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Synthesis and Structural Characterization of New Polyether Complexes of Germanium(II) and Tin(II)

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To Neil Burford: a mentor, role model, and friend.

Abstract

A series of germanium(II) and tin(II) bromide polyether complexes have been synthesized. Specifically, [GeBr([15]crown-5)][GeBr₃], [GeBr([18]crown-6)][GeBr₃], [GeBr(triglyme)][GeBr₃], [GeBr(tetraglyme)][GeBr₃], [SnBr([18]crown-6)][SnBr₃], [Sn([15]crown-5)₂][SnBr₃]₂, [SnBr(triglyme)][SnBr₃] and [SnBr(tetraglyme)][SnBr₃] have been fully characterized including by single crystal X-ray diffraction. The synthesis of [GeBr(dibenzo[24]crown-8)][GeBr₃] and [GeCl(dibenzo[24]crown-8)][GeCl₃] are also reported, along with the crystal structure of the latter's water adduct, which features a water molecule adjacent to the GeCl⁺ ion within the cavity of the crown ether.

Introduction

The chemistry involving group 14 cations and polyethers ligands has been an area of great interest over the last decade.¹ The complexation of lead(II) ions by macrocyclic polyethers in solution was well established by the early 80s,² and accordingly, lead(II) and tin(II) were the first group 14 elements to form polyether complexes which were structurally confirmed by single crystal X-ray diffraction.^{3,4} While it was generally thought that low valent germanium centers require stabilization by strongly bound covalent ligands, the isolation of cryptand[2.2.2]-encapsulated germanium(II) dication **A** (Figure 1) by the Baines group in 2008 caused this paradigm to shift⁵ and paved the path for the isolation of many other polyether complexes of germanium(II) in the years which followed.^{6–9} Many of the resulting compounds hold great potential for further reactivity in that they may act as Lewis acids to simple nucleophiles like water and ammonia while retaining a non-bonding electron pair.¹⁰

An overwhelming majority of these cationic crown or glyme complexes are paired with triflate counter anions or anions derived from chloride, with the heavier halides being present in only a handful examples.^{7,11} As a part of our group's long-standing interest in the synthesis and reactivity of polyether complexes of group 13 and 14 elements,^{12,13} we sought to fill this gap by examining in detail the reactions between germanium(II) and tin(II) bromide with various cyclic and acyclic polyethers.

Figure 1 Examples of polyether complexes of group 14 cations.

Results and Discussions

Germanium(II) Crown Complexes

We began our investigations with the reactions of various crown ethers with commercially available GeBr_2 . While we obtained crystalline material from several of these reactions, we found that these products were contaminated with significant amounts of ammonium. In several instances, single crystal X-ray diffraction experiments of these materials revealed crown ether ammonium complexes with GeBr_3^- anions (Figure 2 depicts $[\text{NH}_4(\text{benzo}[18]\text{crown-6})][\text{GeBr}_3]$ as an example). We discovered that the source of the contamination was the commercially purchased GeBr_2 : when dissolved in MeCN-d_3 and subjected to a ^1H NMR experiment, the spectrum features a 1:1:1 triplet centered at 5.86 ppm, the multiplicity of which is due to coupling of the protons to the ^{14}N isotope ($I = 1$, 99.63% abundant).

Examination of the early literature suggests that this contamination is introduced as part of the purification process for commercially synthesized GeBr_2 and would likely go unnoticed for other reactions which do not involve ligands with a high affinity for ammonium.¹⁴ While the addition of crown ethers almost certainly produced the desired reaction with GeBr_2 (due to the presence of GeBr_3^- anions), the crown ethers' large binding affinity for ammonium¹⁵ likely resulted in the displacement of the GeBr^+ cation, whose fate remains unknown.

Figure 2 Thermal ellipsoid plot (50% probability surface) of $[\text{NH}_4(\text{benzo}[18]\text{crown-6})][\text{GeBr}_3]$. Hydrogen atoms (except those of ammonium) and the anion are omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): H1c-O1 , 2.20(10); H1b-O3 , 1.88(12); H1d-O5 , 2.10(9).

To solve the problem of ammonium contamination, we decided to synthesize GeBr_2 -dioxane from commercially purchased GeBr_4 , which is produced using a method which does not involve ammonia.¹⁶ Treatment of two equivalents of GeBr_2 -dioxane with one equivalent of [18]crown-6 and [15]crown-5 resulted in clean reactions to yield the salts $[\text{GeBr}([\text{15}]\text{crown-5})][\text{GeBr}_3]$, **1** $[\text{GeBr}_3]$ and $[\text{GeBr}([\text{18}]\text{crown-6})][\text{GeBr}_3]$, **2** $[\text{GeBr}_3]$ respectively. Indeed, NMR data as well as elemental analyses of the materials isolated upon workup show no traces of ammonium and indicate that the materials obtained were analytically pure. The ^1H NMR signals for the crown ether protons in each complex (**1** $[\text{GeBr}_3]$ = 3.83 ppm

and $2[\text{GeBr}_3] = 3.81 \text{ ppm}$) are significantly deshielded from those of the free crowns (ca. 3.5 ppm for both free crowns) which confirms formation of the complexes in solution.

Scheme 1 Synthesis of $1[\text{GeBr}_3]$ and $2[\text{GeBr}_3]$; a) [15]crown-5, b) [18]crown-6

The crystals of $1[\text{GeBr}_3]$ are isomorphous to the chloride analogue reported by our group,⁶ crystallizing in $\text{Pca}2_1$ with four crystallographically independent units in the asymmetric unit. The crown ethers of the cations adopt a folded geometry (figure 3) wherein the germanium centre retains an apparent stereochemically active lone pair adjacent to the Ge-Br bond. The Ge-O distances in all four crystallographically unique cations range between 2.088(10) Å to 3.023(9) Å.

Figure 3 Thermal ellipsoid plot (50% probability surface) of $1[\text{GeBr}_3]$. Only one crystallographically unique cation is displayed for clarity. Hydrogen atoms and the anion are omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Ge3-Br3 , 2.525(2); Ge3-O311 , 2.35(3); Ge3-O32 , 2.135(9); Ge3-O33 , 2.353(9); Ge3-O34 , 2.900(10); Ge3-O35 , 2.857(10).

Recrystallization of the materials to give single crystals suitable for X-ray diffraction was done by adding an appropriate anti-solvent to a dissolved sample, cooling to -30°C and storing over several days. $2[\text{GeBr}_3]$ crystallizes in P-1 with two unique chemical units the asymmetric unit (because both are similar, only one is shown in figure 2). The GeBr^+ fragment is bound in a meridional fashion around the Ge(II) ion, but is slightly off-centre in the crown cavity (i.e. the Ge atom is not located at the centroid of the O_6 ring). As such, the Ge-O distances range from 2.269(2) to 3.300(3) $\text{\AA}$ in the fragment depicted in figure 2. The Ge-O bond lengths of the second crystallographically unique cation also fall within this range. This observation illustrates the relatively poor size match between germanium(II) ion and the [18]crown-6 cavity.

97

98 *Figure 3 Thermal ellipsoid plot (50% probability surface) of 2[GeBr₃]. Hydrogen atoms and the anion are omitted for clarity.*
 99 *Selected bond lengths (Å) and angles (°): Ge1-Br1, 2.3993(5); Ge1-O1, 2.269(2); Ge1-O2, 2.413(3); Ge1-O3, 2.889(3); Ge1-O4,*
 100 *3.300(3); Ge1-O5, 3.043(3); Ge1-O6, 2.556(3).*

101

102 The complexation of germanium using larger crown ether ligands (>[18]crown-6) has been nearly
 103 completely unexplored. The reaction of dibenzo[24]crown-8 with two equivalents of GeBr₂·dioxane in
 104 THF followed by subsequent workup did afford a white solid whose NMR spectra and microanalysis
 105 was consistent with [GeBr(dibenzo[24]crown-8)][GeBr₃], **3**[GeBr₃], however we were unable to obtain
 106 single crystals of this material suitable for X-ray diffraction. The chloride analogue of this compound has
 107 also hitherto eluded report, and thus we investigated the analogous reaction involving GeCl₂·dioxane as
 108 well. Workup of this reaction afforded a white powder whose microanalysis and NMR spectra are
 109 consistent with [GeCl(dibenzo[24]crown-8)][GeCl₃], **4**[GeCl₃] (Scheme 2). However, attempted
 110 recrystallizations of this material in DCM led to the formation of a single crystals of
 111 [H₂O·GeCl(dibenzo[24]crown-8)][GeCl₃], [**4**·H₂O][GeCl₃], presumably due to adventitious amounts of
 112 water in the DCM used for crystallization. The formation of the water complex [**4**·H₂O][GeCl₃] was
 113 further confirmed by elemental analysis and multinuclear NMR spectroscopy of the isolated crystals. The
 114 ¹H NMR spectrum of the crystals clearly indicates the presence of the water protons which appear as a
 115 broad peak at 6.41 ppm. In the solid-state structure of [**4**·H₂O][GeCl₃], the distances between the Ge

atom and the crown ether oxygens ranges from 2.2954(18) Å to 3.5699(19) Å, while the Ge-OH₂ distance is 2.029(4) Å. The protons of the H₂O molecule are hydrogen bonded to the O-atoms of the crown ether (OH-O lengths are 2.07(7) and 1.95(7)), placing the water molecule within the confines of the large crown ether, reminiscent of an example involving indium(III).¹⁷

Scheme 2 Synthesis of $4[\text{GeCl}_3]$ and isolation of $[\text{4} \cdot \text{H}_2\text{O}][\text{GeCl}_3]$

Figure 5 Thermal ellipsoid plot (50% probability surface) of $[\text{4} \cdot \text{H}_2\text{O}][\text{GeCl}_3]$. Hydrogen atoms (except those on H₂O) and the anion are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1-Cl1, 2.2760(12); Ge1-O1, 2.029(4); Ge1-O11, 3.5699(19); Ge1-O12, 2.9941(18); Ge1-O13, 2.2954(18); Ge1-O14', 3.3609(19); H1a-O12', 1.95(7); H1b-O14, 2.07(7).

126

127 Surprisingly, given the considerable reactivity exhibited by most divalent germanium compounds, in
 128 2013 our group reported the first crystallographically characterized water adduct of germanium(II),¹⁰
 129 making this a rare example of such a compound. In a related note, only a handful of structurally
 130 authenticated germanium(IV) water complexes have been reported, but such species all have much
 131 shorter Ge-O distances of less than 2 Å as one might expect.^{18–20} The unexpected isolation of a new
 132 water complex of germanium(II) featuring such a different bonding motif is remarkable given the
 133 foregoing.

134

135 Germanium(II) Bromide Glyme Complexes

136 We next sought to investigate the reaction of GeBr₂ with glymes. The much higher degree of flexibility in
 137 glymes should theoretically give rise to different structural motifs than those observed in the crown
 138 ether analogues. Furthermore, to our knowledge there are no structurally authenticated germanium
 139 glyme complexes yet reported. The treatment of two equivalents of GeBr₂·dioxane with triglyme or
 140 tetraglyme followed by workup led to the isolation of [GeBr(triglyme)][GeBr₃], **5**[GeBr₃] and
 141 [GeBr(tetraglyme)][GeBr₃], **6**[GeBr₃] respectively as analytically pure white solids (Scheme 3). As with
 142 the crown ether complexes, the ¹H NMR spectra of these materials feature signals which are slightly
 143 deshielded compared to those of their respective free glymes, indicative of complexation in solution.

144

145 Scheme 3 Synthesis of **5** and **6**[GeBr₃]; a) triglyme, b) tetraglyme

Figure 5 Thermal ellipsoid plot (50% probability surface) of $5[\text{GeBr}_3]$. Hydrogen atoms and the anion are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1-Br1, 2.4155(9); Ge1-O1, 2.425(4); Ge1-O2, 2.122(3); Ge1-O3, 2.189(3); Ge1-O4, 2.656(4).

Crystals of $6[\text{GeBr}_3]$ suitable for single crystal X-ray diffraction were obtained by diffusion of pentane into a saturated THF solution. The salt crystallizes in $P2_1/c$ with one ion pair in the asymmetric unit. As with the triglyme case, the glyme binds the germanium(II) atom in a *mer*-fashion. The Ge-O distances range between 2.219(3) and 2.805(4) Å, with the more terminal oxygen atoms having the larger Ge-O distances (Figure 6).

Figure 6 Thermal ellipsoid plot (50% probability surface) of $6[\text{GeBr}_3]$. Hydrogen atoms and the anion are omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Ge1-Br1 , 2.4003(7); Ge1-O1 , 2.710(3); Ge1-O2 , 2.389(3); Ge1-O3 , 2.219(3); Ge1-O4 , 2.364(3); Ge1-O5 , 2.805(4).

Tin (II) Bromide Crown Complexes

Our experience with the ammonium contamination of commercially available GeBr_2 prompted us to examine whether the same contamination would be present in commercially purchased SnBr_2 . We were unable to detect any ammonium contamination by NMR spectroscopy of the commercially purchased SnBr_2 and we did not encounter problems with ammonium contamination during our subsequent reactions. Treatment of two equivalents of SnBr_2 with [18]crown-6 affords the complex $[\text{SnBr}([\text{18}]\text{crown-6})][\text{SnBr}_3]$, **7** $[\text{SnBr}_3]$. As with the germanium analogues, the crown ether proton signal in the ^1H NMR spectrum is deshielded with respect to the free crown signal. Upon workup, single crystals were obtained by slow evaporation of a THF solution. The crown ether complexes the SnBr^+ fragment in a *mer*-fashion and the Ge-O bond distances range from 2.703(5) $\text{\AA}$ to 2.855(6) $\text{\AA}$ (Figure 7).

Scheme 4 Synthesis of $7[\text{SnBr}_3]$

Figure 7 Thermal ellipsoid plot (50% probability surface) of $7[\text{SnBr}_3]$. Hydrogen atoms and the anion are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn1-Br1, 2.5979(11); Sn1-O11, 2.855(6); Sn1-O12, 2.745(6); Sn1-O13, 2.703(5); Sn1-O14, 2.764(6); Sn1-O15, 2.733(6), Sn1-O16, 2.740(6).

While the 1:2 reaction between [15]crown-5 and SnBr_2 did not yield any materials which could be confirmed as the $[\text{SnBr}([15]\text{crown-5})][\text{SnBr}_3]$ salt, the 2:3 reaction of those reagents yielded the sandwich complex $[\text{Sn}([15]\text{crown-5})_2][\text{SnBr}_3]_2$, $8[\text{SnBr}_3]_2$, which was isolated as analytically pure single crystals after workup. The structure of this sandwich complex (Figure 8) is isomorphous with the chloride analogue (which was reported in the related $P2_1/a$ setting).²¹ The Sn-O bond lengths range from 2.648(4) Å to 2.795(4) Å and are in good agreement with other analogous sandwich complexes of Sn(II).^{21–23}

Scheme 5 Synthesis of 8[SnBr₃]₂

Figure 8 Thermal ellipsoid plot (50% probability surface) of 8[SnBr₃]₂. Hydrogen atoms and anions are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn1-O1, 2.662(4); Sn1-O2, 2.648(4); Sn1-O3, 2.795(4); Sn1-O4, 2.740(4); Sn1-O5, 2.770(3).

Tin (II) Bromide Glyme Complexes

As with the previously described germanium examples, we sought to also examine the ligand redistribution of SnBr₂ using glymes. Though our group had reported tetraglyme and triglyme complexes of tin(II) triflates,¹³ there have only been two other structurally authenticated example of such complexes since then, and recently such complexes have received attention as metal-containing ionic liquid precursors for high-speed metal electrodeposition.^{24,25} Synthesis of the glyme complexes

203 [SnBr(triglyme)][SnBr₃], **9**[SnBr₃], and [SnBr(tetraglyme)][SnBr₃], **10**[SnBr₃] was accomplished by
 204 treatment of 2 equivalents of SnBr₂ with one equivalent of triglyme and tetraglyme, respectively. For
 205 both reactions, deshielding of the ¹H NMR glyme signals upon coordination is observed, and analytically
 206 pure single crystalline materials were obtained upon workup by slow evaporation of THF filtrates.

208 *Scheme 6 Synthesis of **9**[SnBr₃] and **10**[SnBr₃]; a) triglyme, b) tetraglyme*

210 The crystal structure of **9**[SnBr₃] (figure 9) features one crystallographically unique [SnBr(triglyme)]⁺
 211 fragment where the triglyme complexes the Sn atom in a meridional fashion. The Sn-Br bond length is
 212 2.6751(7) Å and the Sn-O bond lengths range from 2.472(3) Å to 2.585(3) Å, whereby the terminal O
 213 atoms are farther from the Sn atom. Inspection of the packing structure reveals that (unlike the
 214 analogous germanium(II) complex) two of these cations form intermolecular contacts between their
 215 [SnBr]⁺ fragments of 3.2552(7) Å. While this type of head-to-tail dimerization has been observed for
 216 tin(II) chloride fragments (usually featuring strong covalently bound ligands),^{26–29} it is much more rare
 217 for cases involving tin(II) bromide,^{30–33} and the contacts in this instance are very short compared to most
 218 other examples.

Figure 9 Thermal ellipsoid plot (50% probability surface) of $9[\text{SnBr}_3]$. Hydrogen atoms and anions are omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Sn1-Br1 , 2.6751(7); Sn1-Br1' , 3.2552(7); Sn1-O1 , 2.582(3); Sn1-O2 , 2.472(3); Sn1-O3 , 2.475(3); Sn1-O4 , 2.585(3).

The crystal structure of $10[\text{SnBr}_3]$ (Figure 10) does not feature the same type of intermolecular contacts as the triglyme derivative due to the two additional O-donor atoms which completely contour the Sn atom. This salt crystallizes in $P2_1/c$ and the same trend of increased Sn-O bond length for the O atoms at the ends of the tetraglyme is observed, with Sn-O bond distances ranging from 2.434(3) $\text{\AA}$ for the central O atom to 2.715(4) $\text{\AA}$ for one of the terminal O atoms. The Sn-Br distance of 2.6155(7) $\text{\AA}$ is slightly shorter than those of the triglyme complex.

Figure 10 Thermal ellipsoid plot (50% probability surface) of $10[\text{SnBr}_3]$. Hydrogen atoms and anions are omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Sn1-Br1 , 2.6155(7); Sn1-O1 , 2.666(4); Sn1-O2 , 2.556(4); Sn1-O3 , 2.453(4); Sn1-O4 , 2.551(4); Sn1-O5 , 2.715(4).

235 Table 1 Summary of crystallographic data and refinement details

Compound	[NH ₄ (benzo[18]crown-6)][GeBr ₃]	1[GeBr ₃]	2[GeBr ₃]	[4·H ₂ O][GeCl ₃]	5[GeBr ₃]
CCDC	1813785	1813786	1813787	1813788	1813789
Empirical formula	C ₁₆ H ₂₈ Br ₃ GeNO ₆	C ₁₀ H ₂₀ Br ₄ Ge ₂ O ₅	C ₁₂ H ₂₄ Br ₄ Ge ₂ O ₆	C ₂₄ H ₃₄ Cl ₄ Ge ₂ O ₉	C ₈ H ₁₈ Br ₄ Ge ₂ O ₄
Formula weight	642.71	685.08	729.13	753.49	643.04
Color, habit	Colorless, irregular	Colorless, prism	Colorless, prism	Colorless, irregular	Colorless, plate
Crystal size/mm ³	0.276 × 0.27 × 0.125	0.17 × 0.16 × 0.04	0.342 × 0.14 × 0.08	0.19 × 0.15 × 0.078	0.38 × 0.13 × 0.042
Temperature/K	170.01	173(2)	130.01	170.01	159.58
Crystal system	triclinic	Orthorhombic	Triclinic	Monoclinic	Triclinic
Space group (ASP)	P-1	Pca21 (0.41(4))	P-1	C2/c	P-1
a/Å	9.9071(6)	30.7572(8)	12.4881(6)	18.2752(6)	6.4660(6)
b/Å	10.4679(6)	10.1827(3)	14.2168(7)	14.8602(5)	10.5524(10)
c/Å	12.8109(7)	24.6466(7)	14.5248(7)	12.0984(5)	13.8420(13)
α/°	75.657(3)	90	114.3775(18)	90	74.883(4)
β/°	71.941(3)	90	90.5269(19)	112.7480(10)	88.247(4)
γ/°	70.339(3)	90	107.2282(18)	90	82.493(4)
Volume/Å ³	1174.12(12)	7719.1(4)	2217.70(19)	3030.03(19)	903.96(15)
Z	2	16	4	4	2
ρ _{calc} /cm ³	1.818	2.358	2.184	1.652	2.362
μ/mm ⁻¹	6.438	13.683	9.940	2.384	12.167
F(000)	632.0	5184	1392.0	1528.0	604.0
Radiation	MoKα	CuKα	MoKα	MoKα	MoKα
Reflections collected	27805	168614	102138	66191	26357
Independent reflections	4460	11070	12505	3364	5519
R _{int}	0.132	0.101	0.068	0.055	0.067
Data/restraints/parameters	4460/0/269	11070/122/750	12505/0/433	3364/2/203	5519/0/175
Goodness-of-fit on F2	1.023	1.097	1.067	1.132	1.044
Final R indexes [I>2σ (I)]	R ₁ = 0.046 wR ₂ = 0.080	R ₁ = 0.043 wR ₂ = 0.061	R ₁ = 0.040 wR ₂ = 0.063	R ₁ = 0.040 wR ₂ = 0.096	R ₁ = 0.051 wR ₂ = 0.101
Final R indexes [all data]	R ₁ = 0.106 wR ₂ = 0.100	R ₁ = 0.057 wR ₂ = 0.064	R ₁ = 0.063 wR ₂ = 0.069	R ₁ = 0.050 wR ₂ = 0.101	R ₁ = 0.086 wR ₂ = 0.114
Residual density / e Å ⁻³	1.75/-1.80	0.777/-0.734	1.35/-1.66	1.66/-0.79	1.51/-1.71
Data completeness / %	99.4	99.2	99.6	99.7	99.2
Absorption correction	Semi-empirical from equivalents				
Refinement method	Full-matrix least-squares on F2				
R1(F): {Σ(F _o - F _c)/Σ F _o } for reflections with F _o > 4(Σ(F _o)). wR2(F2): {Σw(F _o /2 - F _c /2)/Σw(F _o /2)} ^{1/2} where w is the weight given to each reflection					

236

237 Table 2 Continued summary of crystallographic data and refinement details

Compound	6[GeBr ₃]	7[SnBr ₃]	8[SnBr ₃] ₂	9[SnBr ₃]	10[SnBr ₃]
CCDC	1813790	1813791	1813792	1813793	1813794
Empirical formula	C ₁₀ H ₂₂ Br ₄ Ge ₂ O ₅	C ₁₂ H ₂₄ Br ₄ O ₆ Sn ₂	C ₂₀ H ₄₀ Br ₆ O ₁₀ Sn ₃	C ₁₆ H ₃₆ Br ₈ O ₈ Sn ₄	C ₁₀ H ₂₂ Br ₄ O ₅ Sn ₂
Formula weight	687.09	821.33	1276.05	1470.49	779.29
Color, habit	Colorless, irregular	Colorless, prism	Colorless, prism	Colorless, irregular	Colorless, plate
Crystal size/mm ³	0.276 × 0.270 × 0.125	0.293 × 0.181 × 0.177	0.667 × 0.220 × 0.220	0.425 × 0.258 × 0.158	0.388 × 0.306 × 0.055
Temperature/K	135(2)	170(2)	143(2)	143.2	143.21
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group (ASP)	P2 ₁ /c	P-1	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a/Å	12.5980(7)	16.1157(18)	10.5528(7)	9.724(2)	13.9519(11)
b/Å	13.2256(7)	16.116	20.2328(12)	9.254(2)	11.5896(9)
c/Å	12.9975(7)	20.679(3)	8.8778(5)	20.207(5)	13.0100(11)
α/°	90	90	90	90	90
β/°	109.434(2)	90	111.225(3)	92.466(7)	94.593(3)
γ/°	90	120	90	90	90
Volume/Å ³	2042.21(19)	4651.1(8)	1766.94(19)	1816.7(7)	2096.9(3)
Z	4	8	2	2	4
ρ _{calc} /g/cm ³	2.235	2.346	2.398	2.688	2.468
μ/mm ⁻¹	10.783	9.042	8.932	11.549	10.017
F(000)	1304.0	3072	1200.0	1352.0	1448.0
Radiation	MoKα	MoKα	MoKα	MoKα	MoKα
Reflections collected	165609	134430	130246	111312	120453
Independent reflections	5172	21429	5153	11803	9946
R _{int}	0.063	0.062	0.049	0.059	0.053
Data/restraints/parameters	5172/0/192	21429/0/866	5153/0/178	11803/0/165	9946/0/192
Goodness-of-fit on F2	1.268	1.030	1.128	1.255	1.305
Final R indexes [I>=2σ (I)]	R ₁ = 0.038 wR ₂ = 0.079	R ₁ = 0.034 wR ₂ = 0.070	R ₁ = 0.040 wR ₂ = 0.0880	R ₁ = 0.066 wR ₂ = 0.104	R ₁ = 0.070 wR ₂ = 0.124
Final R indexes [all data]	R ₁ = 0.046 wR ₂ = 0.085	R ₁ = 0.060 wR ₂ = 0.081	R ₁ = 0.042 wR ₂ = 0.089	R ₁ = 0.083 wR ₂ = 0.109	R ₁ = 0.079 wR ₂ = 0.127
Residual density / e Å ⁻³	0.85/-1.11	1.142/-1.977	2.99/-1.96	1.67/-2.17	2.79/-3.74
Data completeness / %	99.9	99.8	99.9	96.2	97.0
Absorption correction	Semi-empirical from equivalents				
Refinement method	Full-matrix least-squares on F2				
R1(F): {Σ(F _o - F _c)/Σ F _o } for reflections with F _o > 4(Σ(F _o)). wR2(F2): {Σw(F _o 2 - F _c 2)/Σw(F _o 2)2}1/2 where w is the weight given to each reflection					

Conclusions

The reactions between commercially available germanium(II) bromide and various crown ethers results in the formation of ammonium-crown ether GeBr_3^- salts due to the presence of ammonium in commercially available germanium(II) bromide. The use of in-house synthesized $\text{GeBr}_2 \cdot \text{dioxane}$ solves the issue of ammonium contamination, and using this precursor, the salts $[\text{GeBr}([15]\text{crown-5})][\text{GeBr}_3]$, $[\text{GeBr}([18]\text{crown-6})][\text{GeBr}_3]$, $[\text{GeBr}(\text{triglyme})][\text{GeBr}_3]$, $[\text{GeBr}(\text{tetraglyme})][\text{GeBr}_3]$, were isolated and their crystal structures determined. The latter two complexes represent the first examples of crystallographically confirmed glyme complexes of germanium. The synthesis of $[\text{GeBr}(\text{dibenzo}[24]\text{crown-8})][\text{GeBr}_3]$ and $[\text{GeCl}(\text{dibenzo}[24]\text{crown-8})][\text{GeCl}_3]$ are also reported. The water adduct of the latter salt, $[\text{H}_2\text{O} \cdot \text{GeCl}(\text{dibenzo}[24]\text{crown-8})][\text{GeCl}_3]$ was characterized by X-ray crystallography and the larger crown ether accommodates the $[\text{GeCl}]^+$ fragment and a water molecule within its cavity and represents a rare example of a germanium(II) water adduct. Commercially available SnBr_2 was used to synthesize the salts $[\text{SnBr}([18]\text{crown-6})][\text{SnBr}_3]$, $[\text{Sn}([15]\text{crown-5})_2][\text{SnBr}_3]_2$, $[\text{SnBr}(\text{triglyme})][\text{SnBr}_3]$ and $[\text{SnBr}(\text{tetraglyme})][\text{SnBr}_3]$, each of which was fully characterized including by X-ray crystallography. This hitherto unreported series of compounds compliments the known chloride and triflate analogues which have only recently been reported. We are currently investigating the synthesis of the heavier iodide analogues as well as further chemistry involving these species.

Experimental

General procedures

All manipulations were carried out using standard inert atmosphere techniques. All chemicals and reagents were purchased from Sigma Aldrich. MeCN-d_3 was dried over calcium hydride or phosphorus

pentoxide and stored over molecular sieves under nitrogen. All other solvents were dried on a series of Grubbs' type columns and were degassed prior to use.³⁴ Glymes were dried over 3Å molecular sieves and degassed prior to use. GeBr₂·dioxane was synthesized by modification of a literature procedure for the synthesis of GeCl₂·dioxane.¹⁶ NMR spectra were recorded at room temperature on Bruker Avance III 500 MHz, Bruker Avance Ultrashield 300 MHz or Bruker Avance DPX 300 MHz spectrometers. Chemical shifts (δ) are reported in ppm relative to internal standards for ¹H and ¹³C (the given deuterated solvent). Coupling constants |J| are given in Hz. Elemental analysis was performed at the University of Windsor Mass Spectrometry Service Laboratory using a Perkin Elmer 2400 combustion CHN analyzer. Melting points were determined under a N₂ atmosphere. Electrospray ionization mass spectrometry was attempted at the McMaster Regional Centre for Mass Spectrometry but none of the species herein withstand the ionization process, and only alkali metal-crown complexes are typically observed in the spectra.

Specific Procedures

1[GeBr₃]

[15]crown-5 (0.154 mL, 0.757 mmol) was added to a GeBr₂·dioxane (0.500 g, 1.56 mmol) solution in THF (ca. 40 mL). The colourless solution stirred for 2 hours at room temperature. All volatile components were then removed under reduced pressure. The resultant oily product was washed with hexanes (5 mL x 3) to provide a white solid. Crystals suitable for SC-XRD were obtained by diffusion of pentane into a saturated THF solution at -30 °C. **Yield:** 86% (0.463 g, 0.675 mmol). **Mp:** 121 – 123 °C. **¹H NMR (CD₃CN, 300 MHz) δ:** 3.83 (s). **¹³C{¹H} NMR (CD₃CN, 300 MHz) δ:** 70.1 (s). Anal. Calcd for C₁₀H₂₀Br₄Ge₂O₅·0.25 THF: C, 18.79; H, 3.15. Found: C, 18.91; H, 3.14 (Anal. Calcd for C₁₀H₂₀Br₄Ge₂O₅: C, 17.53; H, 2.94). The presence a small amount of residual THF was confirmed by ¹H NMR.

284

285 **2[GeBr₃]**

286 A solution of [18]crown-6 (0.080 g, 0.303 mmol) in acetonitrile (ca. 1 mL) was added to a solution of
287 GeBr₂·dioxane (0.200 g, 0.624 mmol) in acetonitrile (ca. 40 mL). After stirring overnight at room
288 temperature all volatile components were removed under reduced pressure. The resultant white solid
289 was washed with hexanes (4 mL x 2) and dried in vacuo. Colourless crystals of **2[GeBr₃]** suitable for SC-
290 XRD were obtained by slow diffusion of Et₂O into a saturated acetonitrile solution at –30 °C. **Yield:** 88%
291 (0.202 g, 0.277 mmol). **Mp:** 94 – 98 °C. **¹H NMR (CD₃CN, 300 MHz) δ:** 3.81 (s). **¹³C{¹H} NMR (CD₃CN, 300**
292 **MHz) δ:** 70.7 (s). Anal. Calcd for C₁₂H₂₄Br₄Ge₂O₆: C, 19.76; H, 3.32. Found: C, 20.16; H, 3.15.

293

294 **3[GeBr₃]**

295 A solution of dibenzo[24]crown-8 (0.140 g, 0.312 mmol) in THF (ca. 1 mL) was added to a solution of
296 GeBr₂·dioxane (0.200 g, 0.624 mmol) in THF (ca. 40 mL). The colourless solution was stirred for 2 hours
297 at room temperature. All volatile components were removed under reduced pressure. The resultant
298 white solid was washed with hexanes (4 mL x 2), yielding a solid powder. **Yield:** 64% (0.184 g, 0.201
299 mmol). **Mp:** 92-94 °C. **¹H NMR (CD₃CN, 300 MHz) δ:** 3.70 (s, 8H), 3.82 (m, 8H), 4.15 (m, 8H), 6.97 (m,
300 8H). **¹³C{¹H} NMR (CD₃CN, 300 MHz) δ:** 69.54 (s), 69.80 (s), 70.43 (s), 115.43 (s), 122.95 (s), 149.54 (s).
301 Anal. Calcd for C₂₄H₃₂O₈Ge₂Br₄: C, 31.55; H, 3.53. Found: C, 31.56; H, 3.37.

302

303 **4[GeCl₃]**

304 A solution of dibenzo[24]crown-8 (0.290 g, 0.646 mmol) in THF (ca. 1 mL) was added to a solution of
305 GeCl₂·dioxane (0.300 g, 1.29 mmol) in THF (ca. 40 mL). The colourless solution was stirred for 2 hours at

room temperature. All volatile components were removed under reduced pressure. The resultant white solid was washed with hexanes (4 mL x 2) and allowed to dry, yielding the analytically pure title compound. **Yield:** 93% (0.432 g, 0.587 mmol). **Mp:** 103-105°C. **^1H NMR (CD_3CN , 300 MHz) δ :** 3.70 (s, 8H), 3.81 (m, 8H), 4.11 (m, 8H), 6.92 (m, 8H). **$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 300 MHz) δ :** 69.43 (s), 70.45 (s), 71.28 (s), 114.91 (s), 122.39 (s), 149.56 (s). Anal. Calcd for $\text{C}_{24}\text{H}_{32}\text{Cl}_4\text{Ge}_2\text{O}_8$: C, 39.18; H, 4.38. Found: C, 39.78; H, 4.45. Recrystallization of this material by slow evaporation of DCM yielded a single crystal of $[\text{4}\cdot\text{H}_2\text{O}][\text{GeCl}_3]$ suitable for SC-XRD, presumably due to adventitious water in the DCM.

$[\text{4}\cdot\text{H}_2\text{O}][\text{GeCl}_3]$

Mp: 105-108°C. **^1H NMR (CD_3CN , 300 MHz) δ :** 3.78 (s, 8H), 3.89 (m, 8H), 4.11 (m, 8H), 6.41 (s, 2H, H_2O), 6.94 (m, 8H). **$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 300 MHz) δ :** 69.64(s), 70.45 (s), 71.35 (s), 115.14 (s), 122.46 (s), 149.71(s). Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{Cl}_4\text{Ge}_2\text{O}_9$: C, 38.25; H, 4.55. Found: C, 38.94; H, 4.29.

$5[\text{GeBr}_3]$

A solution of triglyme (0.141 mL, 0.780 mmol) in THF (ca. 1 mL) was added dropwise to a solution of $\text{GeBr}_2\cdot\text{dioxane}$ (0.500 g, 1.56 mmol) in THF (40 mL). The resultant colourless solution was stirred for 2 hours at room temperature followed by removal of all volatile components under reduced pressure to afford a colourless oil. The oily residue was washed in hexanes (5 mL x 3) and decanted yielding a solid product. Small crystals suitable for SC-XRD were obtained by adding hexanes to a concentrated toluene solution and storing at -30°C. **Yield:** 71 % (0.357 g, 0.555 mmol). **Mp:** 45 – 47 °C. **^1H NMR (CD_3CN , 300 MHz) δ :** 3.41 (s, 6H), 3.60 (m, 4H), 3.79 (m, 8H). **$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 300 MHz) δ :** 58.97 (s), 70.77 (s), 70.82 (s), 72.3 (s). Anal. Calcd for $\text{C}_8\text{H}_{18}\text{Br}_4\text{Ge}_2\text{O}_4$: C, 14.94; H, 2.82. Found: C, 15.43; H, 2.52.

328

329 **6[GeBr₃]**

330 A solution of tetraglyme (0.171 mL, 0.779 mmol) in THF (ca. 1 mL) was added dropwise to a solution of
331 GeBr₂·dioxane (0.500 g, 1.56 mmol) in THF (40 mL). The resultant colourless solution was stirred for 2
332 hours at room temperature followed by removal of all volatile components under reduced pressure to
333 afford a colourless oil. The oily residue was washed in hexanes (5 mL x 3) to give a white solid. Crystals
334 suitable for SC-XRD were obtained by diffusion of pentane into a saturated THF solution at –30 °C. **Yield:**
335 79% (0.422 g, 0.614 mmol). **Mp:** 57 – 60 °C. **¹H NMR (CD₃CN, 300 MHz) δ:** 3.41 (s, 6H), 3.65 (m, 4H), 3.81
336 (m, 8H), 3.88 (m, 4H). **¹³C{¹H} NMR (CD₃CN, 300 MHz) δ:** 58.88 (s), 70.11 (s), 70.68 (s), 70.72 (s), 71.6 (s).
337 Anal. Calcd for C₁₀H₂₂Br₄Ge₂O₅: C, 17.48; H, 3.23. Found: C, 18.09; H, 3.43.

338

339 **7[SnBr₃]**

340 A solution of [18]crown-6 (0.094 g, 0.36 mmol) in THF (ca. 1 mL) was added to a solution of SnBr₂ (0.200
341 g, 0.718 mmol) in THF (ca. 40 mL). The reaction mixture was left to stir overnight at room temperature.
342 After resting without stirring, the clear supernatant was decanted from the white precipitate which was
343 left to dry and characterized as the titled compound. Single crystals suitable for X-ray diffraction studies
344 were obtained through slow evaporation of the clear supernatant. **Yield:** 85% (0.252 g, 0.306 mmol).
345 **Mp:** 167 –170°C. **¹H NMR (CD₃CN, 300 MHz) δ:** 3.78 (s). **¹³C{¹H} NMR (CD₃CN, 300 MHz) δ:** 70.66 (s).
346 Anal. Calcd for C₁₂H₂₄Br₄Sn₂O₆: C, 17.55; H, 2.95. Found: C, 18.27; H, 3.08.

347

348 **8[SnBr₃]₂**

[15]Crown-5 (0.165 mL, 0.835 mmol) was added to a solution of SnBr_2 (0.350 g, 1.26 mmol) in THF (40 mL). The reaction mixture was left to stir overnight at room temperature. After resting without stirring, the clear supernatant was decanted from the white precipitate which was left to dry and characterized as the titled compound. Single crystals suitable for X-ray diffraction studies were obtained through slow evaporation of the clear supernatant. **Yield:** 90% (0.482 g, 0.377 mmol). **Mp:** 147 – 149 °C. ^1H NMR (CD_3CN , 300 MHz) δ : 3.78 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 300 MHz) δ : 70.3 (s). Anal. Calcd for $\text{C}_{20}\text{H}_{40}\text{Br}_6\text{Sn}_3\text{O}_{10}$: C, 18.82; H, 3.15. Found: C, 18.13; H, 3.19.

9[SnBr_3]

A solution of triglyme (0.132 mL, 0.730 mmol) in THF (ca. 1 mL) was added dropwise to a solution of SnBr_2 (0.400 g, 1.44 mmol) in THF (40 mL). The resultant colourless solution was stirred overnight after which all volatile components were removed under reduced pressure to afford a colourless oil. The oil was washed and sonicated with a 1:1.5 mixture of ether:pentane and dried in vacuo to yield the analytically pure title compound. Crystals suitable for SC-XRD were obtained by slow evaporation of a THF solution. **Yield:** 74% (0.392 g, 0.533 mmol). **Mp:** 86 – 88°C. ^1H NMR (CD_3CN , 300 MHz) δ : 3.50 (s, 6H), 3.68 (m, 4H), 3.86 (m, 8H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 300 MHz) δ : 58.43 (s), 69.60 (s), 70.40 (s), 70.48 (s). Anal. Calcd for $\text{C}_8\text{H}_{18}\text{Br}_4\text{Sn}_2\text{O}_4$: C, 13.07; H, 2.47. Found: C, 13.67; H, 2.44.

10[SnBr_3]

A solution of tetraglyme (0.158 mL, 0.718 mmol) in THF (ca. 1 mL) was added dropwise to a solution of SnBr_2 (0.400 g, 1.44 mmol) in THF (40 mL). The resultant colourless solution was stirred overnight after which all volatile components were removed under reduced pressure to afford a colourless oil. The oil

was washed and sonicated with a 1:1.5 mixture of ether:pentane and dried in vacuo to afford the title compound as an analytically pure white powder. Crystals suitable for single x-ray diffraction were obtained by slow evaporation of a THF solution. **Yield:** 92% (0.518 g, 0.664 mmol). **Mp:** 70 – 72 °C. **¹H NMR (CD₃CN, 300 MHz) δ:** 3.42 (s, 6H), 3.64 (m, 4H), 3.79 (m, 8H), 3.83 (m, 4H). **¹³C{¹H} NMR (CD₃CN, 300 MHz) δ:** 58.8 (s), 70.46 (s), 70.94 (s), 71.12 (s), 71.87(s). Anal. Calcd for C₁₀H₂₂ Br₄Sn₂O₅: C, 15.41; H, 2.85. Found: C, 15.64; H, 2.85.

X-ray crystallography

Crystals for investigation were covered in Paratone[®], mounted into a goniometer head, and then rapidly cooled under a stream of cold N₂ of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were then collected using the APEXII software suite³⁵ on a Bruker Photon 100 CMOS diffractometer using a graphite monochromator with MoK_α (λ = 0.71073 Å) or CuK_α (λ = 1.54178 Å) radiation. For each sample, data were collected at low temperature. APEXII software was used for data reductions and SADABS³⁶ was used for absorption corrections (multi-scan; semi-empirical from equivalents). XPREP was used to determine the space group and the structures were solved and refined using the SHELX³⁷ software suite as implemented in the WinGX³⁸ or OLEX2³⁹ program suites. Validation of the structures was conducted using PLATON⁴⁰ and the structures have been deposited in the Cambridge Structural Database (CCDC 1813785-1813794). As with many complexes of this type, several of the compounds exhibited disorder within the polyether groups; this was treated with variable occupancy 2-site models in which appropriate restraints were used to restrain the thermal parameters of related atoms to be approximately equal. Compound **7**[SnBr₃] was solved as a 2-component twin in P-1; all attempts to solve it in higher symmetry space groups led to unstable refinements or residual factors greater than 0.5.

394

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398 **Keywords:** germanium(II) • tin(II) • crown ether • glyme • x-ray crystallography

399

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