Cationic aza-macrocyclic complexes of germanium(II) and silicon(IV)†

Matthew Everett, Andrew Jolleyes, William Levason, Mark E. Light, David Pugh and Gillian Reid*

School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK.
E-mail: G.Reid@soton.ac.uk; Tel: +44 (0)23 8059 3609

Introduction
Elemental silicon and germanium and their compounds with oxygen and chalcogens are key technological materials, with applications in electronics, glasses, ceramics and optics.1–3 We are currently developing routes to electrochemically deposit the elements and their binary and ternary alloys from both organic solvents and supercritical fluids.4–6 In the search for silicon and germanium reagents with appropriate chemical stabilities and solubilities in these media for electrochemical studies, we have explored a variety of coordination complexes, to establish how the properties may be tuned by incorporating various ligands. Most coordination chemistry of germanium(II), germanium(IV) and silicon(IV) involves neutral adducts of the di- or tetra-halides,7 and cationic complexes are rather rare, while Si(II) halide complexes are limited to N-heterocyclic carbenes.8 Aza-macrocyclic complexes reported include [GeF₆(Me₃tacn)]₂[GeF₅] (Me₃tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane),9 [[GeF₆]₂κ²⁺Me₄cyclam]} (Me₄cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane),9 [GeCl₂-Me₄cyclen]⁺[(H₂O)₂Cl₃],10 [SiF₃(Me₃tacn)][SiF₅],11 [Ge(Me₃tacn)]Br·[GeBr₄],12 and [Ge(Me₄cyclam)][GeCl₃]₄.12

Here we report the synthesis of several new Ge(II) monocations and Si(IV) monocations based upon neutral triaza- and tetra-aza macroyclic ligands with a variety of anions. Single crystal X-ray structural studies on representative examples are described and compared.

Experimental
SiCl₄, SiHCl₃, Me₃SiO₃SCF₃, [GeCl₃(dioxane)] and the N-donor ligands were obtained from Sigma Aldrich, except for Me₃tacn which was prepared using the literature route.13 Na[BARF]₃ ([BARF]⁻ = [B₃,5-(CF₃)₂C₆H₃]₄⁻) was synthesised by a modification of Brookhart’s procedure.14 Me₂NCH₂CH₂N(Me)CH₂CH₂NMe₂ (pmdta) was distilled from CaH₂. All experiments were performed under strictly anhydrous conditions using glove-boxes and Schlenk techniques. CH₂Cl₂ was dried by distillation from CaH₂. Toluene was distilled from sodium, hexane was distilled from Na/K alloy and thf was distilled from...
Na/benzophene ketyl. IR spectra were recorded as Nujol mulls between CsI plates using a Perkin Elmer Spectrum 100 spectrometer over the range 4000–200 cm\(^{-1}\). \(^1\)H and \(^19\)F NMR spectra were recorded using a Bruker DPX-400 spectrometer and referenced to the residual solvent resonance and external CFCI\(_4\) respectively. Microanalytical measurements were performed by London Metropolitan University.

\[
\text{[Ge(Me}_4\text{cycalen)]O}_3\text{SCF}_3\text{]}_2
\]

\[\text{[GeCl}_2\text{(dioxane)] (0.058 g, 0.25 mmol) was dissolved in thf (10 mL) and a solution of Me}_5\text{SiO}_3\text{SCF}_3\) (0.115 g, 0.52 mmol) in thf (5 mL) was added with stirring, giving a colourless solution. After 10 min, a solution of Me\(_4\text{cycalen} (0.057 g, 0.25 mmol) in thf (5 mL) was added, causing the formation of a white precipitate. After stirring for a further 1 h, the product was collected by filtration and dried in vacuo. Yield: 0.120 g (80%). Anal. calc. for C\(_{16}\)H\(_{32}\)F\(_6\)GeN\(_4\)O\(_6\)S\(_2\) (627.2): C, 30.65; H, 5.14; N, 8.93. Found: C, 30.65; H, 5.14; N, 8.93.\]

\[
\text{[GeCl}_2\text{(dioxane)] (0.059 g, 0.26 mmol) was suspended in CH}_2\text{Cl}_2 (10 mL) and a solution of Me}_5\text{SiO}_3\text{SCF}_3\) (0.112 g, 0.50 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added with stirring, giving a colourless solution. After 10 min Me\(_4\text{cycalen} (0.044 g, 0.26 mmol) was added, causing the formation of a white precipitate. After stirring for approximately 1 h, the product was collected by filtration and dried in vacuo. Yield: 0.085 g (62%). Anal. calc. for C\(_{14}\)H\(_{28}\)F\(_6\)GeN\(_4\)O\(_6\)S\(_2\) (599.1): C, 28.08; H, 4.61; N, 9.26.\]

\[
\text{[Ge(Me}_4\text{cycalen)]O}_3\text{SCF}_3\text{]}_2
\]

\[\text{[GeCl}_2\text{(dioxane)] (0.059 g, 0.26 mmol) was suspended in CH}_2\text{Cl}_2 (10 mL) and a solution of Me}_5\text{SiO}_3\text{SCF}_3\) (0.112 g, 0.50 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added with stirring, giving a colourless solution. After 10 min Me\(_4\text{cycalen} (0.044 g, 0.26 mmol) was added, causing the formation of a white precipitate. After stirring for approximately 1 h, the product was collected by filtration and dried in vacuo. Yield: 0.085 g (62%). Anal. calc. for C\(_{14}\)H\(_{28}\)F\(_6\)GeN\(_4\)O\(_6\)S\(_2\) (599.1): C, 28.08; H, 4.61; N, 9.26.\]

\[
\text{[Ge(Me}_4\text{cycalen)]O}_3\text{SCF}_3\text{]}_2
\]

\[\text{[GeCl}_2\text{(dioxane)] (0.059 g, 0.26 mmol) was suspended in CH}_2\text{Cl}_2 (10 mL) and a solution of Me}_5\text{SiO}_3\text{SCF}_3\) (0.112 g, 0.50 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added with stirring, giving a colourless solution. After 10 min Me\(_4\text{cycalen} (0.044 g, 0.26 mmol) was added, causing the formation of a white precipitate. After stirring for approximately 1 h, the product was collected by filtration and dried in vacuo. Yield: 0.085 g (62%). Anal. calc. for C\(_{14}\)H\(_{28}\)F\(_6\)GeN\(_4\)O\(_6\)S\(_2\) (599.1): C, 28.08; H, 4.61; N, 9.26.\]

\[
\text{[Ge(Me}_4\text{cycalen)]O}_3\text{SCF}_3\text{]}_2
\]

\[\text{[GeCl}_2\text{(dioxane)] (0.059 g, 0.26 mmol) was suspended in CH}_2\text{Cl}_2 (10 mL) and a solution of Me}_5\text{SiO}_3\text{SCF}_3\) (0.112 g, 0.50 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added with stirring, giving a colourless solution. After 10 min Me\(_4\text{cycalen} (0.044 g, 0.26 mmol) was added, causing the formation of a white precipitate. After stirring for approximately 1 h, the product was collected by filtration and dried in vacuo. Yield: 0.085 g (62%). Anal. calc. for C\(_{14}\)H\(_{28}\)F\(_6\)GeN\(_4\)O\(_6\)S\(_2\) (599.1): C, 28.08; H, 4.61; N, 9.26.\]

\[
\text{[Ge(Me}_4\text{cycalen)]O}_3\text{SCF}_3\text{]}_2
\]

\[\text{[GeCl}_2\text{(dioxane)] (0.059 g, 0.26 mmol) was suspended in CH}_2\text{Cl}_2 (10 mL) and a solution of Me}_5\text{SiO}_3\text{SCF}_3\) (0.112 g, 0.50 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added with stirring, giving a colourless solution. After 10 min Me\(_4\text{cycalen} (0.044 g, 0.26 mmol) was added, causing the formation of a white precipitate. After stirring for approximately 1 h, the product was collected by filtration and dried in vacuo. Yield: 0.085 g (62%). Anal. calc. for C\(_{14}\)H\(_{28}\)F\(_6\)GeN\(_4\)O\(_6\)S\(_2\) (599.1): C, 28.08; H, 4.61; N, 9.26.\]

\[
\text{[Ge(Me}_4\text{cycalen)]O}_3\text{SCF}_3\text{]}_2
\]

\[\text{[GeCl}_2\text{(dioxane)] (0.059 g, 0.26 mmol) was suspended in CH}_2\text{Cl}_2 (10 mL) and a solution of Me}_5\text{SiO}_3\text{SCF}_3\) (0.112 g, 0.50 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added with stirring, giving a colourless solution. After 10 min Me\(_4\text{cycalen} (0.044 g, 0.26 mmol) was added, causing the formation of a white precipitate. After stirring for approximately 1 h, the product was collected by filtration and dried in vacuo. Yield: 0.085 g (62%). Anal. calc. for C\(_{14}\)H\(_{28}\)F\(_6\)GeN\(_4\)O\(_6\)S\(_2\) (599.1): C, 28.08; H, 4.61; N, 9.26.\]
for C_{10}H_{11}Cl_{2}F_{2}N_{3}O_{2}Si (454.8): C, 26.40; H, 4.66; N, 9.24. Found: C, 26.61; H, 4.73; N, 9.25%. \(^1\)H NMR (295 K, CD_{3}CN): 3.54–3.66 (m, [6H], NCH_{3}), 3.31–3.41 (m, [6H], NCH_{3}), 3.17 (s, [9H], NCH_{3}). \(^{13}\)C{\(^1\)H} NMR (295 K, CD_{3}CN): 122.20 (q, \(J_{C-F} = 320\) Hz, CF_{3}), 54.84 (CH_{3}), 53.49 (CH_{3}). \(^{15}\)F{\(^1\)H} NMR (295 K, CD_{3}CN): –78.7 (O_{2}SCF_{3}). IR (Nujol, cm\(^{-1}\)): 231s, 428s (SiCl), 460s (SiCl), 497m, 517m, 574m, 601m, 637s, 754m, 899m, 967m, 998m, 1029s, 1053m, 1155s, 1225m.

Crystals were obtained by layering a concentrated CH_{2}Cl_{2} solution with hexane.

\[\text{SiHCl}_{3} (\text{Me}_{3}\text{tacn})][\text{BARF}^{+}]\]

\[\text{SiHCl}_{3} (0.068 g, 0.50 mmol)\] and Na[BARF] \( (0.443 g, 0.50 mmol)\) were dissolved in toluene \( (10 \text{ mL})\) and stirred for 5 min. A solution of Me_{3}\text{tacn} \( (0.085 g, 0.50 mmol)\) in toluene \( (5 \text{ mL})\) was added then the reaction was stirred for 4 h. After this time, volatiles were removed \textit{in vacuo} and the solid extracted into CH_{2}Cl_{2} \( (5 \text{ mL})\), filtered and hexane \( (30 \text{ mL})\) added to precipitate a white solid. Yield: 0.421 g (74%). Anal. calc. for C_{11}H_{12}BCl_{2}F_{2}N_{2}Si (1134.12): C, 43.98; H, 3.02; N, 3.70. Found: C, 43.45; H, 3.11; N, 3.80%.

\[\text{SiBr}_{3} (\text{pmdta})][\text{BARF}^{+}]\]

\[\text{SiBr}_{3} (0.174 g, 0.50 mmol)\] and NaN[BARF] \( (0.443 g, 0.50 mmol)\) were dissolved in toluene \( (10 \text{ mL})\) and stirred for 5 min. A solution of pmdta \( (0.087 g, 0.50 mmol)\) in toluene \( (5 \text{ mL})\) was added then the reaction was stirred for 4 h. After this time, volatiles were removed \textit{in vacuo} and the solid extracted into CH_{2}Cl_{2} \( (5 \text{ mL})\), filtered and hexane \( (30 \text{ mL})\) added to precipitate a white solid. Yield: 0.291 g (45%). Anal. calc. for C_{41}H_{33}BBr_{3}F_{24}N_{3}Si (1303.93): C, 37.73; H, 2.71; N, 3.22. Found: C, 37.57; H, 2.80; N, 3.26%.

\[\text{SiCl}_{4} (\text{Me}_{3}\text{tacn})][\text{Cl}^{-}]\]

Made similarly using SiCl_{4} \( (0.085 g, 0.50 mmol)\) in place of SiHCl_{3}. Yield: 0.466 g (82%). Anal. calc. for C_{14}H_{13}BCl_{4}F_{3}N_{4}Si (1168.9): C, 41.85; H, 3.08; N, 3.74%.

A concentrated CH_{2}Cl_{2} solution of this complex layered with hexane deposited a few colourless crystals which were identified from an X-ray crystallographic study as \[\text{SiCl}_{4} (\text{Me}_{3}\text{tacn})][\text{Cl}].\] Attempts to prepare the latter directly from \[\text{SiCl}_{4} (\text{Me}_{3}\text{tacn})][\text{Cl} (10 and 24, respectively) which is explained by the presence of multiple cation units with very similar, but not identical, metrical parameters in the asymmetric unit. H atoms attached to C atoms were placed in geometrically assigned positions, with C–H distances of 0.95 Å (CH) and 0.98 Å (CH_{3}) and refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C) (CH_{3}) or 1.5U_{eq}(C) (CH). Si–H and N–H protons were located in the Fourier difference map and allowed to refine freely. enCIFer was used to prepare CIFs for publication.15e

X-ray crystallography

Crystals were obtained as described above. Details of the crystallographic data collection and refinement are in Table 1. Diffractometer: Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E: SuperBright molybdenum rotating anode generator \( (\lambda = 0.71073 \text{ Å})\) with VHF Varimax optics \( (70 \text{ or } 100 \mu \text{m focus})\). Cell determination, data collection, data reduction, cell refinement and absorption correction: CrystalClear-SM Expert 2.0 r7.4.2d Structure solution and refinement were carried out using WinGX or Olex2 and software packages within.15d–e No positional disorder was observed in complexes of [BARF]^{+}, despite this being a common issue with weakly-coordinating anions containing CF_{3} groups, especially [BARF]^{+}.16 [Ge(\text{Me}_{3}\text{tacn})][\text{Cl}_{2} \text{MeCN} crystallised as an inversion twin with a BASF of 0.21. Unusually large Z values were observed for \([\text{Ge(\text{Me}_{4}\text{cyclen})][\text{O}_{3}\text{SCF}_{3}]_{2} \cdot 0.8\text{MeCN} and [\text{SiCl}_{4} (\text{Me}_{3}\text{tacn})][\text{Cl}] (10 and 24, respectively) which is explained by the presence of multiple cation units with very similar, but not identical, metrical parameters in the asymmetric unit. H atoms attached to C atoms were placed in geometrically assigned positions, with C–H distances of 0.95 Å (CH) and 0.98 Å (CH_{3}) and refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C) (CH_{3}) or 1.5U_{eq}(C) (CH). Si–H and N–H protons were located in the Fourier difference map and allowed to refine freely. enCIFer was used to prepare CIFs for publication.15e

This article is licensed under a Creative Commons Attribution 3.0 Unported License.
Germanium(II) complexes

Results and discussion

Germanium(II) complexes

We have previously reported\(^1\)\(^2\) that reaction of GeBr\(_2\) with Me\(_3\)tacn in anhydrous MeCN solution gives colourless \([\text{Ge(}\text{Me}\(_3\)tacn\text{-})\text{Cl}]^{\text{2+}}\) dications (Ge–N = 2.124(3)–2.156(3) Å), with Br\(^{-}\) and [GeBr\(_3\)]\(^{-}\) anions providing charge balance. We find that reaction of \([\text{GeCl}_2\text{(dioxane)}]\) with Me\(_3\)tacn in anhydrous CH\(_2\)Cl\(_2\) followed by addition of Me\(_3\)SiO\(_3\)SCF\(_3\) gave a colourless powder, \([\text{Ge(Me}\(_3\)tacn\text{-})\text{[O}_2\text{SCF}_3\text{]}_2\text{MeCN}\text{-}}\), subsequently obtained as colourless crystals of \([\text{Ge(Me}\(_3\)tacn\text{-})\text{Cl}[\text{O}_2\text{SCF}_3\text{]}_2\text{]}\), by recrystallisation from MeCN/Et\(_2\)O. The structure (Fig. 1) also reveals a pyramidal Ge\(_3\)N\(_3\) unit, however, in this species there are also weak directional Ge...O interactions from one oxygen in each triflate anion at 2.850(2) and 3.176(2) Å, well within the sum of vdw radii for O and Ge (3.79 Å).\(^1\)

While there is no evidence for 2 : 1 Me\(_3\)tacn : Ge species (presumably due to steric clashing of the Me groups on the relatively small Ge(II) centre), the anions present in the products proved to be very sensitive to the reaction conditions; if the reaction of \([\text{GeCl}_2\text{(dioxane)}]\), Me\(_3\)tacn and Me\(_3\)SiO\(_3\)SCF\(_3\) was conducted in MeCN solution as described in the

<table>
<thead>
<tr>
<th>Compound</th>
<th>([\text{Ge(Me}(_3)tacn\text{-})\text{Cl}]^{\text{2+}}\text{MeCN}\text{-}})</th>
<th>([\text{Ge(Me}(_3)tacn\text{-})\text{Cl}[\text{O}_2\text{SCF}_3\text{]}_2\text{]})</th>
<th>([\text{Ge(Me}(_3)tacn\text{-})\text{Cl[O}_2\text{SCF}_3\text{]}_2\text{]})</th>
<th>([\text{Ge(Me}(_3)tacn\text{-})\text{Cl[O}_2\text{SCF}_3\text{]}_2\text{]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>([\text{GeCl}_2\text{(dioxane)}]\text{MeCN}\text{-}})</td>
<td>([\text{Ge(Me}(_3)tacn\text{-})\text{Cl}]^{\text{2+}}\text{MeCN}\text{-}})</td>
<td>([\text{Ge(Me}(_3)tacn\text{-})\text{Cl]}^{\text{2+}}\text{MeCN}\text{-}})</td>
<td>([\text{Ge(Me}(_3)tacn\text{-})\text{Cl]}^{\text{2+}}\text{MeCN}\text{-}})</td>
</tr>
<tr>
<td>M(g mol(^{-1}))</td>
<td>583.07</td>
<td>631.96</td>
<td>438.40</td>
<td>355.83</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Tetragonal</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group (No.)</td>
<td>P2(_1)/n (14)</td>
<td>P4(_1) (\text{c}(103))</td>
<td>P2(_1)/c (14)</td>
<td>Pn(_2) (\text{c}(33))</td>
</tr>
<tr>
<td>(a/\text{Å})</td>
<td>13.541(5)</td>
<td>17.1253(3)</td>
<td>18.152(9)</td>
<td>14.399(5)</td>
</tr>
<tr>
<td>(b/\text{Å})</td>
<td>8.543(5)</td>
<td>17.1253(3)</td>
<td>13.9764(15)</td>
<td>10.139(5)</td>
</tr>
<tr>
<td>(c/\text{Å})</td>
<td>19.620(5)</td>
<td>22.1160(10)</td>
<td>14.2804(16)</td>
<td>21.491(5)</td>
</tr>
<tr>
<td>(α/°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(β/°)</td>
<td>97.495(5)</td>
<td>101.705(7)</td>
<td>101.705(7)</td>
<td>101.705(7)</td>
</tr>
<tr>
<td>(γ/°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Result and discussion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Common items: T = 100 K; wavelength (Mo-K\(_\alpha\)) = 0.71073 Å; \(θ(\text{max}) = 27.5°\). \(R_1 = \sum |F_o| - |F_c||/\sum |F_o|; wR_2 = \sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^{1/2}.\)
Experimental section, concentrated in vacuo, and the solution layered with Et₂O, the product was isolated as rod-like crystals of [Ge(Me₃tacn)]Cl[O₃SCF₃]. The X-ray structure of this species (Fig. 2) shows the complex forms a weakly associated dimer in the solid state via the chloride bridges (Ge···Cl = 3.0254(9), 3.214(1) Å) and with a similar pyramidal ‘Ge¹'[Me₃tacn]’ core. These Ge···Cl interactions are substantially within the sum of vdW radii for Ge and Cl (4.11 Å). One k²-coordinated triflate completes a distorted six-coordinate environment at each germanium centre.

The same reaction conducted in MeCN solution, but worked up after 15 min and placed in a freezer, deposited a few rod-like crystals that were identified as [Ge(Me₃tacn)]·Cl₂·MeCN by X-ray crystallography (Fig. 3). In this case the ‘Ge¹'[Me₃tacn]’ core has two long contacts to the chlorides at 3.028(4) and 3.028(3) Å. The closest intermolecular contact is to a chloride of an adjacent molecule, but the Ge···Cl distance is the same as the sum of vdW radii for Ge and Cl (within experimental error), most likely a consequence of crystal packing.

Comparison of the Ge–N distances in this series of complexes shows only small differences as a function of the anion(s) present, suggesting that the structures are dominated by the ‘Ge¹'[Me₃tacn]’ core. All of the Ge–N distances are considerably longer than the sum of the covalent radii (1.85 Å), but well within the sum of the van der Waals radii (3.66 Å).

The spectroscopic data provide very limited information; the IR spectra show the Me₃tacn and the [O₃SCF₃]⁻ (when present), whilst the ¹H NMR spectra show small high frequency shifts corresponding to coordinated Me₃tacn. The complexes are extremely sensitive to hydrolysis by trace water, readily forming protonated Me₃tacn.

The reaction of [GeCl₂(dioxane)] and Me₃SiO₃SCF₃ in thf followed by addition of Me₆cyclam gave [Ge[Me₆cyclam]][O₃SCF₃]₂. Attempts to obtain crystals of this complex were unsuccessful with recrystallisation from MeCN/Et₂O or CH₂Cl₂/Et₂O giving [Me₆cyclamH₃][O₃SCF₃]₂ (identical crystallographically). We reported the structure of [Ge[Me₆cyclam]][GeCl₃]₃ in our preliminary communication, which revealed an essentially coplanar N₄ with the Ge out of the plane by 0.83 Å, and with no significant interaction with the anions. The data also revealed a spread of Ge–N distances (2.151(2)–2.349(2) Å), suggesting germanium[II] is not a good fit to the relatively large 14-membered macrocyclic cavity; this may correlate with the very ready hydrolysis in solution.

Replacing the 14-membered Me₆cyclam ring by the 12-membered Me₆cyclo (1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotetradecane) gave colourless [Ge[Me₆cyclo]][O₃SCF₃]₂. Crystals of [Ge[Me₆cyclo]][O₃SCF₃]₂·0.8CH₂CN suitable for
X-ray diffraction were obtained by layering an acetonitrile solution of the complex with diethyl ether. The structure (Fig. 4) also shows the Ge(n) centre coordinated to a tetradentate Me3cyclen macrocycle with the Ge–N bonds alternating short-long-short-long around the ring, Ge–N = 2.165(6)–2.244(5) Å, with the Ge lying 1.009(3) Å above the mean N4 plane. In both complexes the methyl substituents on nitrogen are directed to the same side of the plane as the germanium centre. There are no significant interactions to the triflate anions, therefore, the germanium is in a highly distorted square planar, or tetragonal pyramidal, environment.

The reaction of \([\text{SiCl}_3(\text{dioxane})]\) in CH2Cl2 with Me4cyclen in a 3:1 molar ratio gave the corresponding \([\text{Ge}(\text{Me4cyclen})]\)[\([\text{GeCl}_3]\)]2, which was less stable in solution.

**Silicon(\(v\)) complexes**

The reaction of \([\text{SiCl}_4]\), Me3tacn and Me3SiO3SCF3 in anhydrous CH2Cl2 solution produced \([\text{SiCl}_3(\text{Me3tacn})]\)[\([\text{O}_3\text{SCF}_3]\)]2, which is much more hydrolytically sensitive than the \([\text{SiF}_3(\text{Me3tacn})]\)[\([\text{SiF}_5]\)] salt.13 Crystals of this chloro-complex were obtained by layering a concentrated CH2Cl2 solution with hexane. The structure of the cation shows the expected fac-octahedral coordination (Fig. 5). Comparison with the \([\text{SiF}_3(\text{Me3tacn})]\) cation shows negligible differences between the Si–N distances.

The corresponding \([\text{SiCl}_3(\text{Me3tacn})][\text{BAR}^3]\) was obtained by reacting \([\text{SiCl}_4]\) and Na[BAR\(^3\)] in toluene, followed by addition of a solution of Me3tacn. As we have described elsewhere,10 if the reagents are added simultaneously, the product is the sodium complex of the ligand, rather than the silicon cation. Crystals of \([\text{SiCl}_3(\text{Me3tacn})][\text{BAR}^3]\) were not obtained, however, a concentrated CH2Cl2 solution of the \([\text{BAR}^3]\) salt, layered with hexane, produced a few colourless crystals identified by an X-ray structure determination as \([\text{SiCl}_3(\text{Me3tacn})]\)[Cl] (see Fig. S1 in ESI†) which separate adventitiously due to the lower solubility of this salt. Direct reaction of \([\text{SiCl}_4]\) and Me3tacn in CH2Cl2 resulted in precipitation of a pale yellow solid containing the same \([\text{SiCl}_3(\text{Me3tacn})]\)[Cl], however we have been unable to obtain it in analytically pure form by this route.

The \(^1\text{H}\) NMR spectrum of \([\text{SiCl}_3(\text{Me3tacn})]\) in CD3CN at 298 K shows sharp second order multiplets characteristic of symmetrical fac-coordinated Me3tacn in solution.20 Similar reaction of SiHCl3 with Na[BAR\(^3\)] in toluene, followed by addition of Me3tacn, produced the corresponding dichlorosilane complex, \([\text{SiCl}_2(\text{Me3tacn})][\text{BAR}^3]\). The presence of the Si–H group is shown by a singlet in the \(^1\text{H}\) NMR spectrum at \(\delta = 4.78\) and by \(\nu\)(SiH) in the IR spectrum at 2137 cm\(^{-1}\). The presence of the fac-SiHCl3 removes the threefold symmetry of the Me3tacn found in \([\text{SiCl}_3(\text{Me3tacn})]\), and this is reflected in both the \(^1\text{H}\) and \(^13\text{C}\)\(^{\text{[\(\text{H}\)]}}\) NMR spectra, which show two \(\delta\)(Me) resonances and corresponding splitting of the NCH2 resonances. Attempts to determine the structure of this complex have been unsuccessful. Poor quality crystals were obtained, but structure solution showed disordered \([\text{SiCl}_3(\text{Me3tacn})]\) and \([\text{SiHCl}_2(\text{Me3tacn})]\) were both present (note that \([\text{SiCl}_3(\text{Me3tacn})]\) is not present in the NMR spectra of the bulk product). Disproportionation of silane complexes of amine ligands has been noted in other systems, and presumably occurs here slowly over the time taken to grow crystals from the \([\text{SiHCl}_3(\text{Me3tacn})]\) solution.21

Finally, two complexes of the linear triamine, Me2NCH2CH2N(Me)CH2CH2NMe2 (pmdta), \([\text{SiX}_3(\text{pmdta})][\text{BAR}^\text{X}](\text{X} = \text{Cl or Br})\) were isolated by reacting the appropriate SiX3 with Na[BAR\(^3\)] in toluene, followed by addition of pmdta. The X-ray crystal structure of the chloride reveals a mer-geometry (Fig. 6) which contrasts with the fac arrangement found in the Me3tacn complexes. The geometry of the \([\text{SiCl}_3(\text{pmdta})]\) cation is close to octahedral, and the Si–N and Si–Cl distances are little different from those found in \([\text{SiCl}_3(\text{Me3tacn})]\).
despite the different donor arrangements. The geometry is also similar to that found in 

\[ \text{mer}-\text{[SiHCl}_3\text{(pmdta)}]^- \] (which has H trans to Cl).22

The spectroscopic data are unexceptional, but consistent with the mer geometries, although it is notable that the terminal –NMe_2 groups appear as a broad singlet rather than the two resonances expected due to the inequivalence produced by the central –NMe group lying out of the N_3Cl plane. The ease of formation of the \[ \text{[SiX}_3\text{(pmdta)}]^- \] cations \((X_3 = \text{Cl}_3, \text{Br}_3, \text{HCl}_2)\) is in contrast with the \(\text{k}^2\)-coordinated pmdta adduct formed with \(\text{SiF}_4\), reflecting the much higher Si–F bond strength.11

Conclusions

Two series of complexes with neutral aza-macrocyclic coordination to Ge(n) and Si(n) are reported and structurally characterised. The hydrolytically sensitive Ge(n) triaza macrocyclic complexes show pyramidal GeN3 coordination with very weak, but variable, interactions from the chloride and triflate anions. This contrasts with the ‘naked’ dication identified in the previously reported \([\text{Ge(Me}_3\text{tacn)}]\text{Br[GeBr}_3]^-\).12 The tetra-aza macrocyclic complexes of Ge(n) give GeN4 dications in highly distorted square planar geometries, with no significant anion interactions towards Ge(n).

The triaza ligand complexes of Si(n), formed by halide abstraction using either Me_3SiOSCF_3 or Na[BF_4]^-, adopt distorted octahedral coordination geometries, and the chloro-, tribromo- and hydridodichloro-species reported here are significantly more readily hydrolysed than \([\text{SiF}_3(\text{Me}_3\text{tacn})]^-\).11

Acknowledgements

We thank EPSRC for support (EP/I010890/1 and EP/I033394/1). The SCFED Project (http://www.scfed.net) is a multidisciplin-