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-triazacyclononane), Me₄cyclen (1,4,7,10-tetramethyl-1,4,7,10-tetraazaacyclododecane) or Me₄cyclam (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(Me₃tacn)][Cl₂ and [Ge(Me₃tacn)][Cl(O₃SCF₃)] were also isolated; the preparation of [Ge(Me₄cyclen)][GeCl]₂ is also described. The structures of the Me₄tacn 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(Me₄cyclen)][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(Me₃tacn)]Y (Y = O₃SCF₃, BArF; [B{3,5-(CF₃)₂C₆H₃}₄]) and [SiCl₃(Me₄cyclen)][BArF], obtained from reaction of SiCl₄ or SiHCl₃ with Me₃tacn, followed by addition of either Me₂SiO₃SCF₃ or Na[BArF], contain distorted octahedral cations, with facial κ⁵-coordinated Me₃tacn. The open-chain triamine, Me₂NCH₂CH₂N(Me)CH₂CH₂NMe₂ (pmdta), forms [SiCl₂(pmdta)][BArF]⁻ and [SiBr₃(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. We are currently developing routes to electrochemically deposit the elements and their binary and ternary alloys from both organic solvents and supercritical fluids. 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, and cationic complexes are rather rare, while Si(II) halide complexes are limited to N-heterocyclic carbenes. Aza-macrocyclic complexes reported include [GeF₄(Me₃tacn)][GeF₃] (Me₃tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane), [GeCl₄][κ⁵κ⁴-Me₄cyclam] (Me₄cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazaacyclotetradecane), [GeCl₄(Me₄cyclen)][H₂O]Cl₂, [SiF₃(Me₄cyclen)][SiF₅], [Ge(Me₄cyclen)][Br-GeBr₃] and [Ge(Me₄cyclam)][GeCl₃]. Here we report the synthesis of several new Ge(II) monocations and dications 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, SiHCl₃, Me₃SiO₃SCF₃, [GeCl₂(dioxane)] and the N-donor ligands were obtained from Sigma Aldrich, except for Me₄tacn which was prepared using the literature route. 13 Na[BArF]⁻ ([BArF]⁻ = [B{3,5-(CF₃)₂C₆H₃}₄]⁻) was synthesised by a modification of Brookhart’s procedure. 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/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.

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

\[\text{[GeCl}_2\text{(dioxane)] (0.059 g, 0.26 mmol) was dissolved in thf (10 mL) and a solution of Me}_3\text{SiO}_3\text{SCF}_3\text{ (0.115 g, 0.52 mmol) in thf (5 mL) was added with stirring, giving a clear, colourless solution. After 10 min, a solution of Me}_4\text{cyclen (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\(_{10}\)H\(_{21}\)F\(_6\)GeN\(_3\)O\(_6\)S\(_2\) (542.0): C, 24.38; H, 4.71; N, 9.35. Found: C, 28.19; 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\(_2\)). \(^{19}\)F\(^1\)H NMR (CD\(_3\)CN, 298 K): 79.4 (O\(_3\)SCF\(_3\)). IR (Nujol/cm\(^{-1}\)): 474v, 517m, 573m, 639s, 739m, 785m, 917s, 945m, 958s, 1014s, 1024s, 1051s, 1064s, 1151m, 1226s, 1275s, 1298s.\]

\[\text{[Me}_4\text{cyclen]}\text{[GeCl}_3\text{]}_2\]

\[\text{[GeCl}_2\text{(dioxane)] (0.059 g, 0.26 mmol) was dissolved in CH}_2\text{Cl}_2 (10 mL) and a solution of Me}_3\text{SiO}_3\text{SCF}_3\text{ (0.112 g, 0.50 mmol) in CH}_2\text{Cl}_2 (10 mL) was added with stirring, giving a colourless solution. After 10 min Me}_4\text{tacn (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\(_{10}\)H\(_{21}\)F\(_3\)GeN\(_3\)O\(_3\)S (428.4): C, 28.04; H, 4.94; N, 9.81. \(^1\)H NMR (CD\(_3\)CN, 298 K): 3.02 (s, [9H], NCH\(_3\)), 3.34-3.54 (m, [12H], NCH\(_2\)). \(^{19}\)F\(^1\)H NMR (CD\(_3\)CN, 298 K): -79.4 (O\(_3\)SCF\(_3\)). IR (Nujol/cm\(^{-1}\)): 420v, 451w, 516v, 573m, 693s, 739m, 785m, 898m, 982w, 994m, 1030s, 1049m, 1138m, 1167s, 1226s, 1259s.

Crystals of [Ge4tacn][O\(_3\)SCF\(_3\)]\(_2\)-CH\(_3\)CN suitable for X-ray diffraction were obtained by layering an acetonitrile solution with diethyl ether.

\[\text{[Ge}_4\text{tacn]}\text{[Cl}_2\text{[O}_3\text{SCF}_3\text{]}_2\]

In a similar reaction using a 1:1 molar ratio of [GeCl\(_2\)(dioxane)] and Me4tacn, conducted in MeCN solution, the mixture was stirred at room temperature for ca. 3 h following addition of Me3SiO3SCF3, then concentrated in vacuo. This did not cause any precipitation, and the solution was layered with Et2O and stored in the freezer. Small rod-shaped crystals formed, which were found to be [Ge4tacn][Cl2(O3SCF3)] as identified by an X-ray crystal structure determination. Anal. calc. for C\(_{11}\)H\(_{22}\)F\(_6\)GeN\(_4\)O\(_6\)S\(_2\) (542.0): C, 24.38; H, 4.71; N, 9.35. Found: C, 28.19; H, 4.61; N, 9.26%. \(^1\)H NMR (CD\(_3\)CN, 298 K): 3.02 (s, [9H], NCH\(_3\)), 3.34-3.54 (m, [12H], NCH\(_2\)). \(^{19}\)F\(^1\)H NMR (CD\(_3\)CN, 298 K): -79.4 (O\(_3\)SCF\(_3\)). IR (Nujol/cm\(^{-1}\)): 420v, 451w, 516v, 573m, 693s, 739m, 785m, 898m, 982w, 994m, 1030s, 1049m, 1138m, 1167s, 1226s, 1259s.

\[\text{[Ge}_4\text{tacn]}\text{[Cl}_2\text{[GeCl}_3\text{]}_2\]

In a further reaction conducted in MeCN solution, the mixture was stirred at room temperature for ca. 15 min following addition of Me3SiO3SCF3, 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 [Ge4tacn]-Cl2·MeCN.

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

SiCl\(_4\) (0.170 g, 1.0 mmol) and Me3SiO3SCF3 (0.222 g, 1.0 mmol) were dissolved in CH\(_2\)Cl\(_2\) (10 mL) and stirred for 5 min. A solution of Me4tacn (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_{17}Cl_{2}F_{3}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%. 1H NMR (295 K, CD_{2}CN): 3.54–3.66 (m, [6H], NCH3), 3.31–3.41 (m, [6H], NCH2), 3.17 (s, [9H], NCH2). 13C{1H} NMR (295 K, CD_{2}CN): 122.20 (q, 1J_{C-F} = 320 Hz, CF_{3}), 54.86 (CH_{3}), 53.49 (CH_{4}). 19F{1H} NMR (295 K, CD_{2}CN): −78.7 (O_{2}SCF_{3}). IR (Nujol, cm⁻¹): 2313, 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.

\[ \text{[SiHCl}_{\text{Me:tacn}]}\text{[BAr}^\text{F}] \]

SiHCl (0.068 g, 0.50 mmol) and Na[BAr]F (0.443 g, 0.50 mmol) were dissolved in toluene (10 mL) and stirred for 5 min. A solution of Me:tacn (0.085 g, 0.50 mmol) in toluene (5 mL) was added then 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_{35}BCl_{3}F_{24}N_{3}Si (1170.58): C, 42.03; H, 3.01; N, 3.59. Found: 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 [SiCl_{3}(Me3tacn)][BAr]F. Attempts to prepare the latter directly from [SiCl_{3}(Me3tacn)][BAr]F (1): 231s, 428s (SiCl), 449m (SiCl), 480m (SiCl), 683s, 744m, 838m, 888m, 899m, 925w, 955w, 1112s, 1144s, 1279s, 1358s.

\[ \text{[SiBr}_{\text{tdpta}]}\text{[BAr}^\text{F}] \]

SiBr_{4} (0.174 g, 0.50 mmol) and Na[BAr]F (0.443 g, 0.50 mmol) were dissolved in toluene (10 mL) and stirred for 5 min. A solution of tpta (0.087 g, 0.50 mmol) in toluene (5 mL) was added then 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_{33}BCl_{3}F_{24}N_{3}Si (1168.9): C, 42.10; H, 2.85; N, 3.59. Found: C, 41.85; H, 3.08; N, 3.74%.

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

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 (λ_{1} = 0.71073 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 r74. Structure solution and refinement were carried out using WinGX or Olex2 and software packages within. No positional disorder was observed in complexes of [BAr]F⁻, despite this being a common issue with weakly-coordinating anions containing CF_{3} groups, especially [BAr]F⁻. [Ge(Me3tacn)]Cl_{2}-MeCN crystallised as an inversion twin with a BASF of 0.21. Unusually large Z values were observed for [Ge(Me4cyclen)]O_{3}SCF_{3}·0.8MeCN and [SiCl_{4}(Me3tacn)][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 1.5U_{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.
find that reaction of \([\text{GeCl}_2(\text{dioxane})]\) with \(\text{Me}_3\text{tacn}\) in subsequently obtained as colourless crystals of \([\text{Ge(Me}_3\text{tacn})]^{-}\) and \(\text{Me}_3\text{SiO}_3\text{SCF}_3\) in anhydrous \(\text{MeCN}\) solution gives colourless \([\text{Ge-}3\text{Br}_3\text{Cl}_2\text{MeCN}]\text{Br}_3\text{Cl}_2\text{MeCN}\) containing unusual discrete three-coordinate \([\text{Ge(Me}_3\text{tacn})]^{-}\) dications (Ge-N = 2.124(3)–2.156(3) Å), with \(\text{Br}^+\) and \(\text{Br}_3\text{Cl}_2\text{MeCN}\) anions providing charge balance. We find that reaction of \([\text{GeCl}_3(\text{dioxane})]\) with \(\text{Me}_3\text{tacn}\) in anhydrous \(\text{CH}_2\text{Cl}_2\) followed by addition of \(\text{Me}_3\text{SiO}_3\text{SCF}_3\) gave a colourless powder, \([\text{Ge(Me}_3\text{tacn})][\text{O}_3\text{SCF}_3]^{-}\), subsequently obtained as colourless crystals of \([\text{Ge(Me}_3\text{tacn})]^{-}\) and \(\text{Me}_3\text{SiO}_3\text{SCF}_3\) by recrystallisation from \(\text{MeCN/Et}_2\text{O}\). 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).\(^\text{17}\)

### Results and discussion

#### Germanium(II) complexes

We have previously reported\(^\text{12}\) that reaction of \(\text{GeBr}_2\) with \(\text{Me}_3\text{tacn}\) in anhydrous \(\text{MeCN}\) solution gives colourless \([\text{Ge(}3\text{Me}_3\text{tacn})\text{Br}_3\text{GeBr}_3\text{]}\), containing unusual discrete three-coordinate \([\text{Ge(}3\text{Me}_3\text{tacn})]^{-}\) dications (Ge-N = 2.124(3)–2.156(3) Å), with \(\text{Br}^+\) and \(\text{Br}_3\text{GeBr}_3\) anions providing charge balance. We find that reaction of \([\text{GeCl}_3(\text{dioxane})]\) with \(\text{Me}_3\text{tacn}\) in anhydrous \(\text{CH}_2\text{Cl}_2\) followed by addition of \(\text{Me}_3\text{SiO}_3\text{SCF}_3\) gave a colourless powder, \([\text{Ge(}3\text{Me}_3\text{tacn})][\text{O}_3\text{SCF}_3]^{-}\), subsequently obtained as colourless crystals of \([\text{Ge(}3\text{Me}_3\text{tacn})]^{-}\) and \(\text{Me}_3\text{SiO}_3\text{SCF}_3\) by recrystallisation from \(\text{MeCN/Et}_2\text{O}\). 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).\(^\text{17}\)

While there is no evidence for 2:1 \(\text{Me}_3\text{tacn}\):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 \([\text{GeCl}_3(\text{dioxane})]\), \(\text{Me}_3\text{tacn}\) and \(\text{Me}_3\text{SiO}_3\text{SCF}_3\) was conducted in \(\text{MeCN}\) solution as described in the

### Table 1 Selected X-ray crystallographic data\(^a\)

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<th>Compound</th>
<th>[Ge(\text{Me}_3\text{tacn})][\text{O}_3\text{SCF}_3]^{-}\text{MeCN}</th>
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<th>[Ge(\text{Me}_3\text{tacn})]^{-}\text{Cl}[\text{O}_3\text{SCF}_3]^{-}\text{Cl}</th>
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\(^a\) Common items: $T$ = 100 K; wavelength (Mo-K$_\alpha$) = 0.71073 Å; $\theta(\text{max}) = 27.5^{\circ}$; $R$$_1 = \sum |F_o| - |F_c|/\sum |F_o|$; $wR$_2 = \left[ \sum w(F_o^2 - F_c^2)^2/\sum wF_o^2 \right]^{1/2}.

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Experimental section, concentrated in vacuo, and the solution layered with Et2O, the product was isolated as rod-like crystals of \([\text{Ge(Me3tacn)}]\)[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 = 3.028(4), 3.214(1) Å) and with a similar pyramidal ‘Ge\(^{II}\)(Me3tacn)’ core. These Ge···Cl interactions are substantially within the sum of vdW radii for Ge and Cl (4.11 Å). One \(k^1\)-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 \([\text{Ge(Me3tacn)}]\)Cl·MeCN by X-ray crystallography (Fig. 3). In this case the ‘Ge\(^{II}\)(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 ‘Ge\(^{II}\)(Me3tacn)’ core. All of the Ge–N distances are considerably longer than the sum of the covalent radii (1.85 Å),\(^1\) but well within the sum of the van der Waals radii (3.66 Å).\(^1\)

The spectroscopic data provide very limited information; the IR spectra show the Me3tacn and the [O3SCF3]\(^-\) (when present), whilst the \(^1\)H 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 \([\text{GeCl}_2(\text{dioxane})]\) and Me3SiO3SCF3 in thf followed by addition of Me4cyclam gave \([\text{Ge}[\text{Me4cyclam}]]\)[O3SCF3]₂. Attempts to obtain crystals of this complex were unsuccessful with recrystallisation from MeCN/Et2O or CH2Cl2/Et2O giving \([\text{Me4cyclamH}]_2[\text{O3SCF3}]_2\) (identified crystallographically). We reported the structure of \([\text{Ge}[\text{Me4cyclam}]]\)[GeCl3] in our preliminary communication,\(^1\) 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\(^{[n]}\) is not a good fit to the relatively large 14-membered macrocycle cavity; this may correlate with the very ready hydrolysis in solution.

Replacing the 14-membered Me4cyclam ring by the 12-membered Me4cycalen (1,4,7,10-tetramethyl-1,4,7,10-tetraaza-cyclotetradecane) gave colourless \([\text{Ge}[\text{Me4cycalen}]]\)[O3SCF3]₂. Crystals of \([\text{Ge}[\text{Me4cycalen}]]\)[O3SCF3]₂·0.8CH3CN 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(α) centre coordinated to a tetradeinate Me₃cycloen 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 Nₓ 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 [GeCl₂(dioxane)] in CH₂Cl₂ with Me₄cyclen in a 3:1 molar ratio gave the corresponding [Ge(Me₄cyclen)]-[GeCl₂]₂ which was less stable in solution.

Silicon(n) complexes

The reaction of SiCl₄, Me₃tacn and Me₃SiO₃SCF₃ in anhydrous CH₂Cl₂ solution produced [SiCl₄(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 [SiCl₄(Me₃tacn)][BAR₅]²⁺ was obtained by reacting SiCl₄ and Na[BAR₅] in toluene, followed by addition of a solution of Me₃tacn. As we have described elsewhere, the reagents are added simultaneously, the product is the sodium complex of the ligand, rather than the silicon cation. Crystals of [SiCl₄(Me₃tacn)][BAR₅]²⁺ were not obtained, however, a concentrated CH₂Cl₂ solution of the [BAR₅]²⁻ salt, layered with hexane, produced a few colourless crystals identified by an X-ray structure determination as [SiCl₄(Me₃tacn)]Cl (see Fig. S1 in ESIF) 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 [SiCl₄(Me₃tacn)]Cl, however we have been unable to obtain it in analytically pure form by this route.

The ¹H NMR spectrum of [SiCl₄(Me₃tacn)]⁺ in CD₃CN at 298 K shows sharp second order multiplets characteristic of symmetrical fac-coordinated Me₃tacn in solution. Similar reaction of SiHCl₃ with Na[BAR₅] in toluene, followed by addition of Me₃tacn, produced the corresponding dichlorosilane complex, [SiHCl₂(Me₃tacn)][BAR₅]. 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 thefac-SiHCl₂ removes the three-fold symmetry of the Me₃tacn found in [SiCl₄(Me₃tacn)]⁺, and this is reflected in both the ¹H and ¹³C{¹H} NMR spectra, which show two δ(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 [SiCl₄(Me₃tacn)]⁺ and [SiHCl₂(Me₃tacn)]⁺ were both present (note that [SiCl₄(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 [SiHCl₂(Me₃tacn)]⁺ solution.

Finally, two complexes of the linear triamine, Me₂NCH₂CH₂N(Me)CH₂CH₂NMMe₂ (pmdta), [SiX₃(pmdta)][BAR₅] (X = Cl or Br) were isolated by reacting the appropriate SiX₃ with Na[BAR₅] 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 [SiCl₄(pmdta)]⁺ cation is close to octahedral, and the Si–N and Si–Cl distances are little different from those found in [SiCl₄(Me₃tacn)]⁺.
The triaza ligand complexes of Si(IV), formed by halide abstraction using either Me$_3$SiO$_3$SCF$_3$ or Na[BARF], adopt distorted square planar geometries, with no significant anion interactions towards Ge(II).

Two series of complexes with neutral aza-macrocyclic coordination to Ge(II) and Si(IV) are reported and structurally characterised. The hydrolytically sensitive Ge(II) triaza macrocyclic complexes give GeN$_4$ dications in highly distorted square planar geometries, with no significant anion interactions except in the case of SiF$_4$, reflecting the much higher Si–F bond strength.\(^{11}\)

Despite the different donor arrangements, the geometry is also similar to that found in mer-[SiHCl$_2$(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$_3$ 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$_2$Cl plane. The ease of formation of the [SiX$_3$(pmdta)]$^+$ cations (X$_3$ = Cl$_3$, Br$_3$, HCl$_2$) is in contrast with the κ$^2$-coordinated pmdta adduct formed with SiF$_4$, reflecting the much higher Si–F bond strength.\(^{11}\)

**Conclusions**

Two series of complexes with neutral aza-macrocyclic coordination to Ge(II) and Si(IV) are reported and structurally characterised. The hydrolytically sensitive Ge(II) triaza macrocyclic complexes show pyramidal GeN$_3$ 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(Me$_3$tacn)]$^+$.\(^{12}\) The tetra-aza macrocyclic complexes of Ge(II) give GeN$_4$ dications in highly distorted square planar geometries, with no significant anion interactions towards Ge(II).

The triaza ligand complexes of Si(IV), formed by halide abstraction using either Me$_3$SiOSiO$_3$SCF$_3$ or Na[BARF], adopt distorted octahedral coordination geometries, and the trichloro-triromo- and hyridodichloro-species reported here are significantly more readily hydrolysed than [SiF$_4$(Me$_3$tacn)]$^+$.\(^{11}\)

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**References**