

Germanium(II) Dications Stabilized by Azamacrocycles and Crown Ethers**

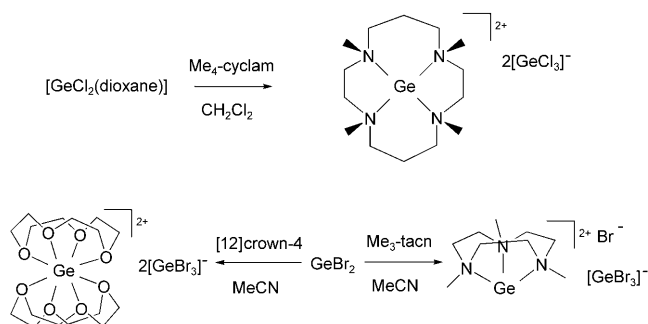
Fei Cheng, Andrew L. Hector, William Levason, Gillian Reid,* Michael Webster, and Wenjian Zhang

The chemistry of the p-block elements has undergone something of a renaissance in recent years, owing to their intrinsic interest, their use in organic chemistry and catalysis, and their importance in electronic materials.^[1,2] Within Group 14 there is a very high level of inherent interest in germanium and silicon compounds and in Ge and Si reagents in organic chemistry and catalysis.^[2–6] The development of low-valent compounds, multiply bonded species, radicals, and clusters is of significant current importance.^[7,8] Cationic Ge and Si compounds are very rare, and notable examples include the $[R_3Ge]^+$ and $[R_3Si]^+$ ions with bulky R groups.^[9,10] With the exceptions of the organogermanium or -silicon species, the majority of Ge^{IV} , Ge^{II} , and Si^{IV} complexes incorporate halide coligands. The neutral triazamacrocycle Me_3 -tacn is capable of displacing a halide ligand from both $GeCl_4$ and GeF_4 , and even from SiF_4 , to give the distorted octahedral $[MX_3(Me_3-tacn)]^+$ monocations (Me_3 -tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane), which have been structurally characterized.^[11–13] Halide-free Ge^{II} mono- or dications are even less common.^[14] Very recent work from Baines and co-workers has produced an extremely unusual Ge^{2+} dication within cryptand[2.2.2],^[15] the structure of which suggests only very weak Ge–N or Ge–O interactions. The success in isolating this species has been attributed to stability gained by encapsulation of the Ge^{II} in the cryptand.

In recent work we have shown that the thiamacrocycles [9]aneS₃, [14]aneS₄, and [16]aneS₄ (1,4,7-trithiacyclononane, 1,4,8,11-tetrathiacyclotetradecane, and 1,5,9,13-tetrathiacyclohexadecane, respectively) react with $[GeCl_2(dioxane)]$ or $GeBr_2$ to form weakly associated chain or sheet polymers involving exocyclic thioether coordination. The macrocycles bridge adjacent GeX_2 units but do not displace the halide ligands.^[16] To develop this chemistry further, we sought to establish whether it would be possible to displace halides from Ge^{II} using other neutral macrocyclic ligands, and herein we report the first halide-free, dicationic Ge^{II} species with N- and O-donor macrocycles.

Reaction of Me_3 -tacn with one molar equivalent of $GeBr_2$ in anhydrous MeCN solution gives $[Ge(Me_3-tacn)]Br[GeBr_3]$ as a colorless solid in good yield. Using the 14-membered-ring tetraazamacrocycle Me_4 -cyclam (1,4,8,11-tetramethyl-

1,4,8,11-tetraazacyclotetradecane) with $[GeCl_2(dioxane)]$ in anhydrous CH_2Cl_2 leads to isolation of a colorless solid formulated as $[Ge(Me_4-cyclam)][GeCl_3]_2$, while reaction of $GeBr_2$ with [12]crown-4 in CH_3CN gives $[Ge([12]crown-4)_2]Br[GeBr_3]$ (Scheme 1). The same $[Ge([12]crown-4)_2]^{2+}$



Scheme 1.

dication was also obtained from reaction of $GeCl_4$ and [12]crown-4 in the presence of Et_3SiH and $LiAlH_4$, similar to the method used for the preparation of $[GeCl_2(dioxane)]$.^[17]

Proton NMR spectra (CD_3CN or $(CD_3)_2CO$) of these compounds shows resonances unshifted from those of the ligands alone, consistent with highly labile complexes. As the structural information from the IR and Raman spectra is very limited (except for the $[GeCl_3]^-$ anions, which have characteristic features and are clearly evident), we have focused on crystal structure determinations to establish structural properties of the complexes unambiguously and to explore how the ligand denticity and donor type influence the structures.

The crystal structure^[18] of $[Ge(Me_3-tacn)]Br[GeBr_3]$ (Figure 1) shows the only significant interactions to Ge^{II} to be through a tridentate Me_3 -tacn ligand coordinated facially to the Ge atom. The Ge–N separations lie in the range

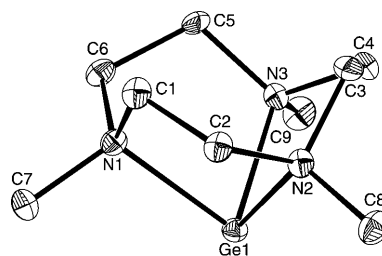


Figure 1. Structure of the $[Ge(Me_3-tacn)]^{2+}$ ion. Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–N1 2.156(3), Ge1–N2 2.124(3), Ge1–N3 2.134(3); N1–Ge1–N2 81.32(11), N1–Ge1–N3 81.69(11), N2–Ge1–N3 82.11(11).

[*] Dr. F. Cheng, Dr. A. L. Hector, Prof. W. Levason, Prof. G. Reid, Dr. M. Webster, Dr. W. Zhang
School of Chemistry, University of Southampton
Southampton SO17 1BJ (UK)
Fax: (+44) 2380-593-781
E-mail: g.reid@soton.ac.uk

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2.124(3)–2.156(3) Å; they are considerably longer than the sum of the covalent radii for Ge (1.17 Å) and N (0.68 Å) and are indicative of weak interactions. The next closest contacts to the Ge atom involve three much more distant interactions to Br atoms, two from adjacent Br[−] ions and one from a Br atom in a pyramidal [GeBr₃][−] ion (Ge⋯Br = 3.14, 3.28, 3.69 Å). Therefore, the coordination is essentially only through the three N atoms of the macrocyclic amine, giving a pyramidal GeN₃ dication.

The crystal structure^[18] of the tetraazamacrocyclic complex [Ge(Me₄-cyclam)][GeCl₃]₂ shows a very different coordination environment within the [Ge(Me₄-cyclam)]²⁺ ion, with two pyramidal [GeCl₃][−] anions balancing the charge. The structure of the discrete cation (Figure 2) shows a rather distorted coordination environment at Ge1, with two shorter (Ge1–N2 2.151(2), Ge1–N4 2.178(2) Å) and two slightly longer Ge–N bonds (Ge1–N1 2.307(2), Ge1–N3 2.349(2) Å); the bond lengths alternate short, long, short, long around the ring. All of these distances are considerably longer than the sum of the covalent radii for Ge and N, and hence they are probably best described as long-range, weak interactions. The four N atoms are approximately coplanar (root-mean-square deviation 0.28 Å), with the Ge1 atom displaced 0.83 Å above the plane and the four Me groups directed to the same side of the plane as the Ge ion. There are no short Ge⋯Cl interactions, although one Ge⋯Ge' separation of 3.531(1) Å is observed between Ge2 and Ge2a (symmetry operation *a* = −*x*, 1−*y*, −*z*). In this endocyclic tetraazamacrocyclic complex [Ge(Me₄-cyclam)][GeCl₃]₂, the ligand is clearly unsuited to tridentate coordination, hence the observed structure probably reflects a size mismatch between the Ge^{II} ion and the macrocycle.

These azamacrocyclic complexes of Ge^{II} present two extremely unusual examples of halide-free dicationic Ge^{II} complexes stabilized by a neutral donor ligand. The different denticities of the macrocycles lead to significantly different structures. The Me₃-tacn ligand coordinates in a tridentate fashion to give a pyramidal species, leaving the other side of the Ge center essentially exposed (and readily accessible to other reagents), while the larger tetraaza ring leads to endocyclic coordination of the Ge^{II} cation.

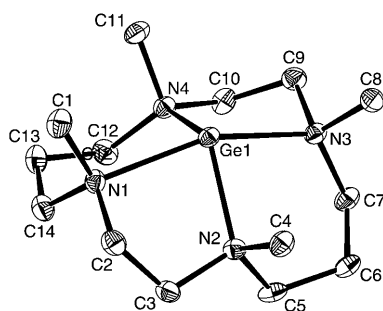


Figure 2. Structure of the [Ge(Me₄-cyclam)]²⁺ ion. Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–N1 2.307(2), Ge1–N2 2.151(2), Ge1–N3 2.349(2), Ge1–N4 2.178(2); N1–Ge1–N2 79.84(8), N1–Ge1–N3 152.93(8), N1–Ge1–N4 86.89(8), N2–Ge1–N3 86.35(8), N2–Ge1–N4 118.41(8), N3–Ge1–N4 79.34(8).

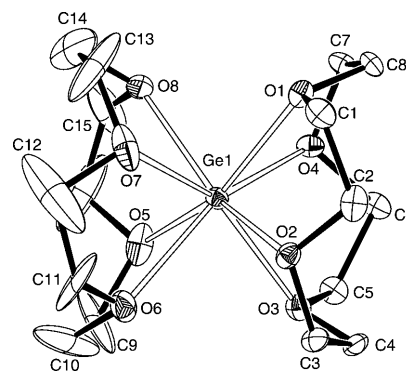


Figure 3. Structure of the [Ge([12]crown-4)₂]²⁺ ion. Thermal ellipsoids are drawn at the 25% probability level and H atoms are omitted for clarity. The crown ether ligand involving atoms O5 to O8 is disordered. Selected bond lengths [Å]: Ge1–O1 2.325(9), Ge1–O2 2.352(9), Ge1–O3 2.284(9), Ge1–O4 2.369(8), Ge1–O5 2.330(11), Ge1–O6 2.361(10), Ge1–O7 2.367(11), Ge1–O8 2.311(11).

Recrystallization of the extremely reactive [Ge([12]crown-4)₂][Br[GeBr₃]] from anhydrous CH₂Cl₂ produced very small crystals of [Ge([12]crown-4)₂][GeBr₃]₂ through anion rearrangement (as is frequently observed in this area of the Periodic Table). The structure of the dication^[18] in this salt (Figure 3) shows that the Ge atom is coordinated to two tetradentate crown ether ligands to give an eight-coordinate square antiprism sandwich structure. One of the crown ether ligands is disordered, hence the geometric parameters associated with this part of the structure are rather unreliable. However, the Ge–O bonds involving the ordered ligand are in the range 2.284(9) to 2.369(8) Å. These bonds are slightly shorter than those reported for the D₃-symmetric [Ge(cryptand[2.2.2])]²⁺ dication (Ge–O 2.4856(16), Ge–N 2.524(3) Å), in which the Ge²⁺ ion is encapsulated by the macrotricyclic ligand.^[15]

These three macrocyclic dications represent a remarkable set of distinctly different structure types involving Ge^{II}, revealing the very considerable influence that ligand structure and denticity have upon the speciation and structures adopted. The macrocyclic structures undoubtedly play a considerable role in stabilizing the dications. It is also significant that the related thioether macrocycles [9]aneS₃, [14]aneS₄, and [16]aneS₄ do not give halide-free cations.^[16]

These results demonstrate that Ge^{II} dications may be readily accessed and stabilized through the use of macrocyclic ligands. The resulting complexes have highly variable coordination numbers (formally three to eight), opening up possibilities for a rich chemistry of this and other p-block cations and exciting prospects for new reaction chemistry.

Experimental Section

Schlenk techniques and a glovebox were used for all manipulations, which were conducted under strictly anhydrous and anaerobic conditions.

[Ge(Me₃-tacn)]Br[GeBr₃]: Me₃-tacn (0.171 g, 1.0 mmol) was added to a solution of GeBr₂ (0.231 g, 1.0 mmol) in CH₃CN (8 mL) at room temperature with stirring. After stirring for 30 min, volatile

components were removed in vacuo, and the white solid residue was washed with petrol ether and dried in vacuo. Yield: 90% (based on GeBr_2). As is commonly found for Si and Ge halide complexes,^[13,19] the product incorporates Br^- and $[\text{GeBr}_3]^-$ ions in different preparations, hence microanalytical data were variable from one sample to another. IR (nujol): $\tilde{\nu} = 341(\text{w}), 273 \text{ cm}^{-1} (\text{w})$. $^1\text{H NMR}$ (CD_3CN): $\delta = 2.85$ (s, 12H, CH_2), 2.40 ppm (s, 9H, Me). Colorless crystals of $[\text{Ge}(\text{Me}_3\text{-tacn})]\text{Br}[\text{GeBr}_3]$ were obtained by slow evaporation of the solvent from an acetonitrile solution.

$[\text{Ge}(\text{Me}_4\text{-cyclam})][\text{GeCl}_2]_2$: $\text{Me}_4\text{-cyclam}$ (0.075 g, 0.30 mmol) was added to a solution of $[\text{GeCl}_2(1,4\text{-dioxane})]$ (0.230 g, 1.00 mmol) in CH_2Cl_2 (10 mL) at room temperature with stirring, which led to precipitation of a white solid. After 30 min the solvent was removed in vacuo to leave a white solid, which was washed with diethyl ether and dried in vacuo. Yield: 95%. Elemental analysis calcd for $\text{C}_{14}\text{H}_{32}\text{Cl}_6\text{Ge}_3\text{N}_4$ (686.9): C 24.5, H 4.7, N 8.2; found: C 25.2, H 5.1, N 8.3%. $^1\text{H NMR}$ ($(\text{CD}_3)_2\text{CO}$): $\delta = 3.17$ (s, CH_2 , 8H), 2.55 (br, CH_2 , 8H), 2.31 (s, Me, 12H), 1.70 ppm (m, CH_2 , 4H). IR (nujol): $\tilde{\nu} = 323(\text{s}), * 277(\text{s}), 227(\text{s}), 192 \text{ cm}^{-1} (\text{m})$. Raman: $\tilde{\nu} = 320(\text{sh}), * 308(\text{s}), 266(\text{s}), * 230(\text{w}), 195 \text{ cm}^{-1} (\text{w})$. $*$ = $[\text{GeCl}_3]^-$.

$[\text{Ge}([12]\text{crown-4})_2]\text{Br}[\text{GeBr}_3]$: $[12]\text{Crown-4}$ (0.352 g, 2.0 mmol) was added to a solution of GeBr_2 (0.231 g, 1.0 mmol) in CH_3CN (8 mL) at room temperature with stirring. After 12 h the volatile components were removed in vacuo. The resulting white solid was washed with diethyl ether and dried in vacuo. Yield: 90% (based on GeBr_2). Elemental analysis calcd for $\text{C}_{16}\text{H}_{32}\text{Br}_4\text{Ge}_2\text{O}_8$ (815.7): C 23.5, H 4.0; found: C 24.3, H 4.6%. $^1\text{H NMR}$ (CD_3CN): $\delta = 3.64$ ppm (s). IR (nujol): $\tilde{\nu} = 45(\text{m}), 266 \text{ cm}^{-1} (\text{w})$. Colorless crystals of $[\text{Ge}([12]\text{crown-4})_2][\text{GeBr}_3]_2$ were obtained by slow evaporation of the CH_2Cl_2 filtrate.

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