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

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

[GeCl₂(dioxane)] reacts with the neutral aza-macrocyclic ligands L, L = Me₃tacn (1,4,7-trimethyl-1,4,7-triazaacyclononane), Me₂cyclem (1,4,7,10-tetramethyl-1,4,7,10-tetraazaacyclodecane) or Me₂cyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazaacyclotetradecane) and two mol. equiv. of Me₂SiO₃SCF₃ in thf solution to yield the unusual and hydrolytically very sensitive [Ge(L)[O₃SCF₃]₂] as white solids in moderate yield. Using shorter reaction times [Ge(Me₂tacn)]Cl₂ and [Ge(Me₂tacn)]Cl[O₃SCF₃] were also isolated; the preparation of [Ge(Me₂cyclem)][GeCl₃]₂ is also described. The structures of the Me₂tacn complexes show κ⁵-coordination of the macrocycle, with the anions interacting only weakly to produce very distorted five- or six-coordination at germanium. In contrast, the structure of [Ge(Me₂cyclem)][O₃SCF₃]₂ shows no anion interactions, and a distorted square planar geometry at germanium from coordination to the tetra-aza macrocycle. Crystal structures of the Si(IV) complexes, [SiCl₂(Me₂tacn)]Y (Y = O₃SCF₃, BArF; [B{3,5-(CF₃)₂C₆H₃}₄]) and [SiCl₂(Me₄cyclen)][BArF] were also prepared from reaction of Me₂SiO₃SCF₃ with Me₂tacn, followed by addition of either Me₂SiO₃SCF₃ or Na[BarF], contain distorted octahedral cations, with facial κ³-coordinated Me₂tacn. The open-chain triamine, Me₂NCH₂CH₂N(Me)CH₂CH₂NMe₂ (pmdta), forms [SiCl₂(pmdta)][BarF] and [SiBr₂(pmdta)][BarF] under similar conditions, containing mer-octahedral cations.

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) 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 [GeF₃(Me₃tacn)]₂[GeF₄] (Me₃tacn = 1,4,7-trimethyl-1,4,7-triazaacyclononane),⁹ [[GeF₂L]κ³-κ⁵-Me₂cyclam] (Me₂cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazaacyclotetradecane),⁹ [GeCl₄-(Me₂tacn)][(H₂O₂)₂Cl₆],¹⁰ [SiF₂(Me₂tacn)][SiF₅],¹¹ [Ge(Me₂tacn)]Br-[GeBr₄]₁² and [Ge(Me₂cyclam)]Cl[GeCl₃]₁². Here we report the synthesis of several new Ge(II) monocations and Si(IV) monocations based upon neutral triaza- and tetra-aza macrocyclic ligands with a variety of anions. Single crystal X-ray structural studies on representative examples are described and compared.

Experimental

SiCl₄, SiHCl₄, Me₂SiO₃SCF₃, [GeCl₃(dioxane)] and the N-donor ligands were obtained from Sigma Aldrich, except for Me₂tacn which was prepared using the literature procedure.¹³ Na[BarF] ([BarF]⁻ = [B{3,5-(CF₃)₂C₆H₃}]⁻) 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

School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK.
E-mail: G.Reid@soton.ac.uk; Tel: +44 (0)23 8059 3609
†Electronic supplementary information (ESI) available: CCDC 1430051 ([Ge(Me₃tacn)][O₃SCF₃])·MeCN, 1430052 ([Ge(Me₃tacn)][O₃SCF₃]·0.3MeCN), 1430053 ([Ge(Me₃tacn)][O₃SCF₃]·0.6MeCN), 1430054 ([Ge(Me₃tacn)][Cl]·MeCN), 1430055 ([SiCl₂(Me₄cyclen)][O₃SCF₃]), 1430056 ([SiCl₂(Me₄cyclen)][Cl]·MeCN), 1430058 ([SiCl₂(pmdta)][BArF]), 1430057 ([SiCl₂(pmdta)][BArF]). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt03941j

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Na/benzophenone 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 CFCl$_3$, respectively. Microanalytical measurements were performed by London Metropolitan University.

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

$\text{[GeCl}_4\text{(dioxane)] (0.058 g, 0.25 mmol) was dissolved in thf (10 mL) and a solution of Me$_2$SiO$_2$SCF}_3$$_2$ (0.115 g, 0.52 mmol) in thf (5 mL) was added with stirring, giving a colourless solution. After 10 min, a solution of Me$_2$cylen (0.057 g, 0.25 mmol) in thf (5 mL) was added, causing the formation of a white precipitate. After stirring for a further 1 h, the product was collected by filtration and dried in vacuo. Yield: 0.120 g (80%). Anal. calc. for C$_{14}$H$_{28}$F$_6$GeN$_4$O$_6$S$_2$: C, 28.08; H, 4.61; N, 9.26%. $^1$H NMR (CD$_3$CN, 298 K): 2.78 (s, [12H], NCH$_3$), 3.20–3.40 (m, [16H], NCH$_2$$_2$), $^{19}$F{$_1$H} NMR (CD$_3$CN, 298 K): −79.4 (O$_2$SCF$_3$). IR (Nujol/cm$^{-1}$): 743w, 757w, 802w, 1011m, 1034s, 1160s, 1226m, 1256s, 1278s.

$\text{[Ge(Me$_4$cylen)}]_2\text{GeCl}_2$

$\text{[GeCl}_4\text{(dioxane)] (0.058 g, 0.25 mmol) was dissolved in thf (10 mL) and a solution of Me$_2$SiO$_2$SCF}_3$$_2$ (0.115 g, 0.52 mmol) in thf (5 mL) was added with stirring, giving a colourless solution. After 10 min a solution of Me$_2$cylen (0.065 g, 0.26 mmol) in thf (5 mL) was added with stirring, giving a colourless solution. After 10 min Me$_4$cyclam (0.065 g, 0.25 mmol) was dissolved in thf (10 mL) was added with stirring, giving a colourless solution. After 10 min Me$_4$cyclen (0.057 g, 0.26 mmol) was added, causing the formation of a white precipitate. After stirring for approximately 1 h, the product was collected by filtration and dried in vacuo. Yield: 0.085 g (62%). Anal. calc. for C$_{14}$H$_{28}$F$_6$GeN$_4$S$_2$ (542.0): C, 24.38; H, 3.91; N, 7.75. Found: C, 24.51; H, 3.74; N, 7.84%. $^1$H NMR (CD$_3$CN, 298 K): 3.02 (s, [9H], NCH$_3$), 3.34–3.54 (m, [12H], NCH$_2$$_2$). $^{19}$F{$_1$H} NMR (CD$_3$CN, 298 K): −79.4 (O$_2$SCF$_3$). IR (Nujol/cm$^{-1}$): 420m, 451w, 517m, 574m, 639, 739m, 793w, 919w, 960w, 1030s, 1068w, 1155s, 1225s, 1260s.

Crystals of [Ge(Me$_4$cyclen)]O$_2$SCF$_3$$_2$·CH$_3$CN suitable for X-ray diffraction were obtained by layering an acetonitrile solution with diethyly ether.

$\text{[Ge(Me$_4$cylen)]Cl}[\text{O}_3\text{SCF}_3]$

In a similar reaction using a 1:1 molar ratio of [GeCl$_4$(dioxane)] and Me$_4$cyclen, conducted in MeCN solution, the mixture was stirred at room temperature for ca. 3 h following addition of Me$_2$SiO$_2$SCF$_3$, then concentrated in vacuo. This did not cause any precipitation, and the solution was layered with Et$_2$O and stored in the freezer. Small rod-shaped crystals formed, which were found to be [Ge(Me$_4$cyclen)]Cl[O$_3$SCF$_3$] as identified by an X-ray crystal structure determination. Anal. calc. for C$_{14}$H$_{28}$F$_6$GeN$_4$S$_2$ (428.4): C, 28.04; H, 4.94; N, 9.81. Found: C, 28.76; H, 4.85; N, 9.77%. $^1$H NMR (298 K, CD$_2$Cl$_2$): 2.94 (s, [9H], NCH$_3$), 3.21–3.47 (m, [12H], NCH$_2$$_2$). (A second minor species is also evident in the NMR spectrum.) $^{19}$F{$_1$H} NMR (CD$_3$CN, 298 K): −79.4 (O$_2$SCF$_3$).

$\text{[Ge(Me$_4$cylen)}]_2\text{Cl}_2$

In a further reaction conducted in MeCN solution, the mixture was stirred at room temperature for ca. 15 min following addition of Me$_2$SiO$_2$SCF$_3$, then concentrated in vacuo. This caused the rapid precipitation of a white solid, which redissolved on warming. Storage of this solution in the freezer furnished colourless rod-shaped crystals which were found by X-ray crystallographic analysis to be [Ge(Me$_4$cyclen)]-Cl$_2$·MeCN.

$\text{[SiCl}_4\text{(Me$_4$tacn)]O}_2\text{SCF}_3$$_2$

SiCl$_4$ (0.170 g, 1.0 mmol) and Me$_2$SiO$_2$SCF$_3$ (0.222 g, 1.0 mmol) were dissolved in CH$_2$Cl$_2$ (10 mL) and stirred for 5 min. A solution of Me$_4$cyclen (0.171 g, 1.0 mmol) in CH$_2$Cl$_2$ (5 mL) was added and the reaction was stirred for 16 h. After this time, a white solid had formed. This was collected by filtration and dried in vacuo. Yield: 0.204 g (45%). Anal. calc.
for C_{10}H_{12}Cl_{2}F_{3}N_{2}O_{2}Si (454.8): C, 26.40; H, 4.66; N, 9.24.
Found: C, 26.61; H, 4.73; N, 9.25%. 1H NMR (295 K, CD_{2}CN): 3.54–3.66 (m, [6H], NCH_{2}), 3.31–3.41 (m, [6H], NCH_{2}), 3.17 (s, [9H], NCH_{3}). 13C{1H} NMR (295 K, CD_{2}CN): 122.20 (q, J_{C-F} = 320 Hz, CF_{3}), 54.84 (CH_{3}), 53.49 (CH_{2}). 19F{1H} NMR (295 K, CD_{2}CN): –78.7 (O_{2}SCF_{3}). IR (Nujol, cm\(^{-1}\)): 2313, 428s (SiCl), 497m, 517m, 574m, 601m, 637s, 754m, 899m, 3200–20900 | 20898–20905 

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Crystallography

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

[SiHCl_{2}(Me_{3}tacn)][BaF]\(^{+}\)

SiHCl\(_{2}\) (0.068 g, 0.50 mmol) and Na[BaF] (0.443 g, 0.50 mmol) were dissolved in toluene (10 mL) and stirred for 5 min. A solution of Me_{3}tacn (0.085 g, 0.50 mmol) in toluene (5 mL) was added when the reaction was stirred for 4 h. After this time, volatiles were removed in vacuo and the solid extracted into CH_{2}Cl_{2} (5 mL), filtered and hexane (30 mL) added to precipitate a white solid. Yield: 0.421 g (74%). Anal. calc. for C_{41}H_{34}BCl_{2}F_{24}N_{3}Si (1134.12): C, 43.38; H, 3.02; N, 3.70. Found: C, 43.45; H, 3.11; N, 3.80%. 1H NMR (295 K, CD_{2}Cl_{2}): 7.72 (s, [8H], BArF H_{2/6}), 7.57 (s, [4H], BArF H_{4}), 2.76 (t, \(J_{C-F} = 320 \text{ Hz}, \text{CF}_{3}\)), 54.84 (CH_{3}), 53.49 (CH_{2}). 19F{1H} NMR (295 K, CD_{2}CN): –78.7 (O_{2}SCF_{3}). IR (Nujol, cm\(^{-1}\)): 2313, 428s (SiCl), 497m, 517m, 574m, 601m, 637s, 754m, 899m, 3200–20900 | 20898–20905 

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Crystallography

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

[SiBr_{4}(pmdta)][BaF]\(^{+}\)

SiBr_{4} (0.174 g, 0.50 mmol) and Na[BaF] (0.443 g, 0.50 mmol) were dissolved in toluene (10 mL) and stirred for 5 min. A solution of pmdta (0.087 g, 0.50 mmol) in toluene (5 mL) was added when the reaction was stirred for 4 h. After this time, volatiles were removed in vacuo and the solid extracted into CH_{2}Cl_{2} (5 mL), filtered and hexane (30 mL) added to precipitate a white solid. Yield: 0.291 g (45%). Anal. calc. for C_{41}H_{35}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%. 1H NMR (CD_{2}Cl_{2}): 7.72 (s, [8H], BaF H_{2/6}), 2.77 (t, \(J_{C-F} = 320 \text{ Hz}, \text{CF}_{3}\)), 54.72, 57.42 (CH 2), 45.08 (N(CH 3)2), 44.51 (NCH3). IR (Nujol, cm\(^{-1}\)): 363 m (SiBr), 471w, 521w, 584w, 682w, 712s, 838m, 887m, 898m, 925w, 955w, 1112s, 1144s, 1279s, 1358s.

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 or 100 µm focus). Cell determination, data collection, data reduction, cell refinement and absorption correction: CrystalClear-SM Expert 2.0 r7.4. Structure solution and refinement were carried out using WinGX or Olex2 and software packages within. No positional disorder was observed in complexes of [BaF]\(^{+}\), despite this being a common issue with weakly-coordinating anions containing CF\(_{3}\) groups, especially [BaF]\(^{+}\). \[\text{Ge(Me}_{3}\text{tacn)}\]Cl\(_{2}\)-MeCN crystallised as an inversion twin with a BASF of 0.21. Unusually large Z values were observed for [Ge(Me}_{4}\text{cyclen)}]O_{3}\text{SCF}_{3}\_{2}\cdot0.8\text{MeCN} and [SiCl}_{4}\cdot \text{(Me}_{3}\text{tacn)}\]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\(_{3}\)) or 0.99 Å (CH\(_{2}\)) and refined using a riding model, with \(U_{iso}(H) = 1.2U_{eq}(C)\) (CH\(_{3}\)) or 1.5\(U_{eq}(C)\) (CH\(_{2}\)). 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.
Germanium(II) complexes

We have previously reported12 that reaction of GeBr2 with Me3tacn in anhydrous MeCN solution gives colourless \([\text{GeMe}_3\text{tacn}])\cdot\text{MeCN}\), containing unusual discrete three-coordinate \([\text{Ge(Me}_3\text{tacn})]^{2+}\) cations (Ge–N = 2.124(3)–2.156(3) Å), with Br\(^–\) and \([\text{BrGeBr}_3]^{–}\) anions providing charge balance. We find that reaction of \([\text{GeCl}_2\text{dioxane}]\) with Me3tacn in anhydrous CH\(_2\)Cl\(_2\) followed by addition of Me\(_3\)SiO\(_3\)SCF\(_3\) gave a colourless powder, \([\text{GeMe}_3\text{tacn}])\cdot[\text{O}_2\text{SCF}_3]_2\text{MeCN}\), subsequently obtained as colourless crystals of \([\text{GeMe}_3\text{tacn}])\cdot[\text{O}_2\text{SCF}_3]_2\text{MeCN}\) by recrystallisation from MeCN/Et\(_2\)O. The structure (Fig. 1) also reveals a pyramidal GeN\(_3\) 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 3.179(2) Å, well within the sum of vdW radii for O and Ge (3.79 Å).17

<table>
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<th>Compound</th>
<th>([\text{GeMe}_3\text{tacn}])\cdot\text{MeCN})</th>
<th>([\text{GeMe}_3\text{tacn}])\cdot[\text{O}_2\text{SCF}_3]_2\text{MeCN})</th>
<th>([\text{GeMe}_3\text{tacn}])\cdot[\text{O}_2\text{SCF}_3]_2\text{MeCN})</th>
<th>([\text{GeMe}_3\text{tacn}])\cdot[\text{O}_2\text{SCF}_3]_2\text{MeCN})</th>
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<tr>
<td>Formula</td>
<td>C(<em>{13})H(</em>{22})F(_4)Ge(_n)O(_4)S(_2)</td>
<td>C(<em>{15})H(</em>{30}).(_4)F(_4)Ge(_n).O(_4)S(_2)</td>
<td>C(<em>{18}).H(</em>{21})Cl(_{11})Ge(_n)O(_4)S</td>
<td>C(<em>{41})H(</em>{35}).BCl(_3)Ge(_n)</td>
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<td>631.96</td>
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<tr>
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<td>1593.2(3)</td>
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<td>(wR_2) [all data]</td>
<td>0.142</td>
<td>0.142</td>
<td>0.116</td>
<td>0.119</td>
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</table>

Common items: \(T = 100 \) K; wavelength (Mo-K\(_\alpha\)) = 0.71073 Å; \(θ(\max) = 27.5°\). \(R_1 = \sum ||F_o|-|F_c||/\sum |F_o|; wR_2 = (\sum w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)\)^{1/2}.
These Ge\cdots vdW radii for Ge and Cl (4.11 Å). One few rod-like crystals that were identified as [Ge(Me3tacn)]- worked up after 15 min and placed in a freezer, deposited a manium centre. completes a distorted six-coordinate environment at each ger-

Experimental section, concentrated in vacuo, and the solution layered with Et2O, the product was isolated as rod-like crystals of [Ge(Me\_tacn)]\text{[O3SCF3]}\_2. 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\cdots Cl = 3.0254(9), 3.214(1) Å) and with a similar pyramidal 'Ge\textsuperscript{II}(Me\_tacn)' core. These Ge\cdots Cl interactions are substantially within the sum of vdW radii for Ge and Cl (4.11 Å). One k\textsuperscript{2}-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(Me\_tacn)]\_2Cl\_2MeCN by X-ray crystallography (Fig. 3). In this case the 'Ge\textsuperscript{II}(Me\_tacn)' 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\cdots 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\cdots 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 'Ge\textsuperscript{II}(Me\_tacn)' core. All of the Ge\cdots 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 Me\_tacn and the [O3SCF3]\_2^{-} (when present), whilst the \textsuperscript{1}H NMR spectra show small high frequency shifts corresponding to coordinated Me\_tacn. The complexes are extremely sensitive to hydrolysis by trace water, readily forming protonated Me\_tacn.

The reaction of [GeCl\_2(dioxane)] and Me\_4SiO3SCF\_3 in thf followed by addition of Me\_4cyclam gave [Ge(Me\_4cyclam)] [O3SCF\_3]\_2. Attempts to obtain crystals of this complex were unsuccessful with recrystallisation from MeCN/Et\_2O or CH\_2Cl\_2/ Et\_2O giving [Me\_4cyclamH\_2][O3SCF\_3]\_2 (identified crystallographically). We reported the structure of [Ge(Me\_4cyclam)] [GeCl\_3]\_2 in our preliminary communication,\textsuperscript{12} which revealed an essentially coplanar N\_4 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\cdots N distances (2.151(2)–2.349(2) Å), suggesting germanium\textsuperscript{[n]} 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 Me\_4cyclam ring by the 12-membered Me\_6cyclen (1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotetradecane) gave colourless [Ge(Me\_6cyclen)][O3SCF\_3]\_2. Crystals of [Ge(Me\_6cyclen)][O3SCF\_3]\_2·0.8CH\_2CN 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 tetradeutate Me₆cycloen 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 [GeCl₃(dioxane)] in CH₂Cl₂ with Me₆cycloen in a 3 : 1 molar ratio gave the corresponding [Ge(Me₆cycloen)]- [GeCl₄]₂ which was less stable in solution.

**Silicon(IV) complexes**

The reaction of SiCl₄, Me₃tacn and Me₃SiO₂SCF₃ in anhydrous CH₂Cl₂ solution produced [SiCl₃(Me₃tacn)][O₃SCF₃], which is much more hydrolytically sensitive than the [SiF₃(Me₃tacn)][SiF₅] salt.

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 [SiF₃(Me₃tacn)]⁺ cation shows negligible differences between the Si–N distances.

The corresponding [SiCl₃(Me₆cycloen)][BAR₃] was obtained by reacting SiCl₄ and Na[BAR₃] in toluene, followed by addition of a solution of Me₆cycloen. As we have described elsewhere,† if the reagents are added simultaneously, the product is the sodium complex of the ligand, rather than the silicon cation. Crystals of [SiCl₃(Me₆cycloen)][BAR₃] were not obtained, however, a concentrated CH₂Cl₂ solution of the [BAR₃]⁻ salt, layered with hexane, produced a few colourless crystals identified by an X-ray structure determination as [SiCl₃(Me₆cycloen)]Cl (see Fig. S1 in ESI†) which separate adventitiously due to the lower solubility of this salt. Direct reaction of SiCl₄ and Me₃tacn in CH₂Cl₂ resulted in precipitation of a pale yellow solid containing the same [SiCl₃(Me₃tacn)]Cl, however we have been unable to obtain it in analytically pure form by this route.

The ¹H NMR spectrum of [SiCl₃(Me₆tacn)] in CD₂CN at 298 K shows sharp second order multiplets characteristic of symmetrical fac-coordinated Me₆tacn in solution.

Similar reaction of SiHCl₃ with Na[BAR₃] in toluene, followed by addition of Me₆tacn, produced the corresponding dichlorosilane complex, [SiHCl₂(Me₆tacn)][BAR₃]. The presence of the Si–H group is shown by a singlet in the ¹H NMR spectrum at δ = 4.78 and by ν(SiH) in the IR spectrum at 2137 cm⁻¹. The presence of the fac-SiHCl₂ removes the threefold symmetry of the Me₆tacn found in [SiCl₃(Me₆tacn)]⁻, and this is reflected in both the ¹H and ³¹C{¹H} NMR spectra, which show two δ(Me) resonances and corresponding splitting of the NCH₃ resonances. Attempts to determine the structure of this complex have been unsuccessful. Poor quality crystals were obtained, but structure solution showed disordered [SiCl₃(Me₆tacn)]⁻ and [SiHCl₂(Me₆tacn)]⁻ were both present (note that [SiCl₃(Me₆tacn)]⁻ 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 [SiHCl₂(Me₆tacn)]⁻ solution.

Finally, two complexes of the linear triamine, Me₂NCH₂CH₂N(Me)CH₂CH₂NMMe₂ (pmdta), [SiX₃(pmdta)][BAR₃] (X = Cl or Br) were isolated by reacting the appropriate SiX₃ with Na[BAR₃] 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 Me₆tacn complexes. The geometry of the [SiCl₃(pmdta)]⁺ cation is close to octahedral, and the Si–N and Si–Cl distances are little different from those found in [SiCl₃(Me₆tacn)]⁻.
Despite the different donor arrangements. The geometry is also similar to that found in mer-[SiHCl2[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 –NMe₂ 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 N₂Cl plane. The ease of formation of the [SiX₃[pmdta]]⁺ cations (X₃ = Cl₃, Br₃, HCl₂) is in contrast with the κ²-coordinated pmdta adduct formed with SiF₄, 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 [Ge(Me₃tacn)]Br[GeBr₃].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 Me₃SiOSiCl₃ or Na[BArF₄], adopt distorted octahedral coordination geometries, and the trichloro-, tribromo- and hydridodichloro-species reported here are significantly more readily hydrolysed than [SiF₄(Me₃tacn)]⁺.¹¹

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### References