Chlorine-35 Solid-State NMR Spectroscopy as an Indirect Probe of Germanium Oxidation State and Coordination Environment in Germanium Chlorides

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ABSTRACT: Due to the prevalence of Ge−Cl bonds in germanium chemistry and the inherent challenges of germanium-73 NMR spectroscopy, chlorine-35 NMR spectroscopy was investigated as an indirect method of characterization for these ubiquitous and useful compounds. Chlorine-35 NMR parameters were correlated with structural metrics as well as the oxidation state of germanium.

INTRODUCTION

Germanium chlorides are a fundamentally important class of compounds. GeCl4 and GeCl2·dioxane are useful, convenient, and ubiquitous starting materials for the synthesis of germanium-(IV) and germanium(II) compounds, respectively. In recent years, a wealth of unprecedented stable low valent germanium complexes have been synthesized, most of which are made starting from a germanium chloride and many retain an interaction between germanium and the halogen. Given the prevalence and importance of germanium chlorides, it is important to have an understanding of the electronic structure at the reactive center including the oxidation state of germanium; however, methods for the determination of the oxidation state of germanium are not readily available, and furthermore, the oxidation state of the heavier group 14 elements is not always readily assigned.

Thus far, the most useful tool for the characterization of low valent and cationic germanium halides has been X-ray crystallography. However, accurate crystallographic characterization requires high quality single crystals of a suitable size, which can be very challenging to grow. Additionally, crystallography provides insight into the coordination environment, but not the electronic structure of the molecule. While Mössbauer spectroscopy can be used to assess oxidation states, it is only commonly employed for iron, tin, antimony, and iodine, while many other elements, germanium included, lack an appropriate gamma ray source. A useful tool for assessing oxidation states is a synchrotron technique, X-ray Absorption Near Edge Structure (XANES). While XANES is feasible for main group compounds, a more readily accessible methodology is desirable.

It is increasingly possible to obtain structural and electronic information from powder samples by solid-state NMR (SSNMR) spectroscopy. The quadrupolar parameters of 93Nb have previously been shown to be sensitive to the oxidation state of the niobium center, with niobium(V) compounds exhibiting larger $C_Q$ [93Nb] values than niobium(I). Additionally, a relationship was observed between the oxidation state of metals in the second coordination sphere of octahedral niobates and the CSA [93Nb] tensor. Niobium is a nucleus for which Mössbauer spectroscopy is not available, and thus, oxidation states are generally assessed by X-ray photoelectron spectroscopy (X-ray PES). A major obstacle to the application of SSNMR spectroscopy for the characterization of germanium compounds is the unfavorable NMR properties of 73Ge. While its homologues 13C, 29Si, 119Sn, and 207Pb, all with a spin of 1/2, are relatively routine nuclei for NMR spectroscopy, germanium possesses considerably less favorable NMR properties. 73Ge, the only NMR active isotope of germanium, is quadrupolar with a spin of 9/2 and has a moderate quadrupole moment of $-19.6 \text{ mb}$. 73Ge also has a low natural abundance (7.76%); however, the greatest challenge is that 73Ge has one of the smallest gyromagnetic ratios in the periodic table, corresponding to a Larmor frequency of only 31.4 MHz at 21.1 T (900 MHz for 1H). While 73Ge is a challenging nucleus, higher field instruments, which offer a more favorable Boltzmann distribution as well as diminished broadening from the second order quadrupolar interaction, and new sensitivity-enhancement pulse sequences have made 73Ge NMR spectroscopy accessible under favorable conditions of either high symmetry at germanium or high (>4 Ge atoms/1000 Å³)20 germanium content in the sample. However, perfect spherical symmetry at germanium is not common.

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Furthermore, many interesting germanium compounds are kinetically stabilized by bulky ligands, and as a consequence, the overall germanium content in a given volume is low. Lower concentrations of germanium in the unit cell lead to lower signal-to-noise ratios, much like in solution. As a result, it has not been possible to obtain sufficient data to determine whether there is a relationship between $^{73}$Ge NMR parameters and the oxidation state of germanium.

Due to the prevalence of Ge–Cl bonds in germanium chemistry, we are interested in exploring solid-state $^{35}$Cl NMR spectroscopy as an indirect method for obtaining information about germanium. Using spectra of an attached atom is not unprecedented, for example, $^{31}$P J-coupling constants have been shown to be related to rhodium oxidation states. Phosphorus has also been used to provide additional information about quadrupolar nuclei. To assess chlorine as a potential source of information, we chose to undertake a systematic investigation of various compounds containing Ge–Cl bonds to determine what information about the germanium oxidation state and coordination environment might be determined from the $^{35}$Cl NMR parameters. To fully examine the scope of the technique, we included examples of both germanium(II) and the more common germanium(IV) compounds.

There are two NMR active isotopes of chlorine: $^{35}$Cl and $^{37}$Cl. Both are quadrupolar with a spin of 3/2 and have large quadrupole moments ($Q = -81.65$ mb for $^{35}$Cl, $-64.35$ mb for $^{37}$Cl), which results in extremely broad NMR signals in the absence of spherical symmetry. Both isotopes are considered to be low gamma with Larmor frequencies of 88.19 MHz ($^{35}$Cl) and 73.41 MHz ($^{37}$Cl) at 21.1 T. Due to the much higher natural abundance of $^{35}$Cl (75% versus 25% for $^{37}$Cl), it is generally the preferred isotope for NMR spectroscopy; however, $^{37}$Cl studies are also feasible and are sometimes used as a method of verifying $^{35}$Cl parameters. Extremely broad quadrupole NMR spectra are much more easily acquired at ultrahigh (>18.8 T) magnetic field due to the inverse relationship between the second order quadrupolar broadening and the magnetic field strength. Additionally, the study of these nuclei has benefited greatly from the use of Quadrupolar Carr Purcell Meiboom Gill (QCPMG) and related pulse sequences. In the QCPMG sequence, a 90° pulse is followed by a 180° refocusing pulse, as in the standard spin–echo experiment. Rather than allowing the magnetization to decay normally, it is instead repeatedly refocused by a series of 180° pulses. When the echo train is Fourier transformed, the broad signal is collected into a series of spikelets, leading to an improved signal-to-noise ratio. Due to the extreme breadth of typical $^{35}$Cl NMR spectra, it is often necessary to acquire multiple subspectra at evenly spaced transmitter frequencies which are then added together to give the total spectrum. Recently introduced adiabatic Wideband Uniform Rate Smooth Truncation (WURST) pulses have greatly improved the excitation profile of the QCPMG sequence. While stepwise spectral acquisition is often still required, the overall number of subspectra required is greatly reduced, thereby considerably shortening the total acquisition time.

Several recent reviews on $^{35}$Cl NMR spectroscopy have been published. Through a combination of stepwise acquisition and the WURST-QCPMG pulse sequence, it has become increasingly feasible to study chlorine in a covalent environment in addition to simple ionic inorganic chlorides. Recently, a series of chloride substituted group IV transition metal catalysts was examined. Through the use of $^{35}$Cl SSNMR spectroscopy and DFT calculations, a structure was proposed for Schwartz’s reagent, an important catalyst for which X-ray quality single crystals had not been obtained. Particularly notable is an investigation of organic chlorides featuring chlorine covalently bound to carbon, which have the largest quadrupolar coupling constants observed by NMR spectroscopy to date ($Q_{\text{Cl}}[^{35}\text{Cl}] = 66–75$ MHz). Uncomplexed GeCl$_2$ has also been studied by $^{35}$Cl SSNMR spectroscopy. A single narrow signal was observed under static conditions with an estimated $\eta_\text{Q}$ of less than 40 kHz. The crystal structure of GeCl$_2$ is unknown and had previously been proposed to be similar in structure to the distorted octahedral GeBr$_2$. However, the combined $^{35}$Cl and $^{73}$Ge SSNMR data suggest a structure similar to the regularly octahedral GeI$_2$, with high symmetry at both germanium and chlorine and a single halogen site. This illustrates the potential utility of $^{35}$Cl SSNMR spectroscopy in probing the coordination environment of germanium.

In comparison to the relatively few examples of $^{35}$Cl NMR spectroscopic studies of group 14 chlorides, there have been a considerable number of investigations of germanium chlorides by nuclear quadrupole resonance (NQR) spectroscopy. These investigations have largely focused on compounds with germanium in the higher oxidation state due to the prevalence of (IV) compounds compared to germanium(II) compounds. At the time of these studies, there were very few stable compounds with germanium in the +2 oxidation state. A particularly notable study used ab initio calculations of NQR frequencies to relate the quadrupolar frequency to the Ge–O bond length. A considerable advantage of NMR spectroscopy over NQR is the ability to directly measure the value of $\eta_\text{Q}$, which provides additional information about the symmetry around chlorine.

In this study, we focus on a variety of low valent germanium chlorides stabilized by a donor and shown in Figure 1. Solid-state NMR parameters are strongly influenced by structure, and thus, the most prominent structural features of the germanium chlorides 1–6 are reviewed here.

While GeCl$_2$ is a nominally stable germylene, it is only isolated in polymeric form. A more convenient starting material for the synthesis of germanium(II) compounds is germanium dichloride complexed with dioxane (GeCl$_2$-dioxane, 1). This complex is readily synthesized from GeCl$_4$ and is stable under inert conditions. GeCl$_2$-dioxane is a coordination polymer composed of infinite chains of alternating GeCl$_2$ and dioxane units. There is one crystallographically unique germanium site ($C_2$ symmetry) and one unique chlorine site ($C_2$ symmetry). The germanium atom has two strong covalent bonds to chlorine atoms (Ge–Cl bond

![Figure 1. Germanium(II) complexes examined in this study.](image-url)
length = 2.281 Å) and two weak bonds to the oxygen of the dioxane (Ge−O distance = 2.3999 Å; a typical Ge−O bond length falls in the range of 1.75−1.85 Å42). Additionally, there are two nonbonded chlorides found at a distance of 3.463 Å from the adjacent Ge, resulting in an overall pseudo-octahedral geometry at germanium and a pseudobridging environment for chlorine (Figure 2).

Two N-heterocyclic carbene (NHC) complexes of GeCl2 (243 and 3 (iPrNHCGeCl2)44) were also included in the investigation. Complex 2, with methyl groups on the nitrogen of the NHC ligand, features a long-range (3.732 Å) interaction between the chloride of one complex and the germanium of the adjacent molecule (Figure 2). With larger isopropyl groups on nitrogen, as in complex 3, the molecules are not in close enough proximity to each other for a chloride to interact with the germanium of an adjacent complex (shortest Ge( adjacent)−Cl distance > 6.9 Å), leading to a truly terminal environment for the chloride.

Two GeCl2 complexes with neutral nitrogen donors, 2,2′-bipyridine (4; bipyrGeCl2) and 1,10-phenanthroline (5), were also investigated. The bipyridine complex 4 resembles GeCl2-dioxane in that a long-range Ge−Cl contact (3.658 Å) leads to a pseudo-octahedral environment at germanium.71 Unlike GeCl2-dioxane, the covalent Ge−Cl bonds in the bipyridine complex are of different lengths (Ge−Cl(1) = 2.5428 Å and Ge−Cl(2) = 2.7195 Å) leading to two crystallographically distinct chlorine sites. In contrast, the phenanthroline complex 5 (phenGeCl2) is a weakly associated centrosymmetric dimer with one terminal chloride site (Ge−Cl = 2.3145 Å) and the other chloride (Ge−Cl = 2.6276 Å) forming a weak bridging interaction (Figure 2).71

A cationic germanium(II) complex stabilized by benzo-15-crown-5 (6; benzo-15-cr-5-GeCl+) was also included in this study.45 In this case, the single chloride is in a terminal position, with a Ge−Cl bond length of 2.288 Å and no interaction with the adjacent ions. While a series of cationic crown ether complexes is known,45,46 the benzo-15-crown-5 derivative was specifically selected for this study because the counterion is triflate rather than GeCl3−, simplifying the expected 35Cl NMR spectrum.

As the +4 oxidation state is far more common in germanium chemistry, two prototypical germanium(IV) chlorides were also investigated (Figure 3). The two related compounds, dichlorodimesitylgemane (7) and chlorotrimesitylgemane (8), are, given the large size of the mesityl group, believed to feature chlorine in a terminal environment as is typical in germanium(IV) chemistry.42 Neither of these compounds have a known crystal structure.

To complement the Ge−Cl study, a cationic cryptand complex of tin chloride (9)47 was included (Figure 3). While a cryptand is used instead of a crown ether, 9 is, in general terms, quite similar to 6: a macrocyclic ether is used to stabilize a reactive group 14 cation in the +2 oxidation state. As would be expected for a larger atom, the Sn−Cl bond length (2.532 Å) is notably longer than what was observed for the germanium cation.

■ RESULTS

**Solid-State NMR Spectroscopy.** Attempts were made to obtain 73Ge spectra for compounds 1−5 and 7, but only the spectrum of 1 was successfully acquired.48 GeCl2-dioxane has a very high germanium concentration, making it possible to obtain a spectrum with a reasonable signal-to-noise ratio despite the large CQ value leading to a broad signal. The ligands in 2−5 and 7 are much bulkier than dioxane, leading to a lower overall germanium content in the unit cell. Additionally, in some cases the quadrupolar chlorines may result in short T2 relaxation times. Since the QCPMG signal enhancement comes in part from the ability to refocus the signal repeatedly before decay, a short T2 leads to minimal benefit. As direct observation of the germanium center was not a feasible method of characterization for compounds 2−8, we investigated 35Cl SSNMR spectroscopy as an alternate means of characterization.

A summary of the experimental 35Cl NMR results is presented in Table 1. The 35Cl SSNMR spectra of complexed gemenylenes 1−6 differed considerably from that of uncomplexed GeCl2.35 While GeCl2 gave rise to remarkably narrow lines, the signals in this study are more typical of covalent chlorides with pronounced quadrupolar lineshapes. Clearly, the environment around germanium has an impact on the 35Cl NMR parameters, particularly in cases where there is a strongly bound electron donor altering the symmetry at germanium.
Table 1. Summary of Experimental $^{35}$Cl NMR Parameters from Static NMR Spectra Acquired at 21.1 T

<table>
<thead>
<tr>
<th>compound</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$C_Q$ [$^{35}$Cl] (MHz)</th>
<th>$\eta_Q$</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa^a$</th>
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<tr>
<td>1</td>
<td>300(50)</td>
<td>28.3(1)</td>
<td>0.055(10)</td>
<td>250(100)</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>200(50)</td>
<td>29.3(1)</td>
<td>0.12(2)</td>
<td>300(100)</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>150(50)</td>
<td>28.6(3)</td>
<td>0.23(5)</td>
<td>n.a.$^b$</td>
<td>n.a.$^b$</td>
</tr>
<tr>
<td>4</td>
<td>200(50)</td>
<td>15.3(1)</td>
<td>0.13(2)</td>
<td>n.a.$^b$</td>
<td>n.a.$^b$</td>
</tr>
<tr>
<td>5</td>
<td>250(50)</td>
<td>14.1(1)</td>
<td>0.10(2)</td>
<td>250(100)</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>250(50)</td>
<td>13.8(1)</td>
<td>0.15(2)</td>
<td>200(100)</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>300(50)</td>
<td>29.6(1)</td>
<td>0.18(2)</td>
<td>n.a.$^b$</td>
<td>n.a.$^b$</td>
</tr>
<tr>
<td>8</td>
<td>300(100)</td>
<td>25.1(1)</td>
<td>0.10(2)</td>
<td>350(100)</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>200(100)</td>
<td>43.0(5)</td>
<td>0.1(1)</td>
<td>n.a.$^b$</td>
<td>n.a.$^b$</td>
</tr>
<tr>
<td>10</td>
<td>200(50)</td>
<td>41.5(5)</td>
<td>0</td>
<td>n.a.$^b$</td>
<td>n.a.$^b$</td>
</tr>
<tr>
<td>11</td>
<td>200(50)</td>
<td>19.0(1)</td>
<td>0.15(5)</td>
<td>n.a.$^b$</td>
<td>n.a.$^b$</td>
</tr>
</tbody>
</table>

$^a$Euler angles were set to $\alpha = \beta = \gamma = 0$ due to the small effect of CSA. $^b$ n.o. = not observed.

The $^{35}$Cl SSNMR spectrum of 1 provides an excellent illustration of the advantages of the WURST-QCPMG pulse sequence over the simple QCPMG sequence. The QCPMG spectrum of 1 (Figure 4A) required the acquisition of 13 individual subspectra at 100 kHz offset over a total of 9 h. The use of the WURST-QCPMG sequence (Figure 4B) reduced the number of subspectra required to two and the total acquisition time to 45 min. Additionally, the overall line shape of the coadded spectrum was much smoother using the WURST-QCPMG sequence, making the central discontinuity easier to detect and thus increasing the accuracy of the $^{35}$Cl NMR parameters extracted from analytical simulations.

Although the interaction between the electric field gradient (EFG) and the quadrupole moment of the chlorine nucleus is the dominant interaction for $^{35}$Cl, it was not possible to accurately reproduce the position of the central discontinuity of the spectrum of GeCl2·dioxane without including chemical shielding anisotropy (CSA; Figure 4B). Proper positioning of the central discontinuity of the spectrum required a span of approximately 250 ppm ($\kappa = 1$). Due to the small effect of the CSA on the spectrum, Euler angles were all left at zero, although there is no symmetry element requiring this. The quadrupolar coupling constant of 28.3 MHz is consistent with the low symmetry environment around chlorine$^{41}$ and falls within the range observed for group 13 chlorides$^{49}$ and well below the values determined for organic chlorides containing covalent C–Cl bonds.$^{34}$ The quadrupolar asymmetry parameter ($\eta_Q = 0.055$) corresponds to an essentially axially symmetric environment despite the fact that there is not a $C_3$ or higher axis through the Ge–Cl bond. Terminal chlorides tend to have small ($<$0.2) $\eta_Q$ values even in the absence of axial symmetry, while bridging chlorides tend to have larger $\eta_Q$ values,$^{33,50}$ suggesting that the long-range pseudobridging interaction observed in the X-ray structure of$^{41}$ is not strong enough to disrupt the overall symmetry of the EFG tensor.

While the two NHC complexes of GeCl2 (2 and 3) are extremely similar in structure as determined by X-ray crystallography$^{35,44}$ the $^{35}$Cl SSNMR spectra exhibit distinct differences (Figure 5). Complex 2 has a somewhat broader $^{35}$Cl spectrum than GeCl2·dioxane, with a $C_Q$ [$^{35}$Cl] value of 29.3 MHz. To fit the spectrum of 2 acquired at 21.1 T accurately, a small amount of CSA interaction ($\Omega = 300$ ppm) must be included. The parameters were verified by fitting the spectrum acquired at 9.4 T (Figure S1) with the same values. The sharp signal around 0 ppm in both spectra is likely the hydrochloride salt of the N-heterocyclic carbene arising as a decomposition product due to the air and moisture sensitivity of these compounds. The considerably poorer signal-to-noise ratio of 3 can be attributed to the shorter $T_2$ relaxation as estimated from the FID leading to decreased signal enhancement from the WURST-QCPMG pulse sequence. The rapid relaxation likely arises from crystal packing effects allowing greater mobility in the isopropyl groups when compared to the methyl groups in 2. The spectrum of 3 was fit with $C_Q$ [$^{35}$Cl] = 28.6 and $\eta_Q = 0.23$. Due to the poor signal-to-noise ratio, it was not possible to determine any contributions from CSA.

The $^{35}$Cl SSNMR spectrum of 4 (Figure 6) shows two distinct overlapping signals, one with $C_Q$ [$^{35}$Cl] = 14.1 MHz and the other with $C_Q$ [$^{35}$Cl] = 15.3 MHz. A WURT-Echo spectrum was acquired in addition to the WURST-QCPMG spectrum in order to resolve the high frequency discontinuities of the individual signals. Both signals have nonzero $\eta_Q$ values (0.10 and 0.13, respectively) which suggest somewhat less than axial symmetry. A small CSA ($\Omega = 250$ ppm) was required to fit the narrower signal, but the overlap of the two signals meant that the central discontinuity that has proven crucial for CSA determination in the other complexes was not visible for the broader signal in this spectrum. While both chlorides in 4 are found in similar...
pseudobridging environments, the Ge–Cl bond lengths differ by 0.3 Å, \(^{71}\) which leads to different EFG tensors, a difference which was also observed at 9.4 T (Figure S2). The resolution of the two signals is notable as it is uncommon (though not unprecedented\(^ {34}\)) to observe separate chlorine sites except in cases where one Site corresponds to which signal. The dramatic difference in chlorine site symmetry. To see Table S2 for experimental conditions.

The dramatic difference is readily explained by the fact that one chlorine site is weakly bridging while the other is terminal, although it is not possible to conclude from the data alone which site corresponds to which signal.

Consistent with the low symmetry of a terminal chloride, the \(^{35}\)Cl SSNMR spectrum of [benzo-15-crown-5-GeCl][OTf], 6, has a \(\eta \) value of 0.18. A skew value indicative of axial symmetry was consistent with the near axial \(\eta \) value (0.1). On the basis of the relatively small magnitude of the CSA in comparison to the EFG interaction, the error is quite large on the former.

The \(^{35}\)Cl SSNMR spectrum of Mes\(_2\)GeCl\(_2\) (7; Figure 8) differed considerably from the spectra of the germanium(II) compounds. The signal was considerably broader, spanning approximately three megahertz at 21.1 T. The quadrupolar coupling constant of 43 MHz was the largest observed in this study, though larger are known.\(^ {24,52}\) The \(^{35}\)Cl SSNMR spectrum of Mes\(_2\)GeCl (8) exhibited similar features, with a \(\eta \) value of 41.5 MHz. Notably, organic chlorides, for which all published data concerns carbon(IV), exhibit \(\eta \) values even larger than those observed for the germanium(IV) compounds.\(^ {38}\) While there are no other \(^{35}\)Cl data available for germanium(IV) compounds, studies by nuclear quadrupole resonance (NQR) exhibited quadrupolar frequencies ranging from 17.8 to 25.7 MHz, corresponding to \(\eta \) values of approximately 35.6 to 51.4 MHz.\(^ {37}\) Interestingly, CsGeCl\(_3\), a germanium(II) compound, has a quadrupolar frequency of 12.1 MHz, corresponding to a \(\eta \) value of approximately 24.2 MHz.

The \(^{35}\)Cl SSNMR spectrum of the tin cryptand complex 9 (Figure 9) was quite similar to that of the germanium(II) complexes. The signal has a similar \(\eta \) value at 0.15 and a \(\eta \) value of 19 MHz, which falls well within the range determined for the germanium(II) compounds. The quadrupolar coupling constant is somewhat smaller than that observed for the cationic crown ether complex 6. Unlike the crown ether complex, the counterion for the tin cation contains chlorine, SnCl\(_3\).\(^ {72}\) DFT calculations (vide infra) were, thus, required to determine whether the signal observed arose from the cation or the anion or the two signals being similar enough to be unresolvable.

**DISCUSSION**

Overall, the clearest trend observed is the relationship between the magnitude of the quadrupolar coupling constant and the presumed oxidation state of the attached germanium (Figure 10). Both germanium(IV) compounds exhibit considerably larger \(\eta \) values (\(\eta > 40 \text{ MHz}\)) than any of the germanium(II) compounds studied (\(\eta \) = 10–30 MHz). Due to the small values of \(\eta \) observed by SSNMR spectroscopy, doubling the quadrupole frequency observed by NQR gives a reasonable approximation of the \(\eta \) value for a compound, and thus, values obtained from NQR spectroscopy\(^ {35}\) are included to better illustrate the \(\eta \) range of germanium(IV) compounds. Out of 26 examples of germanium(IV) compounds collected by Semin et al., 23 have \(\eta \) values greater than 40 MHz, with the remaining three examples having \(\eta \) values between 34 and 40 MHz.\(^ {35}\) This marked difference between the +4 and +2 oxidation states can be attributed to the covalent bond distorting the electron

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**Figure 5.** Static \(^{35}\)Cl WURST-QCPMG NMR spectra of (A) 2 and (B) 3 at 21.1 T. Dotted traces indicate empirical simulations. An impurity of the hydrochloride salt of the carbene is indicated by an asterisk. The rightmost discontinuity in the spectrum of 3 was confirmed by an additional experiment with a longer acquisition time of 16 h (shown as inset, see Table S2 for experimental conditions).
distribution around chlorine. A higher oxidation state at germanium causes more electron density to be polarized away from chlorine, and thus, a larger electric field gradient, leading to the higher $C_Q$ values. Larger electric field gradients in species with extensive covalent bonding are described by the Townes–Dailey theory in nuclear quadrupole resonance.\textsuperscript{53} The marked difference makes $^{35}$Cl SSNMR spectroscopy a potentially useful tool for the assessment of oxidation states.
The SSNMR approach would require only that there be a chloride attached to the metalloid. This technique may complement the use of XANES, X-ray PES, and Mössbauer spectroscopy. Notably, GeCl, the only germanium(I) chloride studied by $^{35}$Cl NMR spectroscopy, has an average $C_Q[^{35}\text{Cl}]$ value of 5.5 MHz. Notably organic chlorides of carbon(IV) also exhibit very large $C_Q[^{35}\text{Cl}]$ values.

The $C_Q[^{35}\text{Cl}]$ values observed for the germanium(II) series are similar to those observed for transition metal metallocene complexes, consistent with a less covalent bond than in organic chlorides.

Within the germanium(II) series, complexes with related ligands had similar $C_Q[^{35}\text{Cl}]$ values. For example, the $C_Q[^{35}\text{Cl}]$ of complexes with oxygen donors at Ge (e.g., 1 and 6) fall within a 5 MHz range. The $C_Q$ of ligands with carbon donor atoms (e.g., 2 and 3) fall within an even smaller 1 MHz range. However, while three of the four signals from complexes with nitrogen donors fall
within a 5 MHz range, the terminal site of complex 5 has a much larger $C_\phi$ value, suggesting that the relationship between ligands arises because similar donor strengths lead to similar Ge−Cl bond lengths rather than any direct impact of the ligand on $C_\phi$ values.

The $C_\phi$ values for 1−9 range from 0 for the axially symmetric Mes$_3$GeCl (8) to 0.23 for the isopropyl-substituted NHC complex of GeCl$_2$ (3). $C_\phi$ values of less than 0.2 generally indicate near axial symmetry at the nucleus of interest; however, it is notable that the largest $C_\phi$ values of compounds where the chlorine is bound to carbon was observed for an aryl chloride ($C_\phi = 0.139$) despite the absence of C$_3$ or higher axis through the C−Cl bond.34

To develop solid-state NMR spectroscopy as a tool for structural characterization, it is necessary to determine if spectroscopic parameters can be correlated to structural metrics. Thus, correlations between the crystallographically determined structural metrics and the NMR spectral parameters were examined. A relationship between longer M−Cl bond lengths and smaller $C_\phi$ [35Cl] value has been observed previously for the Cp$_2$MCl series.35 Within the series germanium(II) complexes 1−6, there was a linear relationship ($R^2 = 0.90$) between the inverse of the Ge−Cl bond length cubed and the magnitude of $C_\phi$ [35Cl] (Figure 11A), with longer bonds leading to smaller $C_\phi$ values. If the germanium(IV) complexes are included in the fit, the trend becomes less linear ($R^2 = 0.74$). The trend in $C_\phi$ [35Cl] values may be a consequence of the covalency of the Ge−Cl bond and may also explain the low $C_\phi$ value for GeCl$_2$ as the germanium(I) halides are not expected to have traditional covalent bonds.34 Likewise, the high symmetry in GeCl$_2$ may arise from the Ge−Cl bonds having low covalent character.35 Indeed, Natural Bond Order calculations on complexes 1−6 at the TPSSTPSS/6-311+G** level revealed Ge−Cl bond orders well below the value of 1 expected for a traditional covalent bond. While the germanium(IV) compounds are predicted to have shorter Ge−Cl bonds from the geometry-optimized structures, the experimental $C_\phi$ [35Cl] values fall well above those predicted by extrapolation of the trend observed for the germanium(II) compounds. Apparently, the distortion of the electron distribution around chlorine resulting from proximity to germanium is greater when there is a higher germanium oxidation state. The experimental $C_\phi$ value for 9 also does not follow the exact trend due to the difference in electronegativity between germanium and tin.

The average angle between chlorine, germanium, and the donor atom correlated weakly to $C_\phi$ (Figure 11B), with wider bond angles corresponding to larger $C_\phi$ values in a linear manner ($R^2 = 0.76$). If the covalently bound substituents are regarded as being donors, the germanium(IV) compounds 7 and 8 fit the trend of wide angles corresponding to large $C_\phi$ values (using the geometry-optimized structures).

**Computational Investigations.** Theoretical calculations are increasingly used as a complement to SSNMR spectroscopy. In complexes 4, 5, and 9, where two distinct chloride sites exist, calculations are the only way to assign the observed signal(s) by comparison of the experimental to the predicted parameters. The calculation of SSNMR parameters also makes it possible to determine the orientations of the individual tensor components, which can then be used to rationalize the trends observed.
experimentally. Finally, the accurate calculation of NMR parameters can offer support for a geometry-optimized structure when there is not an X-ray structure available.

Previous calculations of $^{35}$Cl SSNMR parameters have been performed using plane wave pseudopotentials using CASTEP.\textsuperscript{35,50,55} The CASTEP code is optimized for calculations on periodic inorganic solids.\textsuperscript{56} Calculations model electron distribution throughout the entire unit cell, and thus, require extensive computational resources for substances with large unit cells. Of the compounds included in this study, only GeCl$_2$-dioxane (1) had a unit cell small enough for CASTEP calculations. The other complexes crystallized in unit cells with too large (>1000 Å) to model in CASTEP with the available computational resources. The experimental $^{35}$Cl SSNMR parameter ($\eta_Q$ and $C_Q$) values of organic chlorides\textsuperscript{34} and trimethylammonium chloride\textsuperscript{37} have been reasonably reproduced using DFT calculations at the B3LYP/6-311+G** level of theory on isolated molecules using the solid-state geometry as determined by X-ray diffraction. As the complexes in this study are molecular solids, Gaussian 09 calculations also appeared appropriate. No thorough investigation of Gaussian methodology for the calculation of $^{35}$Cl SSNMR parameters has been undertaken to date. Model chemistries were assessed using GeCl$_2$-dioxane (1) as it was possible to calculate NMR parameters for this complex using CASTEP, giving a point of comparison to established methodology. A thorough discussion of the assessment can be found in the Supporting Information.

A summary of the computational results is presented in Table 2. As the TPSSTPSS/6-31G* methodology proved to be the most accurate and efficient for GeCl$_2$-dioxane (1), it was employed for all subsequent calculations of $^{35}$Cl NMR parameters. Hydrogen positions were optimized at the TPSSTPSS/6-31G* level. The $^{35}$Cl CSA interaction was overestimated in all cases, ranging from 300 to 600 ppm while the experimental values ranged from 200 to 350. However, the experimental values have large errors due to the large effect of EFG on line shape compared to CSA and CSA only being observable at one field.

The $^{35}$Cl NMR parameters for the methyl-substituted NHClGeCl$_2$ complex 2 were calculated for both the isolated molecule and the dimeric structure apparent from the X-ray data.\textsuperscript{43} Calculation on the monomer gave a $C_Q$ ($^{35}$Cl) value of 34.6 MHz. Inclusion of the pseudobridging interaction with the adjacent molecule offered a modest improvement in agreement with a calculated $C_Q$ value of 33.2 MHz. The small value of $\eta_Q$ was in reasonable agreement. The similarity between the calculated $C_Q$ values for both the monomeric and dimeric structures suggests that the pseudobridging Ge(adjacent)$^-$Cl interaction is not as important for complex 2 as it is for GeCl$_2$-dioxane, for which the difference between the monomeric and cluster structures was dramatic. A similar $C_Q$ value (34 MHz) was calculated for the monomeric isopropyl-substituted NHC-GeCl$_2$ complex 3. Combined with the similar experimental $C_Q$ values for 2 and 3, the computational results support that the long-range pseudobridging Ge$^-$Cl interaction is not as important in the carbene complexes as it is for 1. This is most likely due to the adjacent germanium atom being 0.27 Å closer to the pseudobridging chloride in 1 than in 2, which may in turn arise from the NHC being a better electron donor than dioxane in addition to being more sterically demanding.

While the intermolecular interactions proved to be less important for accurate reproduction of the parameters for 2 and 3 than for GeCl$_2$-dioxane, the interactions were still potentially important, and thus, calculations on the bipyridine complex 4 included the adjacent molecules to either side of the chloride of interest. The quadrupolar coupling constants were overestimated at 23.6 MHz for Cl(1) and 14.8 MHz for Cl(2). The Ge$-$Cl(2) bond length (2.7195 Å) is considerably longer than a typical covalent Ge$-$Cl bond. Indeed, in the related boromine complex, one of the analogous bromides is fully anionic in character.\textsuperscript{71} A longer covalent bond would have a less dramatic effect on the electric field gradient, leading to a lower $C_Q$ value. The relative ordering is also consistent with the general trend observed experimentally (Figure 11). Calculations predict similar $\eta_Q$ values for both chlorine sites of roughly 0.2, which is within experimental error of the experimental values of 0.13 and 0.1. The phenanthroline complex 5 was much less ambiguous with calculated $C_Q$ ($^{35}$Cl) values of 18 MHz for the pseudobridging chloride and 34.7 MHz for the terminal chloride. The calculated values again somewhat overestimated $C_Q$ while accurately reproducing the small $\eta_Q$ values.

The $C_Q$ ($^{35}$Cl) value for the crown ether GeCl complex 6 was slightly overestimated at 27.8 MHz. A difference of 2 MHz, while greater than the experimental error, is still reasonable for such a large $C_Q$ value. The value of $\eta_Q$ was reasonably reproduced.

While there are no X-ray structures available for the two germanium(IV) compounds 7 and 8, calculations were performed using structures optimized at the TPSSTPSS/6-31G* level. Gaussian calculations on compound 7 predicted a $C_Q$ ($^{35}$Cl) of 44.5 MHz and $\eta_Q$ of 0.13. A difference of 1.5 MHz from the experimental $C_Q$ value of 43.0 MHz is very reasonable agreement for such a broad signal. Compound 8 demonstrated a
similar agreement, with a calculated $C_Q$ value of 43.3 MHz overestimating the value of $C_Q$ to the same degree as in 7, and an $\eta_Q$ value of 0, exactly in agreement with experimental results.

For 9, the LAN2DZ basis set was employed for tin, as the 6-311+G** basis set does not include fourth row elements. All other elements in the structure were calculated using the latter basis set. Much like 4 and 5, DFT calculations were required to determine why only one chlorine signal was observed when there are two distinct chlorine environments in 9. The chlorine bound to the cationic tin site was predicted to have a $C_Q^{[35\text{Cl}]}$ value of 22.7 MHz, in reasonable agreement with the 19 MHz observed experimentally. The chlorides of the SnCl$_3^-$ counteranion have a calculated $C_Q^{[35\text{Cl}]}$ value of 105 MHz, confirming that the signal observed is most reasonably assigned to the cationic site. Even considering the trend toward overestimating $C_Q$ in the DFT calculations, the anionic chlorides would be over 10 MHz broad at 21.1 T, and thus, are not observed.

The overall agreement between the calculated and experimental $C_Q^{[35\text{Cl}]}$ values is illustrated in Figure 12. Overall, the correlation between the experimental values is linear, with an $R^2$ value of 0.93. With an ideal 1:1 correlation, the slope of the line of best fit would be 1; it is instead 0.92, suggesting that the overall agreement between theory and experiment is reasonable. The $C_Q$ values of the germanium(IV) compounds 8 and 9 were reasonably reproduced using geometry-optimized structures.

The orientation of the EFG tensor components (Figure S5) can often provide insight into the specific structural effects on the NMR parameters. In the majority of the germanium(II) complexes, the largest tensor component ($V_{33}$) was oriented along the Ge–Cl bond, with the remaining components oriented perpendicular, explaining the general relationship observed between the Ge–Cl bond length and the magnitude of $C_Q$. The $V_{22}$ and $V_{11}$ components of 2–6 are not orientated toward any particular structural feature, providing a possible explanation for the similar $\eta_Q$ values observed for all compounds. Notably, the situation is somewhat different for GeCl$_2$·dioxane (1), with the intermediate component ($V_{22}$) being oriented along the Ge–Cl bond and the largest component ($V_{33}$) being oriented toward the adjacent germanium atom. This was not seen in any of the other complexes which feature a long-range Ge–Cl contact (2, 4, and 5), offering a possible explanation for why GeCl$_2$·dioxane is an outlier in the structural trend relating $C_Q$ to bond angle (Figure 11). The greater influence of the long-range contact may be attributed to the adjacent germanium atom being 0.2 Å closer in GeCl$_2$·dioxane than in 4, with 5 having an even more distant contact.

The same tensor orientation pattern is observed in germanium(IV) compounds (Figure S6). While the geometry-optimized Ge–Cl bond lengths (2.224 Å for Mes$_3$GeCl$_2$ and 2.277 Å for Mes$_3$GeCl) are the shortest Ge–Cl bond lengths in this study, the bond lengths are not sufficiently different from those of the germanium(II) complexes to reasonably be the only explanation for the dramatic difference observed in $C_Q$ values. The oxidation state at germanium, thus, appears to be the most important influence on the value of $C_Q$; however it is likely that bond length will play a role in determining the magnitude of $C_Q^{[35\text{Cl}]}$ within the subcategory of germanium(IV) compounds.

Finally, the same tensor orientation pattern, with the $V_{33}$ component aligned with the element–Cl bond, is also observed for the tin complex 9 (Figure S6). While this is a single example, it points to the possibility that the same trends might be observed for other group 14 compounds.

## CONCLUSIONS

All the compounds examined in this study gave rise to broad $^{35}$Cl solid-state NMR spectra as is expected for terminal, covalently bound chlorides. Through the use of the WURST-QCPMG pulse sequence and piecewise acquisition, it was possible to obtain spectra suitable for extraction of quadrupolar parameters through spectral simulation. This is in marked contrast to attempts to obtain $^{73}$Ge SSNMR spectra for the same compounds. While $^{73}$Ge NMR spectroscopy was attempted for the majority of the selected compounds, it was only possible to obtain a reasonable $^{73}$Ge SSNMR spectrum for GeCl$_2$·dioxane, which, nonetheless, still required 1 week of acquisition time at 21.1 T.48

Examination of the $^{35}$Cl parameters revealed apparent relationships to several properties of germanium including the Ge–Cl bond length and the donor–Ge–Cl bond angle which can provide insights into the coordination environment about germanium. However, the most dramatic observation is the distinct relationship between the assigned oxidation state of germanium and the $^{35}$Cl quadrupolar coupling constant. Germanium(IV) compounds exhibit considerably broader ($C_Q^{[35\text{Cl}]} > 40$ MHz) signals than germanium(II) compounds ($C_Q^{[35\text{Cl}]} = 10–30$ MHz), providing a possible indicator of oxidation state at germanium. Indeed, the difference in the magnitudes of the $C_Q^{[35\text{Cl}]}$ exceeded that which could be accounted for by the tendency of germanium(IV) compounds to have shorter Ge–Cl bonds. If the observed correlation persists in additional samples, $^{35}$Cl SSNMR spectroscopy could prove to be a more accessible alternative to synchrotron techniques for assessing oxidation states of main group chlorides. In tin chemistry, oxidation states are often determined by Mössbauer spectroscopy; however, there is no appropriate gamma ray source for the Mössbauer spectroscopy of germanium compounds, adding to the value of the oxidation state information available from $^{35}$Cl SSNMR spectroscopy. A comparative study of the oxidation states of tin determined by Mössbauer spectroscopy and by $^{35}$Cl SSNMR spectroscopy may provide an independent and experimentally based validation for the hypothesized connection between quadrupolar coupling data and oxidation state.58

![Figure 12. Agreement between calculated and experimental $C_Q^{[35\text{Cl}]}$ values. The solid line represents an ideal 1:1 correlation, while the dashed line represents a line of best fit ($y = 0.92x + 5.5$, $R^2 = 0.93$).](image-url)
In the extreme, when the distortion of the electron density results in an ionic bond, the magnitudes of the C\(_Q\) [\(^{35}\text{Cl}\)] can be smaller than predicted based on oxidation states. Indeed, the \(^{35}\text{Cl}\) SSNMR data reported focuses on ionic inorganic chlorides,\(^{24}\) which have considerably narrower spectra than covalent organic chlorides.\(^{33}\) Symmetry at chlorine will also influence the magnitude of C\(_Q\). Nonetheless, the observed correlation is notable, and further studies are required to determine and understand the factors influencing the magnitude of C\(_Q\) [\(^{35}\text{Cl}\)] in main group chlorides.

Within the series of germanium(II) complexes studied, ligands with common donor atoms gave rise to signals with similar C\(_Q\) [\(^{35}\text{Cl}\)] values, most likely due to the similar electronic environment at germanium. The largest EFG tensor component of the majority of the germanium(II) complexes was oriented along the Ge−Cl bond, as determined by TPSSTPSS/6-311+G** model chemistry. This suggests that the general relationship noted between the donor atom and the value of C\(_Q\) [\(^{35}\text{Cl}\)] is likely due to similar germanium chlorine bond lengths due to comparable structures. GeCl\(_2\)-dioxide is a notable exception as the V\(_3\) component is, oriented toward the adjacent germanium atom, which explains why the pseudobridging Ge−Cl interaction (which is the closest such interaction seen in this study) has the largest influence on C\(_Q\). The V\(_3\) tensor orientation for the germanium(IV) compounds (7 and 8) was also along the Ge−Cl bond, suggesting that there may be a similar relationship between C\(_Q\) [\(^{35}\text{Cl}\)] and Ge(IV)−Cl bond length. Finally, the cationic tin complex also has an EFG tensor with the largest component oriented along the E−Cl bond, leading to the possibility of extending this study into the rest of the group 14 elements.

**Experimental Section**

**Materials.** GeCl\(_2\)-dioxide (1),\(^{50}\) \(^{2,43}\) \(^{3,45}\) \(^4,7f\) \(^5,7f\) \(^6,6^f\) Mes\(_2\)GeCl\(_2\) (7),\(^{50}\) Mes\(_2\)GeCl\(_4\) (8),\(^{59}\) and 9\(^{7f}\) were all prepared according to literature procedures. The identities of the compounds were confirmed by solution state \(^1\)H NMR spectroscopy.

**Solid-State NMR Spectroscopy.** \(^{35}\text{Cl}\) SSNMR spectra were acquired on a Bruker Avance 900 MHz spectrometer at the National Ultrahigh Field NMR Facility for Solids (http://nmr900.ca).\(^{35}\) Experimental setup and pulse calibrations were performed on 1 M KCl in H\(_2\)O, and chemical shift referencing was performed relative to this sample. Spectra were acquired under static conditions on a dual channel H/X 7 mm low gamma probe with high power \(^1\)H decoupling. With the exception of the spectrum of 1 shown in Figure 4A, which was acquired using the QCPMG\(^{25}\) pulse sequence, and the spectrum of 4 shown in Figure 6B, which was acquired using a WURST-echo sequence, all spectra were acquired using a WURST-QCPMG\(^{76}\) sequence with a 50 \(\mu\)s WURST-80 pulse for both excitation and refocusing and \(t_1 = 25 \mu\)s, \(t_2 = t_3 = t_4 = 26 \mu\)s. Specific acquisition parameters for individual compounds are given in Table S2.

Low field data were acquired on a Varian Infinity 400 spectrometer. The WURST-QCPMG experimental setup was performed on solid CaCl\(_2\)-2H\(_2\)O and chemical shift referencing was performed relative to solid KCl (8.5 ppm relative to 0.1 M NaCl in H\(_2\)O at 0 ppm). Spectra were acquired in a piecewise manner with a 150 kHz offset between subspectra. A 50 \(\mu\)s WURST-80 pulse was used for both excitation and refocusing.

**NMR Spectral Simulations.** Experimental NMR parameters were determined from analytical simulations using WSolids.\(^{60}\) Errors were determined by visual comparison to the experimental spectrum. Starting from the best fit value, the parameter being evaluated was varied systematically in both directions while all others were held constant until a visible change was observed.

**Theoretical Calculations.** First-principles calculations were performed using Gaussian 09\(^{61}\) on the Shared Hierarchical Academic Research Computing Network (SHARCNET, www.sharcnet.ca).

Calculations were performed on a four core Opteron 2.4 GHz CPU with 32 GB of memory or an eight core Xeon 2.83 GHz CPU with 16 GB of memory. CSA tensors were computed using the gauge-including atomic orbitals (GIAO) method. For structures with available X-ray structures, atomic coordinates were taken directly from the CIF file and hydrogen positions optimized at the TPSSTPSS/6-31G** level. The compounds without available crystal structures were fully geometry-optimized at the same level. Basis sets and methods were used as indicated. The results of the Gaussian calculations were analyzed using EFGShield.\(^{62}\)

**Associated Content**

**Supporting Information**

Six figures, two tables and optimization of computational methodology. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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**References**

(1) Parkin, G. J. Chem. Educ. 2006, 83, 791. We note that the oxidation state is the same as the valence of germanium in the complexes studied in this paper.


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