Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2015, **44**, 20898

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

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

[$GeCl_2$(dioxane)] reacts with the neutral aza-macrocyclic ligands L, L = Me_3tacn (1,4,7-trimethyl-1,4,7-triazacyclononane), Me_4cyclen (1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane) or Me_4cyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) and two mol. equiv. of $Me_3SiO_3SCF_3$ in thf solution to yield the unusual and hydrolytically very sensitive [Ge(L)][O_3SCF_3]$_2$ as white solids in moderate yield. Using shorter reaction times [Ge(Me_3tacn)]Cl_2 and [Ge(Me_3tacn)]Cl[O_3SCF_3] were also isolated; the preparation of [Ge(Me_4cyclen)][$GeCl_3$]$_2$ is also described. The structures of the Me_3tacn complexes show κ^3-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(Me_4cyclen)][O_3SCF_3]$_2$ 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, [$SiCl_3$(Me_3tacn)]Y (Y = O_3SCF_3, BAr^F; [B{3,5-$(CF_3)_2C_6H_3$}$_4$]) and [$SiHCl_2$(Me_3tacn)][BAr^F], obtained from reaction of $SiCl_4$ or $SiHCl_3$ with Me_3tacn, followed by addition of either $Me_3SiO_3SCF_3$ or Na[BAr^F], contain distorted octahedral cations, with *facial* κ^3-coordinated Me_3tacn. The open-chain triamine, $Me_2NCH_2CH_2N(Me)CH_2CH_2NMe_2$ (pmdta), forms [$SiCl_3$(pmdta)][BAr^F] and [$SiBr_3$(pmdta)][BAr^F] under similar conditions, containing *mer*-octahedral cations.

Received 8th October 2015,
Accepted 6th November 2015

DOI: 10.1039/c5dt03941j

www.rsc.org/dalton

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 [GeF_3(Me_3tacn)]$_2$[GeF_6] (Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane),[9] [$(GeF_4)_2$($\kappa^2\kappa'^2$-Me_4cyclam)] (Me_4cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane),[9] [$GeCl_3$-(Me_3tacn)]$_2$(H_3O)$_2Cl_3$,[10] [SiF_3(Me_3tacn)][SiF_5],[11] [Ge(Me_3tacn)]Br-[$GeBr_3$],[12] and [Ge(Me_4cyclam)][$GeCl_3$]$_2$.[12]

Here we report the synthesis of several new Ge(II) mono- 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

$SiCl_4$, $SiHCl_3$, $Me_3SiO_3SCF_3$, [$GeCl_2$(dioxane)] and the N-donor ligands were obtained from Sigma Aldrich, except for Me_3tacn which was prepared using the literature route.[13] Na[BAr^F] ([BAr^F]$^-$ = [B{3,5-$(CF_3)_2C_6H_3$}$_4$]$^-$) was synthesised by a modification of Brookhart's procedure.[14] $Me_2NCH_2CH_2N(Me)CH_2CH_2NMe_2$ (pmdta) was distilled from CaH_2. All experiments were performed under strictly anhydrous conditions using glove-boxes and Schlenk techniques. CH_2Cl_2 was dried by distillation from CaH_2, 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(Me_3tacn)][O_3SCF_3]$_2$·MeCN), 1430052 ([Ge(Me_4cyclen)][O_3SCF_3]$_2$·0.8MeCN), 1430053 ([Ge(Me_3tacn)]Cl[O_3SCF_3]$_2$), 1430054 ([Ge(Me_3tacn)]Cl_2·MeCN), 14300555 ([$SiCl_3$(Me_3tacn)][O_3SCF_3]), 1430056 ([$SiCl_3$(Me_3tacn)]Cl) and 1430057 ([$SiCl_3$(pmdta)][BAr^F]). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt03941j

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}. ^1H 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.

[Ge(Me$_4$cyclen)][O$_3$SCF$_3$]$_2$

[$GeCl_2$(dioxane)] (0.059 g, 0.26 mmol) was dissolved in thf (10 mL) and a solution of $Me_3SiO_3SCF_3$ (0.112 g, 0.50 mmol) in thf (5 mL) was added with stirring, giving a clear, colourless solution. After 10 min, a solution of Me_4cyclen (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 $C_{14}H_{28}F_6GeN_4O_6S_2$ (599.1): C, 28.08; H, 4.71; N, 9.35. Found: C, 28.19; H, 4.61; N, 9.26%. ^1H NMR (CD_3CN, 298 K): 2.78 (s, [12H], NCH_3), 3.20–3.40 (m, [16H], NCH_2). $^{19}F\{^1H\}$ NMR (CD_3CN, 298 K): −79.4 (O_3SCF_3). IR (Nujol/cm^{-1}): 474w, 517m, 573m, 638s, 749m, 793w, 919w, 960w, 1030s, 1068w, 1155s, 1225s, 1260s.

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

[Ge(Me$_4$cyclam)][O$_3$SCF$_3$]$_2$

[$GeCl_2$(dioxane)] (0.058 g, 0.25 mmol) was dissolved in thf (10 mL), and a solution of $Me_3SiO_3SCF_3$ (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_4cyclam (0.065 g, 0.25 mmol) in thf (5 mL) was added, causing the formation of a white, microcrystalline precipitate. After 1 h, the product was collected by filtration, washed with diethyl ether and dried *in vacuo*. Yield: 0.092 g (59%). Anal. calc. for $C_{16}H_{32}F_6GeN_4O_6S_2$ (627.2): C, 30.65; H, 5.14; N, 8.93. Found: C, 30.81; H, 5.17; N, 8.86%. ^1H NMR (CD_3CN, 298 K): 1.96 (s, [4H], NCH_2CH_2), 2.56 (br s, [12H], NCH_3), 2.94–2.99 (v br, [16H], overlapping $NCH_2CH_2CH_2$ and NCH_2CH_2N). $^{19}F\{^1H\}$ NMR (CD_3CN, 298 K): −79.4 (O_3SCF_3). ^1H NMR (DMF-d_7, 298 K): 2.09 (quintet, [4H], $^3J_{HH}$ = 6.3 Hz, NCH_2CH_2), 2.68 (br s, [12H], NCH_3), 3.08 (v br, [8H], $NCH_2CH_2CH_2$) 3.21 (br s, [8H], NCH_2CH_2N). $^{19}F\{^1H\}$ NMR (DMF-d_7, 298 K): −79.38 (O_3SCF_3). IR (Nujol/cm^{-1}): 517m, 574m, 592w, 639s, 743w, 757w, 802w, 1011m, 1034s, 1160s, 1226m, 1256s, 1278s, 1354m.

[Ge(Me$_4$cyclen)][GeCl$_3$]$_2$

[$GeCl_2$(dioxane)] (0.104 g, 0.45 mmol) was suspended in CH_2Cl_2 (20 mL) and a solution of Me_4cyclen (0.035 g, 0.15 mmol) in CH_2Cl_2 (10 mL) was added with stirring, giving a dense white suspension. After stirring at room temperature for 2 h, the product was collected by filtration, washed with Et_2O and dried *in vacuo*. Yield: 0.048 g (48%). Anal. calc. for: $C_{12}H_{28}Cl_6Ge_3N_4$ (658.9): C, 21.87; H, 4.28; N, 8.50. Found: C, 22.02; H, 4.19; N, 8.41%. ^1H NMR (CD_3CN, 298 K): 2.78 (s, [12H], NCH_3), 3.20–3.38 (m, [16H], NCH_2). IR (Nujol/cm^{-1}): 277s, vbr $[GeCl_3]^-$, 317s, 413w, 472m, 547m, 737s, 747s, 791m, 917s, 945m, 958s, 1014s, 1024s, 1051s, 1064s, 1151m, 1262s, 1275s, 1298s.

[Ge(Me$_3$tacn)][O$_3$SCF$_3$]$_2$

[$GeCl_2$(dioxane)] (0.059 g, 0.26 mmol) was suspended in CH_2Cl_2 (10 mL) and a solution of $Me_3SiO_3SCF_3$ (0.112 g, 0.50 mmol) in CH_2Cl_2 (10 mL) was added with stirring, giving a colourless solution. After 10 min Me_3tacn (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 $C_{11}H_{21}F_6GeN_3O_6S_2$ (542.0): C, 24.38; H, 3.91; N, 7.75. Found: C, 24.51; H, 3.74; N, 7.84%. ^1H NMR (CD_3CN, 298 K): 3.02 (s, [9H], NCH_3), 3.34–3.54 (m, [12H], NCH_2). $^{19}F\{^1H\}$ NMR (CD_3CN, 298 K): −79.4 (O_3SCF_3). IR (Nujol/cm^{-1}): 420m, 451w, 516m, 573m, 639s, 739m, 785m, 898m, 982w, 994m, 1030s, 1049m, 1138m, 1167s, 1226s, 1259s.

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

[Ge(Me$_3$tacn)]Cl[O$_3$SCF$_3$]

In a similar reaction using a 1 : 1 molar ratio of [$GeCl_2$(dioxane)] and Me_3tacn, conducted in MeCN solution, the mixture was stirred at room temperature for *ca.* 3 h following addition of $Me_3SiO_3SCF_3$, then concentrated *in vacuo*. This did not cause any precipitation, and the solution was layered with Et_2O and stored in the freezer. Small rod-shaped crystals formed, which were found to be [Ge(Me$_3$tacn)]Cl[O$_3$SCF$_3$] as identified by an X-ray crystal structure determination. Anal. calc. for $C_{10}H_{21}ClF_3GeN_3O_3S$ (428.4): C, 28.04; H, 4.94; N, 9.81. Found: C, 28.76; H, 4.85; N, 9.77%. ^1H NMR (298 K, CD_2Cl_2): 2.94 (s, [9H], NCH_3), 3.21–3.47 (m, [12H], CH_2). (A second minor species is also evident in the NMR spectrum). $^{19}F\{^1H\}$ NMR (298 K, CD_2Cl_2): −79.4 (O_3SCF_3).

[Ge(Me$_3$tacn)]Cl$_2$

In a further reaction conducted in MeCN solution, the mixture was stirred at room temperature for *ca.* 15 min following addition of $Me_3SiO_3SCF_3$, 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$_3$tacn)]-Cl$_2$·MeCN.

[SiCl$_3$(Me$_3$tacn)][O$_3$SCF$_3$]

$SiCl_4$ (0.170 g, 1.0 mmol) and $Me_3SiO_3SCF_3$ (0.222 g, 1.0 mmol) were dissolved in CH_2Cl_2 (10 mL) and stirred for 5 min. A solution of Me_3tacn (0.171 g, 1.0 mmol) in CH_2Cl_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 $C_{10}H_{21}Cl_3F_3N_3O_3SSi$ (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_3CN): 3.54–3.66 (m, [6H], NCH_2), 3.31–3.41 (m, [6H], NCH_2), 3.17 (s, [9H], NCH_3). $^{13}C\{^1H\}$ NMR (295 K, CD_3CN): 122.20 (q, $^1J_{C-F}$ = 320 Hz, CF_3), 54.86 (CH_2), 53.49 (CH_3). $^{19}F\{^1H\}$ NMR (295 K, CD_3CN): −78.7 (O_3SCF_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_2Cl_2 solution with hexane.

[SiHCl$_2$(Me$_3$tacn)][BAr^F]

$SiHCl_3$ (0.068 g, 0.50 mmol) and $NaBAr^F$ (0.443 g, 0.50 mmol) were dissolved in toluene (10 mL) and stirred for 5 min. A solution of Me_3tacn (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_2Cl_2 (5 mL), filtered and hexane (30 mL) added to precipitate a white solid. Yield: 0.421 g (74%). Anal. calc. for $C_{41}H_{34}BCl_2F_{24}N_3Si$ (1134.12): C, 43.38; H, 3.02; N, 3.70. Found: C, 43.45; H, 3.11; N, 3.80%. ^{1}H NMR (295 K, CD_2Cl_2): 7.74 (s, [8H], BAr^F H2/6), 7.59 (s, [4H], BAr^F H4), 4.78 (s, [1H], Si–H), 3.54–3.70 (m, [4H], NCH_2), 3.26 (s, [3H], NCH_3), 3.21 (s, [4H], NCH_2), 3.12–3.17 (m, [4H], NCH_2), 2.99 (s, [6H], NCH_3). $^{13}C\{^1H\}$ NMR (295 K, CD_2Cl_2): 162.33 (q, $^1J_{C-B}$ = 49.8 Hz, BAr^F C1), 135.42 (CH, BAr^F C2/6), 129.48 (C, q, $^1J_{C-F}$ = 3.3 Hz, BAr^F C3/5), 125.22 (C, q, $^1J_{C-F}$ = 272 Hz, CF_3), 118.11 (CH, BAr^F C4), 54.72, 53.77, 51.41, 50.45 (NCH_2 and NCH_3). IR (Nujol, cm^{-1}): 449 m (SiCl), 480 m (SiCl), 683s, 744m, 838m, 888m, 899m, 1005m, 1056m, 1086m, 1114s, 1163s, 1280s, 1289s, 1356s, 1612w, 2137w (SiH).

[SiCl$_3$(Me$_3$tacn)][BAr^F]

Made similarly using $SiCl_4$ (0.085 g, 0.50 mmol) in place of $SiHCl_3$. Yield: 0.466 g (82%). Anal. calc. for $C_{41}H_{33}BCl_3F_{24}N_3Si$ (1168.9): C, 42.10; H, 2.85; N, 3.59. Found: C, 41.85; H, 3.08; N, 3.74%.

A concentrated CH_2Cl_2 solution of this complex layered with hexane deposited a few colourless crystals which were identified from an X-ray crystallographic study as **[SiCl$_3$(Me$_3$tacn)]Cl**. Attempts to prepare the latter directly from $SiCl_4$ and Me_3tacn in CH_2Cl_2 gave a pale yellow solid which was very poorly soluble in chlorocarbons and which was not analytically pure.

[SiCl$_3$(pmdta)][BAr^F]

$SiCl_4$ (0.085 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 pmdta (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_2Cl_2 (5 mL), filtered and hexane (30 mL) added to precipitate a white solid. Yield: 0.447 g (76%). Anal. calc. for $C_{41}H_{35}BCl_3F_{24}N_3Si$ (1170.58): C, 42.03; H, 3.01; N, 3.59. Found: C, 41.88; H, 3.12; N, 3.71%. ^{1}H NMR (295 K, CD_2Cl_2): 7.72 (s, [8H], BAr^F H2/6), 7.57 (s, [4H], BAr^F H4), 2.76–2.98 (br s, [4H], NCH_2), 2.65 (v br s, [16H], $N(CH_3)_2$ and NCH_2), 2.35 (s, [3H], NCH_3) ppm. $^{13}C\{^1H\}$ NMR (295 K, CD_2Cl_2): 162.37 (q, $^1J_{C-B}$ = 49.7 Hz, BAr^F C1), 135.41 (CH, BAr^F C2/6), 129.45 (C, q, $^1J_{C-F}$ = 3.3 Hz, BAr^F C3/5), 125.22 (C, q, $^1J_{C-F}$ = 272 Hz, CF_3), 118.10 (CH, BAr^F C4), 57.91, 57.16 (CH_2), 45.08 ($N(CH_3)_2$), 44.51 (NCH_3). IR (Nujol cm^{-1}): 448w, 506w (SiCl), 522w (SiCl), 682m, 713m, 889w, 1112s, 1143s, 1358s, 1367s.

Crystals were obtained by layering a concentrated CH_2Cl_2 solution with hexane.

[SiBr$_3$(pmdta)][BAr^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 pmdta (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_2Cl_2 (5 mL), filtered and hexane (30 mL) added to precipitate a white solid. Yield: 0.291 g (45%). Anal. calc. for $C_{41}H_{35}BBr_3F_{24}N_3Si$ (1303.93): C, 37.73; H, 2.71; N, 3.22. Found: C, 37.57; H, 2.80; N, 3.26%. ^{1}H NMR (CD_2Cl_2): 7.72 (s, [8H], BAr^F H2/6), 7.57 (s, [4H], BAr^F H4), 2.76–2.98 (br s, [4H], NCH_2), 2.65 (br s, [16H], $N(CH_3)_2$ and NCH_2), 2.35 (s, [3H], NCH_3). IR (Nujol, cm^{-1}): 363 m (SiBr), 471w, 521w, 584w, 682s, 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 (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 r7.4.[15a] Structure solution and refinement were carried out using WinGX or Olex2 and software packages within.[15b–d] 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 $[BAr^F]^-$.[16] $[Ge(Me_3tacn)]Cl_2{\cdot}MeCN$ crystallised as an inversion twin with a BASF of 0.21. Unusually large Z values were observed for $[Ge(Me_4cyclen)][O_3SCF_3]_2{\cdot}0.8MeCN$ and $[SiCl_3(Me_3tacn)]Cl$ (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), 0.98 Å (CH_3) or 0.99 Å (CH_2) and refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C) (CH, CH_2) or 1.5U_{eq}(C) (CH_3). 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]

Table 1 Selected X-ray crystallographic data[a]

Compound	[Ge(Me$_3$tacn)]-[O$_3$SCF$_3$]$_2$·MeCN	[Ge(Me$_4$cyclen)]-[O$_3$SCF$_3$]$_2$·0.8MeCN	[Ge(Me$_3$tacn)]-Cl[O$_3$SCF$_3$]	[Ge(Me$_3$tacn)]-Cl$_2$·MeCN
Formula	$C_{13}H_{24}F_6GeN_4O_6S_2$	$C_{15.6}H_{30.4}F_6GeN_{4.8}O_6S_2$	$C_{10}H_{21}ClF_3GeN_3O_3S$	$C_{11}H_{24}Cl_2GeN_4$
M/g mol^{-1}	583.07	631.96	438.40	355.83
Crystal system	Monoclinic	Tetragonal	Monoclinic	Orthorhombic
Space group (No.)	$P2_1/n$ (14)	$P4cc$ (103)	$P2_1/c$ (14)	$Pna2_1$ (33)
a/Å	13.541(5)	17.1253(3)	8.1521(9)	14.399(5)
b/Å	8.543(5)	17.1253(3)	13.9764(15)	10.139(5)
c/Å	19.620(5)	22.1160(10)	14.2804(16)	21.491(5)
α/°	90	90	90	90
β/°	97.495(5)	90	101.705(7)	90
γ/°	90	90	90	90
U/Å^3	2250.3(17)	6486.1(4)	1593.2(3)	3138(2)
Z	4	10 (Z' = 1.25)	3	8
μ(Mo-Kα)/mm^{-1}	1.634	1.425	2.267	2.284
F(000)	1184	3236	872	1472
Total reflections	10 515	34 358	8862	11 548
Unique reflections	5123	7099	3647	5491
R_{int}	0.041	0.042	0.074	0.0823
Goodness-of-fit on F^2	1.036	1.030	0.987	1.025
R_1 [b] [$I_o > 2\sigma(I_o)$]	0.037	0.054	0.047	0.061
R_1 (all data)	0.050	0.071	0.060	0.108
wR_2 [b] [$I_o > 2\sigma(I_o)$]	0.082	0.131	0.108	0.103
wR_2 (all data)	0.088	0.142	0.116	0.119

Compound	[SiCl$_3$(Me$_3$tacn)][O$_3$SCF$_3$]	[SiCl$_3$(Me$_3$tacn)]Cl	[SiCl$_3$(pmdta)][BAr^F]
Formula	$C_{10}H_{21}Cl_3F_3N_3O_3SSi$	$C_9H_{21}Cl_4N_3Si\cdot{}^2/_3(CH_2Cl_2)$	$C_{41}H_{35}BCl_3F_{24}N_3Si$
M/g mol^{-1}	454.80	397.80	1170.97
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group (no.)	$P\bar{1}$ (2)	$C2/c$ (15)	$Pbca$ (61)
a/Å	6.997(2)	34.475(8)	17.728(5)
b/Å	10.820(4)	26.707(6)	19.613(6)
c/Å	11.974(4)	11.820(3)	26.662(8)
α/°	99.110(7)	90	90
β/°	93.245(5)	106.684(5)	90
γ/°	92.108(8)	90	90
U/Å^3	892.7(5)	10 425(4)	9270(5)
Z	2	24 (Z' = 3)	8
μ(Mo-Kα)/mm^{-1}	0.743	0.946	0.357
F(000)	468	4944	4704
Total reflections	7788	46 773	17 463
Unique reflections	4019	10 659	8124
R_{int}	0.019	0.114	0.070
Goodness-of-fit on F^2	1.042	1.107	1.176
R_1 [b] [$I_o > 2\sigma(I_o)$]	0.032	0.094	0.097
R_1 (all data)	0.039	0.121	0.147
wR_2 [b] [$I_o > 2\sigma(I_o)$]	0.069	0.227	0.137
wR_2 (all data)	0.072	0.247	0.155

[a] Common items: T = 100 K; wavelength (Mo-Kα) = 0.71073 Å; θ(max) = 27.5°. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^2]^{1/2}$.

Results and discussion

Germanium(II) complexes

We have previously reported[12] that reaction of $GeBr_2$ with Me_3tacn in anhydrous MeCN solution gives colourless [Ge(Me$_3$tacn)]Br[$GeBr_3$], containing unusual discrete three-coordinate [Ge(Me$_3$tacn)]$^{2+}$ dications (Ge–N = 2.124(3)–2.156(3) Å), with Br^- and [$GeBr_3$]$^-$ anions providing charge balance. We find that reaction of [$GeCl_2$(dioxane)] with Me_3tacn in anhydrous CH_2Cl_2 followed by addition of $Me_3SiO_3SCF_3$ gave a colourless powder, [Ge(Me$_3$tacn)][O$_3$SCF$_3$]$_2$, subsequently obtained as colourless crystals of [Ge(Me$_3$tacn)][O$_3$SCF$_3$]$_2$·MeCN by recrystallisation from MeCN/Et_2O. 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]

While there is no evidence for 2 : 1 Me_3tacn : 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 [$GeCl_2$(dioxane)], Me_3tacn and $Me_3SiO_3SCF_3$ was conducted in MeCN solution as described in the

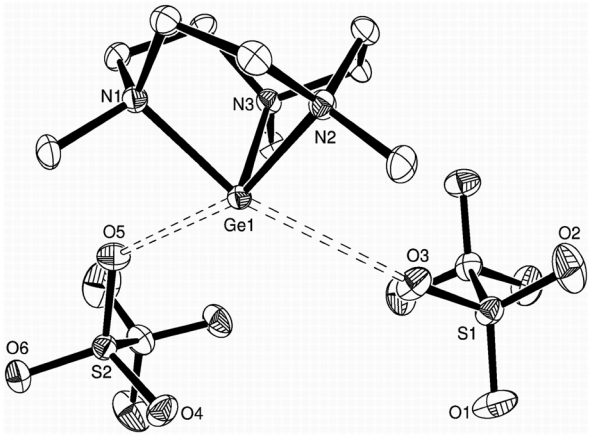

Fig. 1 The X-ray structure of $[Ge(Me_3tacn)][O_3SCF_3]_2$·MeCN. Thermal ellipsoids are drawn at 50% probability, and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): N1–Ge1 = 2.084(2), N2–Ge1 = 2.106(2), N3–Ge1 = 2.089(2), O5···Ge1 = 2.850(2), O3···Ge1 = 3.179(2), N1–Ge1–N3 = 82.73(8), N1–Ge1–N2 = 82.84(8), N3–Ge1–N2 = 83.23(9).

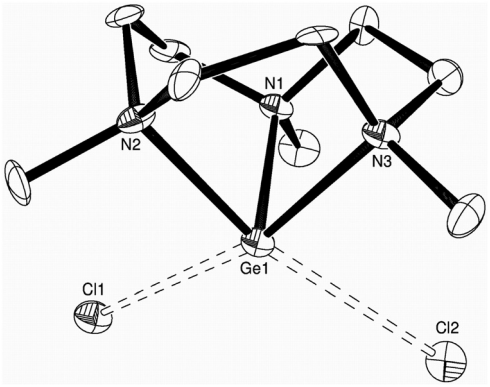

Fig. 3 The X-ray structure of $[Ge(Me_3tacn)]Cl_2$·MeCN showing the Ge1-centred molecule. The crystallographically independent Ge2-centred molecule is very similar. Thermal ellipsoids are drawn at 50% probability, and hydrogen atoms omitted for clarity Selected bond lengths (Å) and angles (°): N1–Ge1 = 2.124(10), N2–Ge1 = 2.147(10), N3–Ge1 = 2.154(9), Cl1···Ge1 = 3.028(4), Cl2···Ge1 = 3.028(3), N1–Ge1–N3 = 80.9(3), N1–Ge1–N2 = 81.2(4), N3–Ge1–N2 = 80.8(4).

Experimental section, concentrated *in vacuo*, and the solution layered with Et_2O, the product was isolated as rod-like crystals of $[Ge(Me_3tacn)]Cl[O_3SCF_3]$. 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 '$Ge^{II}(Me_3tacn)$' core. These Ge···Cl interactions are substantially within the sum of vdW radii for Ge and Cl (4.11 Å). One κ^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 $[Ge(Me_3tacn)]Cl_2$·MeCN by X-ray crystallography (Fig. 3). In this case the '$Ge^{II}(Me_3tacn)$' 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.

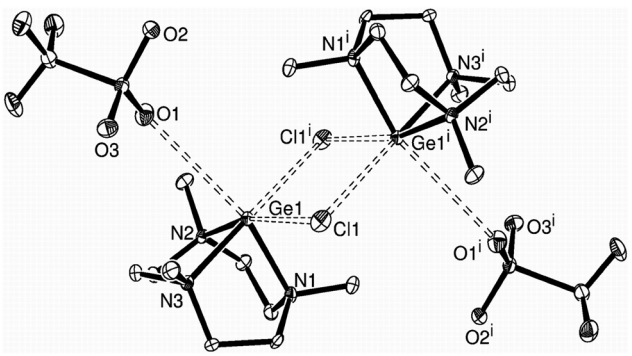

Fig. 2 The X-ray structure of $[Ge(Me_3tacn)]Cl[O_3SCF_3]$ showing the dimeric unit. Thermal ellipsoids are drawn at 50% probability, and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): N1–Ge1 = 2.119(3), N2–Ge1 = 2.139(3), N3–Ge1 = 2.130(2), Cl1···Ge1 = 3.0254(9), O1···Ge1 = 3.381(2), $Cl1^i$···Ge1 3.214(1), N1–Ge1–N3 = 82.48(10), N1–Ge1–N2 = 81.63(10), N3–Ge1–N2 = 80.98(10).

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 '$Ge^{II}(Me_3tacn)$' core. All of the Ge–N distances are considerably longer than the sum of the covalent radii (1.85 Å),[18] but well within the sum of the van der Waals radii (3.66 Å).[17]

The spectroscopic data provide very limited information; the IR spectra show the Me_3tacn and the $[O_3SCF_3]^-$ (when present), whilst the ^1H NMR spectra show small high frequency shifts corresponding to coordinated Me_3tacn. The complexes are extremely sensitive to hydrolysis by trace water, readily forming protonated Me_3tacn.

The reaction of $[GeCl_2(dioxane)]$ and $Me_3SiO_3SCF_3$ in thf followed by addition of $Me_4cyclam$ gave $[Ge(Me_4cyclam)][O_3SCF_3]_2$. Attempts to obtain crystals of this complex were unsuccessful with recrystallisation from MeCN/Et_2O or CH_2Cl_2/Et_2O giving $[Me_4cyclamH_2][O_3SCF_3]_2$ (identified crystallographically). We reported the structure of $[Ge(Me_4cyclam)][GeCl_3]_2$ in our preliminary communication,[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–N distances (2.151(2)–2.349(2) Å), suggesting germanium(II) 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 $Me_4cyclam$ ring by the 12-membered $Me_4cyclen$ (1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotetradecane) gave colourless $[Ge(Me_4cyclen)][O_3SCF_3]_2$. Crystals of $[Ge(Me_4cyclen)][O_3SCF_3]_2$·$0.8CH_3CN$ suitable for

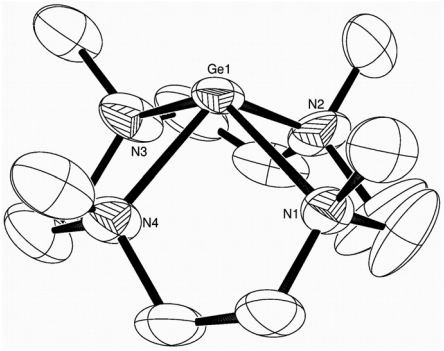

Fig. 4 The X-ray structure of the dication present in $[Ge(Me_4cyclen)][O_3SCF_3]_2 \cdot 0.8CH_3CN$ showing the Ge1-containing molecule. Thermal ellipsoids are drawn at 50% probability, and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1–N1 = 2.244(5), Ge1–N2 = 2.168(9), Ge1–N3 = 2.206(6), Ge1–N4 = 2.165(6), N1–Ge1–N3 = 131.8(2), N2–Ge1–N4 = 118.5(3), N2–Ge1–N1 = 78.2(2), N2–Ge1–N3 = 77.6(3), N4–Ge1–N1 = 77.8(2), N4–Ge1–N3 = 78.2(2). Symmetry codes: (i) *x*, *y*, 0.5 + *z*; (ii) −*x*, 1 − *y*, 0.5 + *z*.

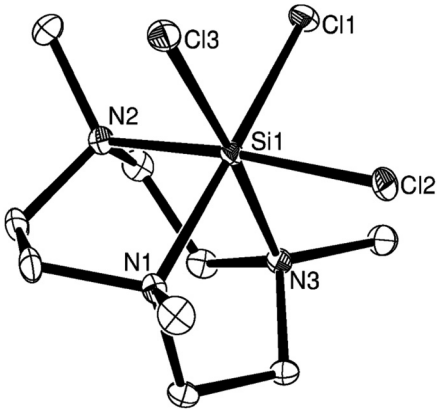

Fig. 5 View of the cation present in $[SiCl_3(Me_3tacn)][O_3SCF_3]$. Thermal ellipsoids are drawn at 50% probability, hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–Cl1 = 2.1867(9), Si1–Cl2 = 2.1688(8), Si1–Cl3 = 2.1416(9), Si1–N1 = 2.010(2), Si1–N2 = 2.013(2), Si1–N3 = 2.026(2); N1–Si1–N2 = 85.61(7), N2–Si1–N3 = 84.70(6), N1–Si1–N3 = 85.37(6), Cl1–Si1–Cl2 = 91.79(4), Cl1–Si1–Cl3 = 92.18(3), Cl2–Si1–Cl3 = 92.76(3).

X-ray diffraction were obtained by layering an acetonitrile solution of the complex with diethyl ether. The structure (Fig. 4) also shows the Ge(II) centre coordinated to a tetradentate Me_4cyclen 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 N_4 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 $[GeCl_2(dioxane)]$ in CH_2Cl_2 with Me_4cyclen in a 3 : 1 molar ratio gave the corresponding $[Ge(Me_4cyclen)][GeCl_3]_2$ which was less stable in solution.

Silicon(IV) complexes

The reaction of $SiCl_4$, Me_3tacn and $Me_3SiO_3SCF_3$ in anhydrous CH_2Cl_2 solution produced $[SiCl_3(Me_3tacn)][O_3SCF_3]$, which is *much* more hydrolytically sensitive than the $[SiF_3(Me_3tacn)][SiF_5]$ salt.[11] Crystals of this chloro-complex were obtained by layering a concentrated CH_2Cl_2 solution with hexane. The structure of the cation shows the expected *fac*-octahedral coordination (Fig. 5). Comparison with the $[SiF_3(Me_3tacn)]^+$ cation shows negligible differences between the Si–N distances.

The corresponding $[SiCl_3(Me_3tacn)][BAr^F]$ was obtained by reacting $SiCl_4$ and $Na[BAr^F]$ in toluene, followed by addition of a solution of Me_3tacn. As we have described elsewhere,[19] if the reagents are added simultaneously, the product is the sodium complex of the ligand, rather than the silicon cation. Crystals of $[SiCl_3(Me_3tacn)][BAr^F]$ were not obtained, however, a concentrated CH_2Cl_2 solution of the $[BAr^F]^-$ salt, layered with hexane, produced a few colourless crystals identified by an X-ray structure determination as $[SiCl_3(Me_3tacn)]Cl$ (see Fig. S1 in ESI†) which separate adventitiously due to the lower solubility of this salt. Direct reaction of $SiCl_4$ and Me_3tacn in CH_2Cl_2 resulted in precipitation of a pale yellow solid containing the same $[SiCl_3(Me_3tacn)]Cl$, however we have been unable to obtain it in analytically pure form by this route.

The ^1H NMR spectrum of $[SiCl_3(Me_3tacn)]^+$ in CD_3CN at 298 K shows sharp second order multiplets characteristic of symmetrical *fac*-coordinated Me_3tacn in solution.[20]

Similar reaction of $SiHCl_3$ with $Na[BAr^F]$ in toluene, followed by addition of Me_3tacn, produced the corresponding dichlorosilane complex, $[SiHCl_2(Me_3tacn)][BAr^F]$. 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*-$SiHCl_2$ removes the three-fold symmetry of the Me_3tacn found in $[SiCl_3(Me_3tacn)]^+$, and this is reflected in both the ^1H and $^{13}C\{^1H\}$ NMR spectra, which show two δ(Me) resonances and corresponding splitting of the NCH_2 resonances. Attempts to determine the structure of this complex have been unsuccessful. Poor quality crystals were obtained, but structure solution showed disordered $[SiCl_3(Me_3tacn)]^+$ and $[SiHCl_2(Me_3tacn)]^+$ were both present (note that $[SiCl_3(Me_3tacn)]^+$ 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 $[SiHCl_2(Me_3tacn)]^+$ solution.[21]

Finally, two complexes of the linear triamine, $Me_2NCH_2CH_2N(Me)CH_2CH_2NMe_2$ (pmdta), $[SiX_3(pmdta)][BAr^F]$ (X = Cl or Br) were isolated by reacting the appropriate SiX_4 with $Na[BAr^F]$ 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 Me_3tacn complexes. The geometry of the $[SiCl_3(pmdta)]^+$ cation is close to octahedral, and the Si–N and Si–Cl distances are little different from those found in $[SiCl_3(Me_3tacn)]^+$

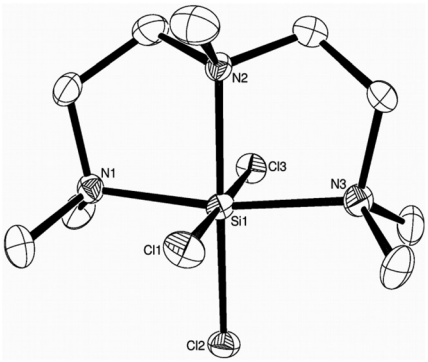

Fig. 6 View of the cation in $[SiCl_3(pmdta)][BAr^F]$. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–Cl1 = 2.147(2), Si1–Cl2 = 2.124(2), Si1–Cl3 = 2.184(2), Si1–N1 = 2.059(5), Si1–N2 = 2.028(5), Si1–N3 = 2.075(5); N1–Si1–N2 = 85.6(2), N2–Si1–N3 = 85.0(2) Cl1–Si1–Cl2 = 91.12(9), Cl2–Si1–Cl3 = 89.82(9).

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_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 $[SiX_3(pmdta)]^+$ 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 $[Ge(Me_3tacn)]Br[GeBr_3]$.[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 $Me_3SiO_3SCF_3$ or $Na[BAr^F]$, adopt distorted octahedral coordination geometries, and the trichloro-, tribromo- and hydridodichloro-species reported here are significantly more readily hydrolysed than $[SiF_3(Me_3tacn)]^+$.[11]

Acknowledgements

We thank EPSRC for support (EP/I010890/1 and EP/I033394/1). The SCFED Project (http://www.scfed.net) is a multidisciplinary collaboration of British universities investigating the fundamental and applied aspects of supercritical fluids.

References

1 D. Vaughn II and R. E. Schaak, *Chem. Soc. Rev.*, 2013, **42**, 2861.
2 S. Raoux, W. Welnic and D. Ielmini, *Chem. Rev.*, 2010, **110**, 240.
3 D. V. Talapin, J. S. Lee, M. V. Kovalenko and E. V. Shevchenko, *Chem. Rev.*, 2010, **110**, 389.
4 (*a*) J. Ke, W. Su, S. M. Howdle, M. George, D. Cook, M. Perdjon-Abel, P. N. Bartlett, W. Zhang, F. Cheng, W. Levason, G. Reid, J. Hyde, J. Wilson, D. C. Smith, K. Mallik and P. Sazio, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 14768; (*b*) J. Ke, P. N. Bartlett, D. Cook, T. L. Easun, M. George, W. Levason, G. Reid, D. C. Smith, W. Su and W. Zhang, *Phys. Chem. Chem. Phys.*, 2014, **16**, 9202.
5 P. N. Bartlett, S. L. Benjamin, C. H. de Groot, A. L. Hector, A. Jolleys, R. Huang, G. P. Kissling, W. Levason, S. J. Pearce, G. Reid and Y. Wang, *Mater. Horizons*, 2015, **2**, 420.
6 (*a*) P. N. Bartlett, C. Y. Cummings, W. Levason, D. Pugh and G. Reid, *Chem. – Eur. J.*, 2014, **20**, 5019; (*b*) J. Ke, P. N. Bartlett, D. Cook, T. L. Easun, M. W. George, W. Levason, G. Reid, D. Smith, W. Su and W. Zhang, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1517.
7 W. Levason, G. Reid and W. Zhang, *Coord. Chem. Rev.*, 2011, **255**, 1319.
8 (*a*) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn and D. Stalke, *Angew. Chem., Int. Ed.*, 2009, **48**, 5683; (*b*) A. C. Filippou, O. Chernov and G. Schnakenburg, *Angew. Chem., Int. Ed.*, 2009, **48**, 5687.
9 F. Cheng, M. F. Davis, A. L. Hector, W. Levason, G. Reid, M. Webster and W. Zhang, *Eur. J. Inorg. Chem.*, 2007, 4897.
10 G. Willey, T. J. Woodman, U. Somasundaram, D. R. Aris and W. Errington, *J. Chem. Soc., Dalton Trans.*, 1998, 2573.
11 F. Cheng, A. L. Hector, W. Levason, G. Reid, M. Webster and W. Zhang, *Chem. Commun.*, 2009, 1334.
12 F. Cheng, A. L. Hector, W. Levason, G. Reid, M. Webster and W. Zhang, *Angew. Chem., Int Ed.*, 2009, **48**, 5152.
13 K. Wieghardt, P. Chaudhuri, B. Nuber and J. Weiss, *Inorg. Chem.*, 1982, **21**, 3086.
14 M. Brookhart, B. Grant and A. F. Volpe Jr., *Organometallics*, 1992, **11**, 3920.
15 (*a*) *CrystalClear-SM Expert 2.0 r7.4*, Rigaku Corporation, Tokyo, Japan, 2011; (*b*) L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849; (*c*) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339; (*d*) G. M. Sheldrick, *Acta Crystal-*

logr., Sect. C: Cryst. Struct. Commun., 2015, **71**, 3; (*e*) F. H. Allen, O. Johnson, G. P. Shields, B. R. Smith and M. Towler, *J. Appl. Crystallogr.*, 2004, **37**, 335.

16 See for example: J. Dyke, W. Levason, M. E. Light, D. Pugh, G. Reid, H. Bhakhoa, P. Ramasami and L. Rhyman, *Dalton Trans.*, 2015, **44**, 13853.

17 M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. A*, 2009, **113**, 5806.

18 B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverrıa, E. Cremades, F. Barragan and S. Alvarez, *Dalton Trans.*, 2008, 2832.

19 M. Everett, A. Jolleys, W. Levason, D. Pugh and G. Reid, *Chem. Commun.*, 2014, **50**, 5843.

20 R. Bhalla, C. Darby, W. Levason, S. K. Luthra, G. McRobbie, G. Reid, G. W. Sanderson and W. Zhang, *Chem. Sci.*, 2014, **5**, 381.

21 (*a*) P. Boudjouk, S. D. Kloos, B.-K. Kim, M. Page and D. Thweatt, *J. Chem. Soc., Dalton Trans.*, 1998, 877; (*b*) H. J. Campbell-Ferguson and E. A. V. Ebsworth, *J. Chem. Soc. A*, 1966, 1508.

22 B.-K. Kim, S.-B. Choi, S. D. Kloos and P. Boudjouk, *Inorg. Chem.*, 2000, **39**, 728.