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Cationic Crown Ether Complexes of Germanium(II)**

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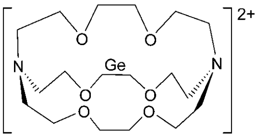
Cations of germanium continue to receive considerable attention owing to the long-standing interest in their comparative chemistry with carbon and silicon.[1–6] Typically, covalently bound substituents on Ge are required to provide steric and electronic stabilization to protect the positively charged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



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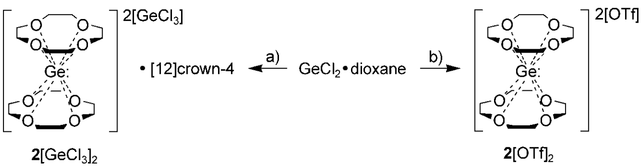
Crown ethers, like cryptands, are renowned for their strong ligating properties towards metallic cations. Coordination complexes with every type of metal ion in the periodic table have been described.[9] In the p block, reported examples of crown ether complexes with metallic cations include aluminum,[10] gallium,[11] indium,[11–14] thallium,[15] tin,[16] lead,[9] and bismuth.[9] Neutral crown ether complexes of nonmetals are also known, although the nonmetal atom is usually situated outside the cavity of the macrocycle.[9,17,18] Only a single example of a nonmetal p-block cation has been reported, namely a [15]crown-5 complex of [SbCl]$^{2+}$.[19]

Many different bonding modes are possible between crown ethers and guest cations; this diversity originates from the relationship between the crown ether cavity size and the ionic radius of the guest. As a consequence, complexes of the same cation with different crown ethers of varying dimensions often exhibit strikingly different structures. For example, In^{+} readily fits into the cavity of [18]crown-6 but forms a crown ether sandwich with two molecules of [15]crown-5.[12–14] We now report that crown ethers can also support germanium cations and allow facile access to a series of unprecedented mono- and dicationic Ge^{II} complexes. We have examined three differently sized crown ethers, [12]crown-4, [15]crown-5, and [18]crown-6,[20] which all form complexes with cationic germanium(II), each with unique structural characteristics.

Reaction of excess [12]crown-4 in a solution of GeCl$_2$·dioxane in THF resulted in the formation of a white solid (Scheme 1).[21] The structure of the product was determined to be the crown ether solvate of the salt [Ge([12]crown-4)$_2$][GeCl$_3$]$_2$ (**2**[GeCl$_3$]$_2$·[12]crown-4) and consists of two [12]crown-4 molecules sandwiching a Ge^{II} dication (Figure 1).[22] The two [GeCl$_3$] counteranions are clearly separated from Ge^{2+}, and the closest Cl$_{anion}$–Ge^{2+} approach is 5.305(2) Å. The structure of **2** is comparable to that of **1**, as both feature an unusual eight-coordinate germanium center; Ge^{II} species typically have coordination numbers of two to four. The Ge–O separations range from 2.383(6) to 2.489(7) Å, which are comparable to the Ge–O interactions in **1** (2.4856(16) Å) and much longer than typical Ge–O single-bond lengths, which range from 1.75 to 1.85 Å.[23,24] Like **1**, complex **2** does not exhibit a stereochemically active lone pair of electrons, which is most likely attributable to the highly symmetrical environment and the positive charge on the germanium ion. Solution ^{1}H NMR spectroscopy experiments on the salt reveal distinct signals for the complexed and free crown ether molecules and



Scheme 1. a) [12]crown-4; b) 2[12]crown-4, 2 Me$_3$SiOTf, −2 Me$_3$SiCl.

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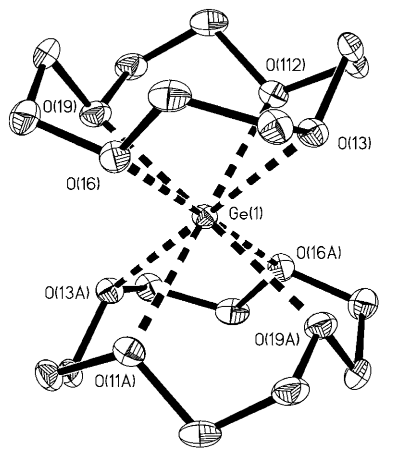


Figure 1. Thermal ellipsoid plot (30% probability surface) of **2**.[22] Hydrogen atoms, the $^{-}$GeCl$_3$ counterions and the [12]crown-4 solvate molecule are omitted for clarity. Selected interatomic distances [Å]: Ge1–O13 2.428(8), Ge1–O16 2.438(6), Ge1–O19 2.383(6), Ge1–O112 2.398(8).

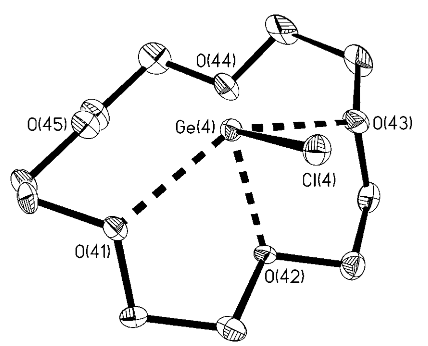
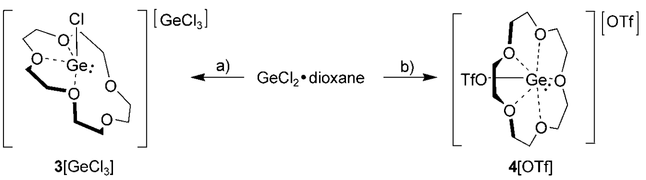


Figure 2. Thermal ellipsoid plot (30% probability surface) of **3**.[27] Only one of the four crystallographically independent cations is illustrated; hydrogen atoms and the $^{-}$GeCl$_3$ counterion are omitted for clarity. Selected interatomic distances [Å] (average for all four cations in brackets): Ge4–Cl4 2.293(2) [2.308(6)], Ge4–O41 2.363(7) [2.353(18)], Ge4–O42 2.104(6) [2.128(15)], Ge4–O43 2.433(10) [2.380(13)], Ge4–O44 3.044(8) [2.985(17)], Ge4–O45 2.835(8) [2.916(15)].

indicate that the dicationic complex remains intact in solution.

In light of the structural features of **2**[GeCl$_3$]$_2$, we reasoned that a similar salt of the dication should be accessible for other anions. Thus, we prepared the germanium(II) triflate (triflate = OTf = O$_3$SCF$_3$) [12]crown-4 complex (Scheme 1) by the treatment of two equivalents of [12]crown-4 with one equivalent of GeCl$_2$·dioxane and two equivalents of Me$_3$SiOTf at room temperature.[25] All of the characterization methods indicate the formation of the related salt **2**[OTf]$_2$, and crystallographic analysis confirms the formation of the anticipated dication (see the Supporting Information).

The structure of **2** clearly shows the germanium center residing outside the cavity of the two [12]crown-4 moieties, suggesting that [12]crown-4 is too small to accommodate a Ge^{2+} ion within its cavity. To determine how a larger crown ether interacts with Ge$^{\text{II}}$, the reaction of one equivalent of [15]crown-5 with two equivalents of GeCl$_2$·dioxane was studied (Scheme 2). Single crystals were grown, and the product was confirmed to be [GeCl([15]crown-5)][GeCl$_3$] (**3**[GeCl$_3$]) by single crystal X-ray diffraction, elemental analysis, and spectroscopic methods. As illustrated in Figure 2, the salt **3**[GeCl$_3$] consists of a $^{+}$GeCl cation encapsulated by [15]crown-5 rather than a dication as observed in **1** and **2**.[26,27] The closest Ge$_{\text{cation}}$–Cl$_{\text{anion}}$ distance of 3.387(2) Å lies well outside of the range for typical covalent bonding interactions and is consistent with a discrete cation–anion system. The Ge4–Cl4 bond length of 2.293(2) Å is comparable to typical Ge–Cl bond lengths of 2.09–2.21 Å.[23] The crown ether adopts a folded conformation in which the plane defined by Ge4, O41, O42, and O43 is almost perpendicular to the plane defined by Ge4, O45, and O44. The $^{+}$GeCl fragment is situated closest to O42 at a distance of 2.104(6) Å, much closer than what was observed in **1** and **2**; two other oxygen atoms, O41 and O43, also show close contacts of 2.363(7) and 2.433(10) Å. These can be compared to the range for typical Ge–O single bonds at 1.75–1.85 Å.[23] The two remaining oxygen atoms, O44 and O45, are situated significantly farther away at 3.044(8) and 2.835(8) Å as result of the folding of the ring. The adoption of a folded conformation by the [15]crown-5 ligand in **3** implies that the $^{+}$GeCl fragment is too large to fit into the cavity of the crown ether and that the germanium center possesses a stereochemically active lone pair of electrons. The salt **3**[GeCl$_3$] is obtained regardless of the stoichiometry employed in the reaction with [15]crown-5.



Scheme 2. a) $^{1}/_{2}$ [15]crown-5; b) [15]crown-5, 2 Me$_3$SiOTf, −2 Me$_3$SiCl.

The synthesis of a germanium(II) triflate [15]crown-5 complex (Scheme 2) was investigated to observe what effect, if any, a change in the substituent at the Ge center would produce. One equivalent of [15]crown-5 was treated with one equivalent of GeCl$_2$·dioxane and two equivalents of Me$_3$SiOTf at room temperature.[25] A white powder was collected and identified as the monocationic complex [GeOTf([15]crown-5)][OTf] (**4**[OTf], Figure 3).[21] The geometry of the crown ether moiety in **4** has changed strikingly from that in **3**. The crown ether in **4** now adopts the more typical planar conformation of the oxygen donors and the germanium center. The germanium ion is situated near the centroid of the ring, with Ge–O$_{\text{crown}}$ separations ranging from 2.233(5) to 2.349(6) Å. One of the triflate groups in **4**[OTf] remains in close proximity to the germanium cation. Although the Ge–O$_{\text{triflate}}$ separation of 2.015(3) Å is longer than a typical Ge–O bond (1.75–1.85 Å),[23] it is comparable to other known Ge–O$_{\text{triflate}}$ covalent interactions.[28] Furthermore, the S1–O1 bond length of 1.451(3) Å is longer than the remaining two sulfur–

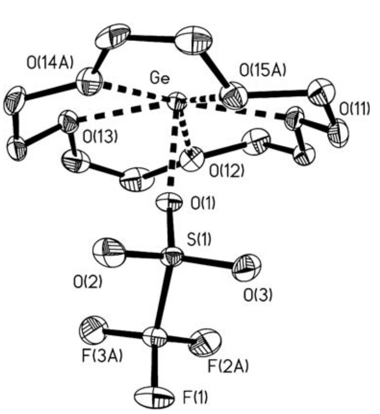
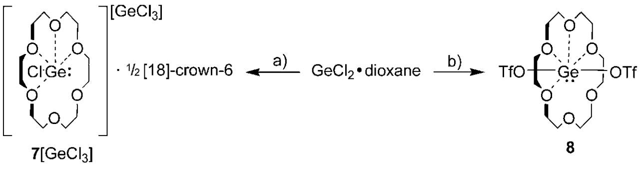


Figure 3. Thermal ellipsoid plot (30% probability surface) of **4**. Hydrogen atoms and the $^{-}$OTf counterion are omitted for clarity. Selected interatomic distances [Å]: Ge–O11 2.260(4), Ge–O12 2.233(5), Ge–O13 2.308(6), Ge–O14A 2.289 (8), Ge–O15A 2.349(6), Ge–O1 2.015 (3), S1–O1 1.451(3), S1–O2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

oxygen bonds (1.416(6) and 1.423(6) Å), which is characteristic of a triflate ion with at least partial covalent bonding to a substituent. The second triflate group in **4**[OTf] is present as a distinctly separate anion in the unit cell, and the closest Ge–$O_{triflate}$ separation is 3.169(6) Å. A possible rationale for the differences between the structures of **3** and **4** is that the Ge–$O_{triflate}$ bond of **4** is much more polarized than the Ge–Cl bond of **3**, thus increasing the effective charge on the Ge center in **4** and decreasing the size of the cation, allowing it to fit more readily into the cavity of the [15]crown-5 ligand.

In spite of the foregoing discussion, crown ethers are notoriously flexible molecules,[9] and the observed geometrical differences between **3** and **4** could be a result of crystal packing effects rather than electronic effects. To examine complexes similar to **3** and **4** featuring a somewhat less flexible framework, the benzocrown ether derivatives of **3** and **4** (**5** and **6**, respectively) were synthesized and characterized.[21] The structures obtained exhibit features virtually identical to those observed in **3** and **4**: in the chloride complex **5**, the crown ether fragment features a folded conformation, while the triflate derivative **6** adopts a typical planar conformation (see the Supporting Information). Therefore, the observed structural differences between **3** and **4** are more likely attributable to the steric and electronic effects of the type described above and not to crystal packing effects.

The direct reaction of two equivalents of $GeCl_2$·dioxane with [18]crown-6 (Scheme 3) resulted in the formation of a new complex with a stoichiometry of Ge_2Cl_4·[18]crown-6.[21] The recrystallization of a preparation containing excess crown ether resulted in the formation of the crown ether solvate of the desired salt. The structure [GeCl([18]crown-6)]-[$GeCl_3$]·$^1/_2$[18]crown-6 (**7**[$GeCl_3$]·$^1/_2$[18]crown-6, Figure 4) shows that the larger crown ether is indeed able to ligate the Cl–Ge^+ fragment in a planar fashion. The Ge center is offset from the centroid of the crown ether oxygen atoms. The closest germanium–oxygen separation is 2.195(3) Å for the Ge1–O11 interaction. The remaining Ge–O distances are significantly longer, ranging from 2.359(4) to 3.237(4) Å; this situation is likely a consequence of the larger cavity size of the [18]crown-6 ring being too large to bind the Ge cation in a symmetrical manner. The structure is also consistent with a stereochemically active lone pair of electrons on the germanium center pointing in a direction orthogonal to the ring, opposite the Ge1–Cl1 bond.



7[$GeCl_3$]

8

Scheme 3. a) 1.5 [18]crown-6; b) [18]crown-6, 2 Me_3SiOTf, −2 Me_3SiCl.

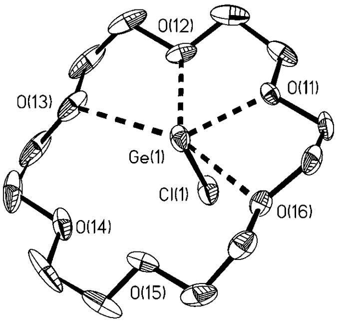


Figure 4. Thermal ellipsoid plot (30% probability surface) of **7**. Hydrogen atoms, the $^{-}GeCl_3$ counterion, and the [18]crown-6 solvate molecule are omitted for clarity. Selected interatomic distances [Å]: Ge1–Cl1 2.201(1), Ge1–O11 2.195(3), Ge1–O12 2.359(4), Ge1–O13 2.869(5), Ge1–O14 3.237(4), Ge1–O15 3.076(4), Ge1–O16 2.640(4).

Finally, to observe the interaction of the larger crown ether with the triflate substituents, $GeCl_2$·dioxane was treated with [18]crown-6 and two equivalents of Me_3SiOTf in THF (Scheme 3).[21] Suitable single crystals were grown and identified as [Ge(OTf)$_2$([18]crown-6)] (**8**), which, surprisingly, consists of a symmetrical Ge(OTf)$_2$ fragment located within the cavity of [18]crown-6 (Figure 5). As in **7**, the germanium atom is located away from the centroid of the oxygen atoms in

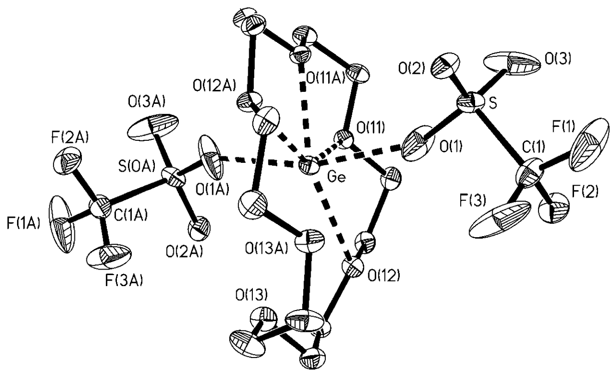


Figure 5. Thermal ellipsoid plot (30% probability surface) of **8**. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å]: Ge–O11 2.218(3), Ge–O12 2.673(3), Ge–O13 3.159(4), Ge–O1 2.204(5), S–O1 1.448(5), S–O2 1.422(4), S–O3 1.397(6).

the crown ether and is much closer to the O11 and O11A atoms (2.218(3) Å) than the remaining oxygen atoms (two at 2.673(3) Å and two at 3.159(4) Å). The crown ether in **8** is noticeably distorted, with the oxygen atoms labeled O13 and O13A located out of the plane defined by the germanium center and the other four oxygen atoms in the ligand. The distant O atoms appear to be oriented in a manner that is not suitable for donation to the Ge center. The $O_{triflate}$–Ge bonds are long (2.204(5) Å) and, although they appear incipient towards ionization, **8** is clearly not an ion-separated system as observed for the salts of **2**–**7**. The structural features of **8** are consistent with a stereochemically active lone pair of electrons on germanium oriented in the direction of O13 and O13A. We postulate that the triflate anions remain in contact with the Ge ion because the larger [18]crown-6 ligand allows for the lone pair of electrons to reside inside the cavity of the crown ether.[29]

We have shown that crown ethers are suitable ligands for the stabilization of cationic germanium(II) systems, the structural properties of which are highly dependent on the size of crown ether used and on the substituents on germanium. The surprising ease with which the crown ethers promote the ionization of Ge^{II} demonstrates the effectiveness of these macrocycles in isolating otherwise elusive cationic germanium species. The simplicity of the synthetic approach may render it applicable to the preparation of other novel nonmetal cations.

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[29] Our supposition is supported by the observation that the analogue of **7** containing the larger tin atom separates into [SnOTf([18]crown-6)][OTf] ions in a similar manner to **3** (see the Supporting Information).