); Sn2–Cl22, 2.483(1); Sn2–Cl23, 2.452(1).

4.3 Conclusions

These results demonstrate that glymes are suitable ligands for the stabilization of cationic germanium(II) and tin(II) centres. The resultant complexes have been characterized by multinuclear NMR spectroscopy, elemental analysis, and X-ray crystallography. Given the flexible nature of the glymes, the solid state structures appear more dependent on the substituent bound to the Ge or Sn centre. While the tin complexes behave as expected, the glyme stabilized GeCl₂ salts behave unexpectedly. In particular, stabilization by triglyme results in a dimeric structure for both the cation and anion where two Ge(II) centres are bridged by two chlorine atoms. Similarly, the tetraglyme stabilized salt features a dimeric anion. While there are several examples of E₂Cl₂ dimers (E =
Group 13, Sn, Pb), this behaviour is unprecedented in Ge(II) chemistry and requires further investigation and confirmation. This may be provided by mass spectrometry or $^{35}$Cl solid-state NMR which can differentiate between terminal and bridging Cl environments.\textsuperscript{23} Additionally, the reactivity of these complexes towards small molecules is currently being investigated, in light of complexes formed by the related $[\text{Ge}[15]\text{crown-5}][\text{OTf}]_2$.\textsuperscript{24}

4.4 Experimental

4.4.1 Reagents and General Methods

All manipulations were carried out under an anhydrous N$_2$ atmosphere using standard Schlenk line and glovebox techniques at room temperature. CH$_2$Cl$_2$, pentane, Et$_2$O, THF, and toluene were dried by passing through Grubbs'-type alumina columns\textsuperscript{25} and then stored over 4 Å molecular sieves. CD$_3$CN was distilled over CaH$_2$ and then stored over 4 Å molecular sieves. Glymes were distilled over sodium under reduced pressure. GeCl$_2$•dioxane and SnCl$_2$ was purchased from Sigma Aldrich and used without further purification.

All NMR spectra were collected at room temperature using a Bruker Avance 500 MHz spectrometer and chemical shifts are reported in ppm. The resonances in the $^1$H and $^{13}$C NMR spectra were referenced to SiMe$_4$ using appropriate solvent resonances as internal standards. The $^{19}$F NMR spectra were referenced externally to CFCI$_3$ (0 ppm). Elemental analysis was performed at University of Windsor, Ontario, Canada.
4.4.2 Synthetic Procedures

Synthesis of [Ge-triglyme][OTf]₂, 4.1[OTf]₂

Triglyme (0.16 mL, 0.860 mmol) in a solution of CH₂Cl₂ (10 mL) was added dropwise over 10 minutes to a suspension of GeCl₂•dioxane (200 mg, 0.806 mmol) in CH₂Cl₂ (40 mL) followed by the addition of Me₃SiOTf (0.38 mL, 1.720 mmol). The resultant colourless solution was stirred overnight at room temperature followed by removal of all volatile components under reduced pressure to afford a colourless oil. The oil was washed and sonicated in a 1:1.5 solution of ether:pentane and decanted, yielding a white paste. The product was dissolved in toluene and slow evaporation of the solvent afforded a colourless crystalline material characterized as the expected 1:1 complex [Ge-triglyme][OTf]₂. Yield: 33% (154 mg, 280 mmol) ᵃ¹H NMR (CD₃CN): 4.10 (m, 8H, CH₂); 3.76 (m, 4H, CH₂); 3.53 (s, 6H, CH₃). ᵃ¹³C{¹H} NMR (CD₃CN): 120.1 (q, 2C, CF₃SO₃); 73.20 (s, 2C, CH₂); 70.91 (s, 2C, CH₂); 70.29 (s, 2C, CH₂); 59.03 (s, 2C, CH₃). ᵃ¹⁹F{¹H} NMR (CD₃CN): -79.08 (s, 6F, CF₃SO₃). Anal. Calcd. for C₁₀H₁₈F₆GeO₁₀S₂: C, 21.88; H, 3.3. Found: C, 21.74; H, 3.59.

Synthesis of [GeCl-triglyme][GeCl₃], 4.2[GeCl₃]

Triglyme (0.078 mL, 0.430 mmol) in a solution of CH₂Cl₂ (10 mL) was added dropwise over 10 minutes to a suspension of GeCl₂•dioxane (200 mg, 0.860 mmol) in CH₂Cl₂ (40 mL). The resultant colourless solution was stirred overnight at room temperature followed by removal of all volatile components under reduced pressure to afford a colourless oil. The oil was washed and sonicated in a 1:1.5 solution of ether:pentane and decanted, still yielding a colourless oil. The product was dissolved in toluene and slow evaporation of the solvent afforded a colourless crystalline material
characterized as the unexpected dimer of [GeCl-triglyme][GeCl₃]. ¹H NMR (CD₃CN): 3.59 (m, 8H, CH₂); 3.50 (m, 4H, CH₂); 3.32 (s, 6H, CH₃). ¹³C{¹H} NMR (CD₃CN): 72.37 (s, 2C, CH₂); 70.96 (s, 2C, CH₂); 70.92 (s, 2C, CH₂); 58.08 (s, 2C, CH₃).

**Synthesis of [Ge-tetraglyme][OTf]₂, 4.3[OTf]₂**

Tetraglyme (0.38 mL, 1.72 mmol) in a solution of CH₂Cl₂ (10 mL) was added dropwise over 10 minutes to a suspension of GeCl₂•dioxane (400 mg, 1.72 mmol) in CH₂Cl₂ (40 mL) followed by the addition of Me₃SiOTf (0.62 mL, 3.44 mmol). The resultant colourless solution was stirred overnight at room temperature followed by removal of all volatile components under reduced pressure to afford a colourless oil. The oil was washed and sonicated in a 1:1.5 solution of ether:pentane and decanted, yielding a white solid. The product was dissolved in CH₂Cl₂ and slow evaporation of the solvent afforded a colourless crystalline material characterized as the expected 1:1 complex [Ge-tetraglyme][OTf]₂. Yield: 66% (677 mg, 1.14 mmol). ¹H NMR (CD₃CN): 3.99 (m, 4H, CH₂); 3.90 (m, 8H, CH₂); 3.70 (m, 4H, CH₂); 3.44 (s, 6H, CH₃). ¹³C{¹H} NMR (CD₃CN): 121.63 (q, 2C, CF₃SO₃); 71.27 (s, 2C, CH₂); 71.18 (s, 2C, CH₂); 71.16 (s, 2C, CH₂); 69.81 (s, 2C, CH₂); 58.12 (s, 2C, CH₃).¹⁹F{¹H} NMR (CD₃CN): -78.71 (s, 6F, CF₃SO₃). Anal. Calcd. for C₁₂H₂₂F₆GeO₁₁S₂: C, 24.3; H, 3.74. Found: C, 24.63; H, 4.27.

**Synthesis of [GeCl-tetraglyme][GeCl₃], 4.4[GeCl₃]**

Tetraglyme (0.095 mL, 0.430 mmol) in a solution of CH₂Cl₂ (10 mL) was added dropwise over 10 minutes to a suspension of GeCl₂•dioxane (200 mg, 0.860 mmol) in CH₂Cl₂ (40 mL). The resultant colourless solution was stirred overnight at room temperature followed by removal of all volatile components under reduced pressure to afford a colourless oil. The oil was washed and sonicated in a 1:1.5 solution of
ether:pentane and decanted, still yielding a colourless oil. The product was dissolved in toluene and slow evaporation of the solvent afforded a colourless crystalline material characterized as [GeCl-tetraglyme][GeCl$_3$] with the anion having unexpectedly dimerized. Yield: 59% (130 mg, 0.255 mmol). $^1$H NMR (CD$_3$CN): 3.92 (m, 4H, CH$_2$); 3.84 (m, 8H, CH$_2$); 3.67 (m, 4H, CH$_2$); 3.42 (s, 6H, CH$_3$). $^{13}$C$[^1$H] NMR (CD$_3$CN): 71.46 (s, 2C, CH$_2$); 70.92 (s, 2C, CH$_2$); 70.85 (s, 2C, CH$_2$); 69.03 (s, 2C, CH$_2$); 58.73 (s, 2C, CH$_3$). Anal. Calcd. for C$_{10}$H$_{22}$Cl$_4$Ge$_2$O$_5$: C, 23.58; H, 4.35. Found: C, 23.59; H, 4.55.

**Synthesis of [SnCl-triglyme][SnCl$_3$], 4.5[SnCl$_3$]**

Triglyme (0.05 mL, 0.264 mmol) in a solution of CH$_2$Cl$_2$ (10 mL) was added dropwise over 10 minutes was added to a suspension of SnCl$_2$ (100 mg, 0.527 mmol) in CH$_2$Cl$_2$ (30 mL). The resultant colourless solution was stirred overnight at room temperature followed by removal of all volatile components under reduced pressure to afford a colourless oil. The oil was washed and sonicated in a 1:1.5 solution of ether:pentane and decanted, still yielding a colourless oil. The product was dissolved in THF and slow evaporation of the solvent afforded a colourless crystalline material characterized as the expected 1:1 complex [SnCl-triglyme][SnCl$_3$]. Yield: 65% (95 mg, 0.170 mmol). $^1$H NMR (CD$_3$CN): 3.74 (m, 4H, CH$_2$); 3.60 (m, 8H, CH$_2$); 3.42 (s, 6H, CH$_3$). $^{13}$C$[^1$H] NMR (CD$_3$CN): 71.96 (s, 2C, CH$_2$); 71.08 (s, 2C, CH$_2$); 70.77 (s, 2C, CH$_2$); 59.11 (s, 2C, CH$_3$). Anal. Calcd. for C$_8$H$_{18}$Cl$_4$O$_4$Sn$_2$: C, 17.24; H, 3.25. Found: C, 17.36; H, 2.99.
Synthesis of \([\text{SnCl-tetraglyme}][\text{SnCl}_3]\), 4.6[SnCl₃]

Tetraglyme (0.06 mL, 0.264 mmol) in a solution of CH₂Cl₂ (10 mL) was added dropwise over 10 minutes was added to a suspension of SnCl₂ (100 mg, 0.527 mmol) in CH₂Cl₂ (30 mL). The resultant colourless solution was stirred overnight at room temperature followed by removal of all volatile components under reduced pressure to afford a colourless oil. The oil was washed and sonicated in a 1:1.5 solution of ether:pentane and decanted, still yielding a colourless oil. The product was dissolved in CH₂Cl₂ and slow evaporation of the solvent afforded a colourless crystalline material characterized as the expected 1:1 complex \([\text{SnCl-tetraglyme}][\text{SnCl}_3]\). Yield: 41% (65 mg, 0.108 mmol). $^1$H NMR (CD₃CN): 3.91 (m, 4H, CH₂); 3.86 (m, 8H, CH₂); 3.69 (m, 4H, CH₂); 3.45 (s, 6H, CH₃). $^{13}$C{$^1$H} NMR (CD₃CN): 71.44 (s, 2C, CH₂); 71.17 (s, 2C, CH₂); 70.85 (s, 2C, CH₂); 70.02 (s, 2C, CH₂); 58.64 (s, 2C, CH₃). Anal. Calcd. for C₁₀H₂₂Cl₄O₅Sn₂: C, 19.97; H, 3.69. Found: C, 20.05; H, 3.39.

4.4.3 X-ray Crystallography

Each subject crystal was covered in Nujol®, mounted on a goniometer head and rapidly placed in the dry N₂ cold-stream of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were collected using the APEX2 software suite on a Bruker D8 Venture with PHOTON 100 diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073 Å) or CuKα radiation (λ = 1.54178 Å). For each crystal, a hemisphere of data was collected using a counting time of 20 or 30 seconds per frame at -100 °C. Data reductions were performed using the using the APEX2 software suite and the data were corrected for absorption using SADABS.
Each structure was solved by direct methods using SHELXS-2013\textsuperscript{28} and refined by full-matrix least-squares on $F^2$ with anisotropic displacement parameters for the heavy atoms using SHELXL-2013\textsuperscript{28} and the WinGX\textsuperscript{29} software package. The solutions were assessed using tools in PLATON,\textsuperscript{30} and thermal ellipsoid plots were produced using SHELXTL.\textsuperscript{31} CIF files are included in the enclosed CD.

Table 4.1: Summary of Crystallographic Data

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<th>[GeCl-triglyme][GeCl\textsubscript{3}]</th>
<th>[Ge-tetraglyme][OTf]\textsubscript{2}</th>
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theta max

Absorption correction
SADABS SADABS SADABS

Max. and min. transmission
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Refinement method
Full-matrix least-squares on F^2

Data / restraints / parameters
3214 / 0 / 192 3491 / 0 / 165 6013 / 0 / 192

Goodness-of-fit on r^2
1.137 1.059 1.045

Final R indices
R1 = 0.0460, R1 = 0.0267, R1 = 0.0356,
wR2 = 0.1155 wR2 = 0.0668 wR2 = 0.0820

R indices (all data)
R1 = 0.0557, R1 = 0.0291, R1 = 0.0489,
wR2 = 0.1219 wR2 = 0.0695 wR2 = 0.0883

Largest diff. peak and hole (e·Å^3)
0.944 and -0.823 0.816 and -0.670 1.312 and -0.849

4.5 References


26. APEX2 - *Software Suite for Crystallographic Programs*, Bruker AXS, Inc.: Madison, WI, **2009**.

27. SADABS, Bruker AXS Inc.: Madison, WI, **2001**.


Chapter 5

Conclusions and Future Work

Having established that crown ethers are suitable ligands for the stabilization of Ge(II) and other low oxidation state main group elements,\textsuperscript{1-4} the primary focus of this thesis has been to explore the reactivity of crown ether stabilized Ge(II) dications. Of particular interest was the [Ge[15]crown-5]\textsuperscript{2+} species due to the less restrictive binding environment which should facilitate the interaction of Ge with other reagents. Indeed, the treatment of [Ge[15]crown-5][OTf]\textsubscript{2} with one equivalent of H\textsubscript{2}O and NH\textsubscript{3}, yielded the first stable water and ammonia adducts of germanium(II). It was found that upon complexation, the protons on water and ammonia were rendered more acidic. Thus, the deprotonation of these complexes was investigated in pursuit of compounds containing unsaturated germanium centres. Currently, only the deprotonation of the water adduct has been studied. This was successful as assessed by \textsuperscript{1}H NMR and XRD of the conjugate acids, however, the hydroxide or monoxide have yet to be structurally characterized. Future work will focus on isolating the aforementioned products, in addition to the deprotonated products of the ammonia, alcohol and amine complexes. The synthetic potential of these complexes, particularly through OH or NH activation, is also of interest.\textsuperscript{5}

While water and ammonia form stable donor-acceptor complexes, the direct addition of H\textsubscript{2}S and PH\textsubscript{3} to [Ge[15]crown-5][OTf]\textsubscript{2} at room temperature results in the precipitation of GeS and GeP as solids or films. Their compositions were confirmed by energy dispersive X-ray spectroscopy (EDS). Both of these products have been noted for their electrical and optical properties and recent work has focused on the fabrication of
thin films, nanoparticles, or nanosheets for use in photovoltaics,\textsuperscript{6,7} batteries,\textsuperscript{8,9} and optical electronics.\textsuperscript{9-11} These materials have been synthesized with a variety of techniques, including sol-gel process, chemical vapour deposition (CVD), and atomic layer deposition (ALD). The approach discussed in this thesis is conducted at room temperature and therefore presents an advantage over the previously mentioned techniques. However, the fabrication of GeS and GeP films is uncontrolled and optimization will require using techniques such as spin coating. The resultant materials will be characterized using various techniques, such as EDS, scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), conductivity and optical measurements.

Lastly, glymes were shown to be suitable ligands for the stabilization of Ge(II) and Sn(II). While the tin complexes behave as expected, the glyme stabilized GeCl\textsubscript{2} salts behave unexpectedly. In particular, stabilization by triglyme results in a dimeric structure for both the cation and anion where two Ge(II) centres are bridged by two chlorine atoms. Similarly, the tetruglyme stabilized salt features a dimeric anion. This behaviour is unprecedented in Ge(II) chemistry. Further investigation and confirmation of the solid state structures can be provided by mass spectrometry or \textsuperscript{35}Cl solid-state NMR which can differentiate between terminal and bridging Cl environments.\textsuperscript{12} Additionally, the reactivity of these complexes towards small molecules are currently being investigated. Given the more flexible nature of the glymes, in comparison to crown ethers, the Ge and Sn centres should be even more amenable to further chemistry. These results will be compared to and contrasted with the products formed by the related [Ge[15]crown-5][OTf]\textsubscript{2}, as outlined in Chapters 2 and 3. Moreover, future work will also investigate the
coordination chemistry of polyethylene glycol (PEG), the polymeric form of glyme. This ligand offers the possibility of isolating Ge(II) and Sn(II) as nanoparticles or “naked” dications. A similar study was conducted by Mills, wherein he successfully isolated Au, Pd, and Ag particles from their respective complexes using PEG and polyvinyl alcohols.\(^\text{13}\)

5.1 References

Appendices

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I, Rajoshree Bandyopadhyay, give Jennifer H. Nguyen permission to use the results and ideas published in the paper entitled “Water and Ammonia Complexes of Germanium(II) Dications” in her thesis. I was the first to synthesize the water and ammonia adducts under the supervision of Dr. Charles L. B. Macdonald.

Rajoshree Bandyopadhyay

September 16, 2014

I, Ala’aeddeen Swidan, give Jennifer H. Nguyen permission to use the results and ideas published in the paper entitled “Water and Ammonia Complexes of Germanium(II) Dications” in her thesis. I characterized the ammonia adduct using $^{14}$N and $^{15}$N NMR under the supervision of Dr. Charles L. B. Macdonald.

Ala’aeddeen Swidan

September 16, 2014
Consent to use work from the unpublished, joint research project featured in Chapter 3 “The Reactivity of Polyether Germanium(II) Dications Towards Hydrogen Sulfide and Phosphine”

I, Jonathan W. Dube, give Jennifer H. Nguyen permission to use the results and ideas published in the chapter entitled “The Reactivity of Polyether Germanium(II) Dications Towards Hydrogen Sulfide and Phosphine” in her thesis. I studied the reactivity of the polyether complexes towards phosphine and characterized the products under the supervision of Dr. Paul J. Ragogna.

Jonathan W. Dube

October 15, 2014

I, Paul J. Ragogna, give Jennifer H. Nguyen permission to use the results and ideas published in the chapter entitled “The Reactivity of Polyether Germanium(II) Dications Towards Hydrogen Sulfide and Phosphine” in her thesis. The work done by Jonathan W. Dube was done under my supervision.

Paul J. Ragogna

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Consent to use work from the unpublished, joint research project featured in Chapter 4 “Glyme Complexes of Germanium(II) and Tin(II)”

I, Warren W. Friedl, give Jennifer H. Nguyen permission to use the results and ideas published in the chapter entitled “Glyme Complexes of Germanium(II) and Tin(II)” in her thesis. I synthesized [Ge-tetraglyme][OTf]₂ under the supervision of Dr. Charles L. B. Macdonald.

Warren W. Friedl

October 15, 2014

I, Joanne Yu, give Jennifer H. Nguyen permission to use the results and ideas published in the chapter entitled “Glyme Complexes of Germanium(II) and Tin(II)” in her thesis. I was supervised by Jennifer when synthesizing [GeCl-triglyme][GeCl₃] under the supervision of Dr. Charles L. B. Macdonald.

Joanne Yu

October 15, 2014

A2: Supplementary Information

Supplementary information for each chapter including CIF files and summaries of the optimized structures, including electronic energies and Cartesian components for each of the atoms are provided with the enclosed CD.
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