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Germanium(II) Adducts

Water and Ammonia Complexes of Germanium(II) Dications**

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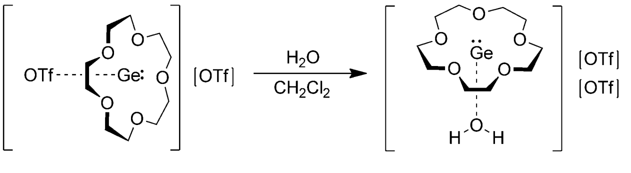
Dedicated to Joseph A. F. Macdonald, Q.C., on the occasion of his 70th birthday

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] Many 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 ions[11]). 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, our group, in collaboration with the Baines group and simultaneously with the Reid group, have demonstrated that crown ethers are also appropriate ligands for the stabilization of unambiguous Ge^{II} dications.[13–15] In that work, we 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, we have undertaken an investigation into the reactivity of the Ge^{II} crown ether complexes with a variety of simple reagents. Herein, we present the first results of our studies regarding the simple coordination chemistry of the dication which include the remarkable formation of the first crystallographically characterized water adduct of germanium(II).



1[OTf]$_2$ **2**[OTf]$_2$

Scheme 1. Synthesis of complex **2**[OTf]$_2$.

The addition of one molar equivalent of water (or D_2O) to a solution of [Ge[15]crown-5][OTf]$_2$ (**1**[OTf]$_2$) in CH_2Cl_2 generates the complexes [Ge[15]crown-5·H_2O][OTf]$_2$ (**2**[OTf]$_2$) and [Ge[15]crown-5·D_2O][OTf]$_2$ ([D$_2$]-**2**[OTf]$_2$), respectively (Scheme 1), as assessed by ^1H NMR spectroscopy in solution. Removal of all volatile components yields a colorless 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**[OTf]$_2$ crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit, as illustrated in Figure 1. The molecular structure of **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 H_2O 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 O_5 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 Ge^{IV} compounds, and it would be anticipated that the Ge^{II}–O distances should be somewhat longer because of the larger ionic radius (Ge^{2+} 87 pm; Ge^{4+} 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) Å[19] to 1.888(4) Å.[20] The Ge–O_{crown} distances range from 2.265(4)–2.361(3) Å and are comparable to those observed in the starting material **1**[OTf]$_2$.[13] The O1–H bond lengths were restrained to be about 0.79 Å; the O1···$O_{triflate}$ distances are 2.631(7) and 2.681(5) Å and are thus well within the accepted range for the inter-oxygen distances (ca. 2.7 Å) in hydrogen-bonded species.[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

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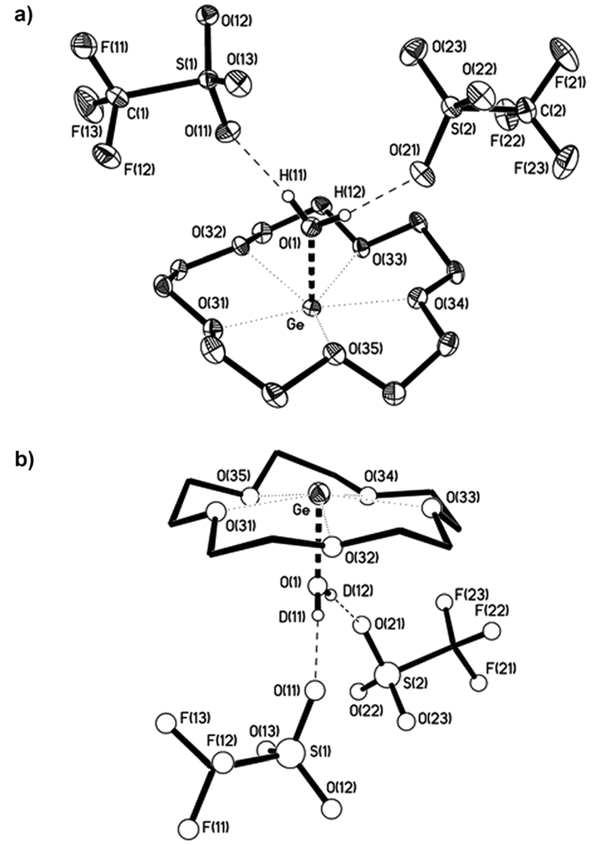


Figure 1. a) ORTEP of [Ge[15]crown-5$\cdot H_2O$][OTf]$_2$ (**2**[OTf]$_2$). Ellipsoids set at 30% probability, most hydrogen atoms have been removed for clarity. b) Ball-and-stick representation of [Ge[15]crown-5$\cdot D_2O$][OTf]$_2$ ([D$_2$]-**2**[OTf]$_2$), highlighting the slightly pyramidal geometry of the oxygen atom in the water moiety. Selected bond distances [Å] and angles [°] (values from [D$_2$]-**2**[OTf]$_2$ are in brackets): Ge–O1 2.003(4) [2.003(4)], O1–H11 0.79(4) [0.75(6)], O1–H12 0.79(4) [0.75(6)], O1$\cdots$O11 2.631(7) [2.649(7)], O1$\cdots$O21 2.681(5) [2.685(5)], Ge–O31 2.282(3) [2.278(3)], Ge–O32 2.265(3) [2.256(3)], Ge–O33 2.356(3) [2.354(3)], Ge–O34 2.276(3) [2.274(3)], Ge–O35 2.361(3) [2.363(3)]; $\Sigma_{<O1}$ 357 [355].

hydrogen-bonded to the H_2O 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 in Figure 1 b.

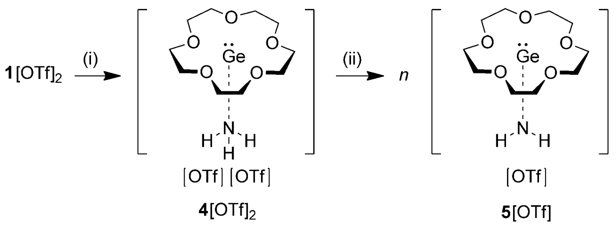
The solid-state FTIR spectra of the protio and deuterio complexes clearly show the presence of H-bonded OH and OD groups with broad signals for stretching frequencies with maxima at 3458 and 1971 cm^{-1}, respectively. Powder X-ray diffraction (pXRD) studies confirm that the only crystalline material present in the bulk samples is consistent with the single-crystal structures.

The ^{1}H and ^{13}C NMR spectra of **2**[OTf]$_2$ in CD_3CN 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_2O-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_2O to $B(C_6F_5)_3$ that increases the acidity of the water.[22–24] It is worth noting that the results of ^{1}H DOSY experiments suggest that adduct **2** is fluxional in solution, and the changes in the appearance and shift of the signal at 8.29 ppm in variable-temperature ^{1}H NMR experiments are consistent with that conjecture (see Supporting Information). The addition of a small excess of water does not appear to degrade **2**[OTf]$_2$ (the ^{1}H NMR shift for the water resonates at the weighted average of the complexed and free values, indicating exchange that is rapid on the NMR timescale), but the addition of bulk amounts of water results in the decomposition of the compound. The potential synthetic utility of **2**[OTf]$_2$ is examined below.

The isolation of a well-characterized water complex of Ge^{II} is remarkable and perhaps unexpected given the considerable reactivity exhibited by most divalent germanium compounds. Roesky demonstrated the preparation of LGeOH complexes with β-diketiminate ligands, but the ready preparation and isolation of **2**[OTf]$_2$ is surprising.[25] Similarly, Driess found that H_2O and NH_3 undergo addition reactions with a related germylene to form analogous complexes.[26] There are a handful of structurally authenticated Ge^{IV} water complexes, but such species are very rare and all have Ge–O distances of less than 2 Å.[27–31]

The presence of potentially acidic hydrogen atoms on the water fragment in **2** suggested that deprotonation reactions might be possible. In practice, the treatment of **2**[OTf]$_2$ with bases, including weak bases (NH_3, pyridine, and *N*-methylimidazole) and relatively strong bases ("proton sponge", DBN, and *N*-heterocyclic carbenes), does indeed result in the formation of the anticipated conjugate acid of the base employed, as shown by NMR and XRD experiments.[32] Given that the dication **2** can be considered as a doubly protonated variant of "**:**Ge≡O**:**",[33] we postulate 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, along with the NMR data from deprotonation reactions, mass spectra of **2**[OTf]$_2$ consistently reveal the presence of a major signal manifold corresponding to [Ge[15]crown-5$\cdot$OH]$^+$, **3**, which may be treated as a trapped singly-protonated germanium monoxide.[34–39]

Given the remarkable stability of the aquo complex **2**[OTf]$_2$, we sought to determine if other simple element hydrides might also be accessible. Gratifyingly, the treatment of **1**[OTf]$_2$ with a solution of NH_3 in dioxane results in the formation of a colorless compound for which there is evidence of complex formation (Scheme 2). Although we have not yet been able to obtain a single crystal structure for the compound, NMR, pXRD, FTIR studies, and microanalysis confirm the formation of the proposed adduct. The FTIR spectrum of the solid contains three broad peaks at 3250, 3200, and 3100 cm^{-1} which correspond to N–H stretching modes. The pXRD spectrum of the solid is almost identical to that of **2**[OTf]$_2$,[40] and the elemental analysis is consistent with a 1:1 adduct of [Ge[15]crown-5][OTf]$_2$ and NH_3, **4**[OTf]$_2$. The ^{1}H NMR spectrum of a CD_2Cl_2 solution of the solid



Scheme 2. Synthesis and reactivity of complex **4**[OTf]$_2$: (i) NH$_3$, CH$_2$Cl$_2$; (ii) *n* NH$_3$, −*n*[NH$_4$][OTf].

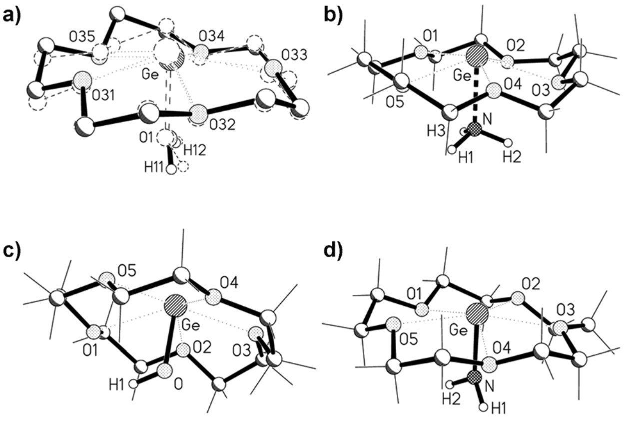


Figure 2. Ball-and-stick representations of geometry-optimized model complexes, including: a) an overlay of the computed structure of [Ge[15]crown-5·H$_2$O]$^{2+}$ **2′** (——) and **2** (-----) (most hydrogen atoms have been removed for clarity); b) the model complex [Ge[15]crown-5·NH$_3$]$^{2+}$ **4′**; c) [Ge[15]crown-5·OH]$^+$ **3′**; and d) [Ge[15]crown-5·NH$_2$]$^+$ **5′**.

Table 1: Selected properties for model ions **2′**, **3′**, **4′**, and **5′** calculated using the M062X/TZVP DFT method.

	2′	**3′**	**4′**	**5′**
$r_{\text{Ge-E}}$[Å]	2.1057	1.8386	2.0988	1.8736
Q_{Ge}[a]	1.495	1.425	1.406	1.331
Q_{E}[a]	−0.974	−1.234	−1.099	−1.436
$Q_{\text{H(av.)}}$[a]	0.541	0.492	0.424	0.387
$\text{WBI}_{\text{Ge-E}}$[b]	0.2178	0.4499	0.3465	0.5797
$\rho_{\text{crit(Ge-E)}}$[c]	0.0631	0.1222	0.0784	0.1257
$\text{cleavage}_{\text{(Ge-E)}}$[d]	hetero[e]	homo[f]	hetero[e]	homo[f]
$E_{\text{Ge-E\_snap}}$[g]	129.46[e]	448.35[f]	182.94[e]	370.19[f]
$\Delta E_{\text{reaction}}$[h]	−106.99	−1141.44	−148.22	−1160.21

[a] NBO charges in au. [b] NBO Wiberg Bond Index. [c] AIM electron density at the bond critical point (E = O,N). [d] Nature of lowest energy bond cleavage (E = O,N). [e] Heterolytic bond cleavage. [f] Homolytic bond cleavage. [g] Bond snapping energy in kJ mol^{-1} (E = O,N). [h] Gas-phase reaction energy [kJ mol^{-1}] for **1′** + donor→complex.

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 [GeOTf[15]crown-5]-[OTf] 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 ($I = 1$; $^1J_{\text{N-H}} = 53.0$ 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 **1**[OTf]$_2$ renders the protons sufficiently acidic to protonate other ammonia molecules.

In theory, removal of all three protons from **4** could produce the germanium analogue of cyanide. However, it should be noted that exposure of **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; see the Supporting Information); alternative bases will be required in pursuit of salts of [:Ge≡N:]$^-$.

Because we were unable to obtain crystal structures for the adduct **4**, we employed DFT calculations to assess the likely structure of the complex. The computed structure of the water adduct **2′**[41] (Figure 2a), reproduces the structure obtained experimentally quite accurately, so it is probable that the computed structure of the adduct **4′** (Figure 2b) 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$^{\text{II}}$−NH$_3$ linkage (2.093(4)–2.107(4) Å), which was obtained unexpectedly from the decomposition of a Ge$^{\text{II}}$-N(SiMe$_3$)$_2$ precursor.[42,43]

The computational data in Table 1 demonstrate that **4′** has a much stronger Ge−E bond than **2′**, as would be anticipated on the basis of relative basicities of NH$_3$ and OH$_2$. Furthermore, the bonds in the deprotonated models **3’** and **5′** are considerably stronger than are those of the corresponding dicationic adducts. For each model compound, the charges of the H-atoms in the complexed form are larger than those calculated for models of H$_2$O (0.457) and NH$_3$ (0.331). Interestingly, it is worth noting that calculated energies for the putative oxidative addition products [H−Ge−OH·[15]crown-5]$^{2+}$ (**6′**) and [H−Ge−NH$_2$·[15]crown-5]$^{2+}$ (**7′**) are found to be less stable than **2′** and **4′** by about 13 kJ mol^{-1} and 57 kJ mol^{-1}, respectively. The uncrowned system favors the Ge$^{\text{II}}$ over Ge$^{\text{IV}}$ to a greater extent and illustrates the effect of crown ether ligation.[44,45] Finally, the relatively small energy difference between **2′** and **6′** suggests that variants of the ligated Ge$^{\text{IV}}$ tautomer might be accessible experimentally.

As might be anticipated, the computational data for the deprotonated model complexes **3′** and **5′** (Figure 2c,d) indicate that these deprotonated variants do indeed feature considerably shorter and stronger Ge−E bonds (E = O,N) than **2′** and **4′**. The NBO analyses identify the presence of polar Ge−E single bonds in **3′** and **5′** but treat the donor and acceptor fragments as separate in **2′** and **4′**.[46] Similarly, the values of relevant quantities in the Wiberg bond indices (WBI), atoms in molecules (AIM)[47] analyses, and the bond snapping energies[48,49] all suggest that the bonds in these monocationic complexes are best considered as covalent bonds whereas those in the dicationic complexes **2′** and **4′** are more consistent with dative bonding.[50,51] Overall, the calculations suggest that deprotonation of these readily made element hydride adducts is a viable approach to new covalently bonded species.

We are presently investigating the further reactivity of these remarkable complexes, their organic analogues (that is, alcohols and amines), their heavier congeners, and the deprotonated variants for their potential use in synthetic chemistry (toward unsaturated molecules), catalysis (by O–H and N–H activation),[52] and as materials precursors.

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