DOI: 10.1002/ejic.200700727

Synthesis, Spectroscopic and Structural Systematics of Complexes of Germanium(IV) Halides (GeX_4, X = F, Cl, Br or I) with Mono-, Bi- and Tri-Dentate and Macrocyclic Nitrogen Donor Ligands

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Keywords: Germanium / Nitrogen ligands / Fluorido complexes

The six-coordinate adducts *cis*-[GeX_4(L–L)] (L–L = 2,2′-bipyridyl, 1,10-phenanthroline, or $Me_2NCH_2CH_2NMe_2$, X = F, Cl or Br) have been synthesised and characterised by IR and VT ^1H and $^{19}F\{^1H\}$ NMR spectroscopy. X-ray crystal structures reveal distorted octahedral geometries and the trends in *d*(Ge–N) with halide are interpreted in terms of varying Lewis acidity within the series. The *trans*-[$GeX_4(py)_2$] were similarly characterised. In contrast, GeI_4 does not form similar adducts, although it appears to co-crystallise with some of the ligands, and the structure of GeI_4·(1,10-phenH)$_3$·I_3 which contains phenanthrolinium cations, iodide anions and tetrahedral GeI_4 molecules is reported. Multidentate nitrogen donor ligands including cyclam (1,4,8,11-tetraazacyclotetradecane) and Me_4-cyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) react with [$GeF_4(MeCN)_2$] to form insoluble compounds [$\{GeF_4\}_2$(macrocycle)] (F_4N_2 donor sets). In contrast, Me_3[9]aneN_3 (1,4,7-trimethyl-1,4,7-triazacyclononane) forms the cation [$GeF_3\{Me_3[9]aneN_3\}]^+$ with a facial geometry (N_3F_3 donor set) which is the first example of displacement of fluoride from GeF_4 by a neutral ligand.
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Introduction

The coordination chemistry of tin(IV), especially complexes derived from the three tetrahalides, SnX_4 (X = Cl, Br or I), is among the most extensive of the *p*-block elements.[1–5] Tin(IV) fluoride has been much less studied (see ref.[4,5] and citations therein), but is a very strong Lewis acid. In marked contrast, the coordination chemistry of the lighter analogue germanium(IV) is little known. Surveys in the 1950–1960s established that germanium(IV) halides exhibited modest Lewis acidity, markedly less than that of the tin(IV) analogues, but provided little detail.[6] A few more examples have been reported in the intervening years,[7–13] but data on series of complexes, solution speciation studies or even establishment of the boundaries of complex formation are elusive. We have begun a detailed examination of the coordination chemistry of germanium(IV), and have recently reported a series of phosphane oxide adducts of the tetrahalides,[14] including *trans*-[$GeF_4(R_3PO)_2$] (R = Me, Et or Ph), *trans*-[$GeCl_4(Et_3PO)_2$], *fac*-[$GeCl_3(Me_3PO)_3$]$_2$-[$GeCl_6$], and *cis*-[$GeX_2(Me_3PO)_4$]X_2 (X = Cl or Br). The ability of R_3PO to displace Cl or Br from the GeX_4 to form the cationic complexes was unexpected and is unknown in the corresponding tin(IV) systems. Similarly, whilst GeF_4 forms *trans*-[$GeF_4(Ph_3AsO)_2$] on reaction with the arsane oxide, reaction of Ph_3AsO or Me_3AsO with $GeCl_4$ leads to the corresponding R_3AsCl_2, again contrasting with the tin(IV) systems.[14]

This present study focuses on nitrogen donor ligands of a variety of architectures and denticities, especially the complexes with GeF_4. A more limited range of examples with $GeCl_4$ and $GeBr_4$ were examined for comparison purposes.

Results and Discussion

Mono- and Bi-Dentate Nitrogen Donor Ligands

The germanium(IV) halides and their complexes are moisture sensitive to varying degrees and all syntheses were carried out using rigorously anhydrous conditions. GeF_4 is a gas (sub. 236 K) and inconvenient to handle in this form, and the nitrile adduct, [$GeF_4(MeCN)_2$][14] is a more convenient precursor. The reaction of [$GeF_4(MeCN)_2$] with the bidentate N-donors 2,2′-bipyridyl, 1,10-phenanthroline and $Me_2N(CH_2)_2NMe_2$ (L–L) in anhydrous MeCN solution afforded white solid [GeF_4(L–L)] complexes which were unaffected by exposure to moist air and stable in solution in dry MeCN or CH_2Cl_2. The $^{19}F\{^1H\}$ NMR spectra in CH_2Cl_2 or MeCN each show two triplets consistent with the presence of *cis* isomers ($^2J_{FF}$ = 55–65 Hz), and the IR spectra show several strong bands in the region 590–660 cm^{-1} assigned as ν(Ge–F) (theory: 4 IR-active stretches $2a_1 + b_1 + b_2$). The ^1H NMR spectra are also simple showing resonances only due to the coordinated ligands. In contrast the

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monodentates, pyridine and Et_3N (L) give $[GeF_4(L)_2]$ which exhibit singlet $^{19}F\{^1H\}$ NMR resonances in $CDCl_3$ solution consistent with *trans* isomers. The ^1H NMR spectra of solutions of $[GeF_4(NEt_3)_2]$ in CH_2Cl_2 at 298 K shows broad δ(Me) and $\delta(CH_2)$ resonances with no couplings, but on cooling four resonances appear, two quartets and two triplets ($^3J_{HH} \approx 7$ Hz) with approximately equal intensities in each case, assigned from their chemical shifts to $[GeF_4(NEt_3)_2]$ and free NEt_3, showing significant ligand dissociation in solution. The presence of only the *trans* isomer contrasts with the behaviour found for $[GeF_4(R_3PO)_2]$ where varying amounts of *cis* and *trans* isomers were found in solution in chlorocarbons.[14]

The structure of [GeF$_4$(2,2′-bipy)][9] is the only literature structure of a GeF_4 adduct with a bidentate N-donor ligand. We have determined the structures of [GeF$_4$(1,10-phenanthroline)] and $[GeF_4(Me_2NCH_2CH_2NMe_2)]$ (Table 1, Figures 1 and 2) which show close to octahedral coordination at the Ge with F–Ge–F angles slightly greater than 90° and F–Ge–N slightly smaller than 90°, and with N–Ge–N 80.0(2)° and 85.2(3)° respectively. The Ge–F$_{transF}$ are typically longer than Ge–F$_{transN}$, with the *trans* F–Ge–F unit bent towards the neutral ligand, as is usually found in compounds of this type.[5,9] The structure of $[GeF_4(py)_2]$ in contrast, is of a *trans* isomer, a centrosymmetric molecule, with unexceptional bond lengths (Table 2, Figure 3).

Table 1. Selected bond lengths [Å] and angles (°) for [GeF$_4$(1,10-phenanthroline)]·0.5MeCN and $[GeF_4(Me_2NCH_2CH_2NMe_2)]$.

(a) [GeF$_4$(1,10-phenanthroline)]·0.5MeCN[a]			
Ge1–F1	1.781(2)	Ge1–F2	1.753(2)
Ge1–N1	2.046(3)		
F1–Ge1–F2	93.11(13)	F1–Ge1–F2a	92.70(12)
F1–Ge1–F1a	171.11(14)	F2–Ge1–F2a	98.40(18)
F1–Ge1–N1	86.58(11)	F1–Ge1–N1a	86.61(12)
F2–Ge1–N1	90.81(12)	N1–Ge1–N1a	79.98(16)
(b) $[GeF_4(Me_2NCH_2CH_2NMe_2)]$			
Ge1–F1	1.773(3)	Ge1–F2	1.763(2)
Ge1–F3	1.756(4)	Ge1–F4	1.774(4)
Ge1–N1	2.087(3)	Ge1–N2	2.068(5)
F1–Ge1–F2	91.6(2)	F1–Ge1–F3	92.0(2)
F1–Ge1–F4	174.6(2)	F2–Ge1–F3	94.7(2)
F2–Ge1–F4	91.6(2)	F3–Ge1–F4	91.9(1)
F1–Ge1–N1	88.4(2)	F3–Ge1–N1	89.5(2)
F4–Ge1–N1	88.0(2)	F1–Ge1–N2	90.0(1)
F2–Ge1–N2	90.4(2)	F4–Ge1–N2	85.7(2)
N2–Ge1–N1	85.3(2)	N1–C3–C4–N2	–54.5(6)

[a] Symmetry operation: *a* = 1 –*x*, 1/2 – *y*, *z*.

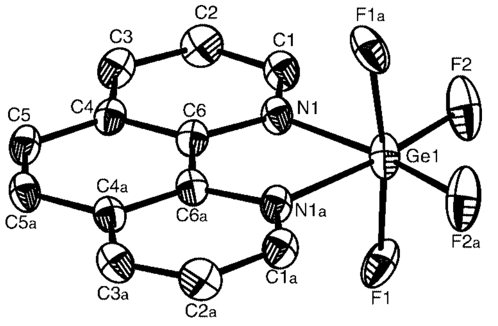

Figure 1. Structure of [GeF$_4$(1,10-phenanthroline)]·0.5MeCN showing the atom labelling scheme. The solvate and the H atoms have been omitted for clarity and the atom displacement ellipsoids are drawn at the 50% probability level. Symmetry operation: *a* = 1 –*x*, 1/2 – *y*, *z*.

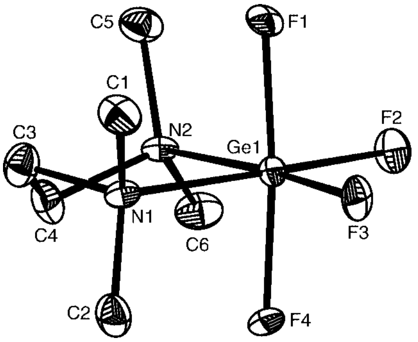

Figure 2. Structure of $[GeF_4(Me_2NCH_2CH_2NMe_2)]$ showing the atom labelling scheme. The H atoms have been omitted for clarity and the atom displacement ellipsoids are drawn at the 50% probability level.

Table 2. Selected bond lengths [Å] and angles (°) for $[GeF_4(py)_2]$.

Ge1–F1	1.780(2)	Ge1–F2	1.782(3)
Ge1–N1	2.011(4)	N1–C	1.348(5), 1.354(5)
F1–Ge1–F2	89.86(12)	F1–Ge1–N1	90.21(13)
F2–Ge1–N1	90.25(13)		

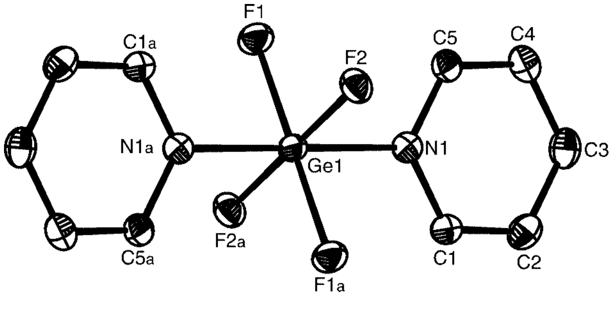

Figure 3. Structure of $[GeF_4(py)_2]$ showing the atom labelling scheme. The H atoms have been omitted for clarity and the atom displacement ellipsoids are drawn at the 50% probability level. The Ge is positioned on a centre of symmetry. Symmetry operation: *a* = –*x*, – *y*, – *z*.

In contrast to the fluorides, the complexes of $GeCl_4$ and $GeBr_4$ are hydrolytically very sensitive and must be handled in a glove box and in dry solvents. The complexes [GeX$_4$(L–L)] (X = Cl or Br; L–L = 2,2′-bipy, 1,10-phen, $Me_2NCH_2CH_2NMe_2$) were obtained as white powders by combining the constituents in dry CH_2Cl_2 solution, and in several cases, as colourless crystals on recrystallisation from dry MeCN in a freezer. The structures of [GeCl$_4$(2,2′-bipy)][12] and $[GeCl_4(Me_2NCH_2CH_2NMe_2)]$[8] have been reported previously, and we report here the structures of [GeX$_4$(1,10-phenanthroline)], [GeBr$_4$(2,2′-bipy)] and [GeBr$_4$-

($Me_2NCH_2CH_2NMe_2$)] (Tables 3, 4, and 5, Figures 4, 5, 6, and 7). The structural features generally mimic those discussed above for the fluorides, with X–Ge–X angles rather greater than 90° and X–Ge–N angles rather less. The N–Ge–N angles are 79.5(1)° [$GeCl_4$(1,10-phenanthroline)], 78.8(3)° [$GeBr_4$(1,10-phenanthroline)], 79.0(2)° [$GeBr_4$(2,2′-bipy)] and 82.3(2)° [$GeBr_4$($Me_2NCH_2CH_2NMe_2$)], reflecting the slightly different ligand bites. The availability of the present data combined with that in the literature permits a detailed comparison of structural features within the [GeX_4(L–L)] series as a function of X and hence an examination of the Lewis acidity of the GeX_4. The trends reflect two major contributions, the strength of the Ge–N bond

Table 3. Selected bond lengths [Å] and angles (°) for [GeX_4(1,10-phenanthroline)] (X = Cl and Br).

(a) [$GeCl_4$(1,10-phenanthroline)]·0.5MeCN[a]

Ge1–Cl1	2.2619(6)	Ge1–Cl2	2.2232(6)
Ge1–Cl3	2.2244(6)	Ge1–Cl4	2.2799(6)
Ge1–N1	2.0716(17)	Ge1–N2	2.0759(17)
Cl1–Ge1–Cl2	93.61(2)	Cl1–Ge1–Cl3	92.15(2)
Cl1–Ge1–Cl4	171.81(2)	Cl2–Ge1–Cl3	96.81(2)
Cl2–Ge1–Cl4	91.65(2)	Cl3–Ge1–Cl4	93.46(2)
N1–Ge1–Cl1	86.40(5)	N1–Ge1–Cl2	92.07(5)
N1–Ge1–Cl4	87.13(5)	N2–Ge1–Cl1	87.21(5)
N2–Ge1–Cl3	91.66(5)	N2–Ge1–Cl4	86.66(5)
N1–Ge1–N2	79.49(7)		

(b) [$GeBr_4$(1,10-phenanthroline)]·0.4CH_2Cl_2

Ge1–Br1	2.3902(14)	Ge1–Br2	2.4289(16)
Ge1–Br3	2.3792(15)	Ge1–Br4	2.4719(17)
Ge1–N1	2.069(7)	Ge1–N2	2.078(7)
Br1–Ge1–Br2	93.52(5)	Br1–Ge1–Br3	95.40(5)
Br1–Ge1–Br4	91.95(5)	Br2–Ge1–Br3	94.99(5)
Br2–Ge1–Br4	171.16(6)	Br3–Ge1–Br4	91.40(5)
N1–Ge1–Br2	86.0(2)	N1–Ge1–Br3	93.4(2)
N1–Ge1–Br4	87.5(2)	N2–Ge1–Br1	92.4(2)
N2–Ge1–Br2	87.6(2)	N2–Ge1–Br4	85.3(2)
N1–Ge1–N2	78.8(3)		

[a] There are two molecules in the asymmetric unit and the second molecule is very similar.

Table 4. Selected bond lengths [Å] and angles (°) for [$GeBr_4$(2,2′-bipy)].

Ge1–Br1	2.4438(7)	Ge1–Br2	2.4202(6)
Ge1–Br3	2.4280(7)	Ge1–Br4	2.4157(6)
Ge1–N1	2.070(3)	Ge1–N2	2.073(4)
Br1–Ge1–Br2	92.64(2)	Br1–Ge1–Br3	173.13(2)
Br1–Ge1–Br4	92.12(2)	Br2–Ge1–Br3	91.70(2)
Br2–Ge1–Br4	92.99(2)	Br3–Ge1–Br4	92.96(2)
N1–Ge1–Br1	86.84(10)	N1–Ge1–Br2	94.09(10)
N1–Ge1–Br3	87.54(10)	N2–Ge1–Br1	87.48(10)
N2–Ge1–Br3	87.57(10)	N2–Ge1–Br4	93.97(10)
N1–Ge1–N2	78.95(14)	N1–C5–C6–N2	0.7(6)

Table 5. Selected bond lengths [Å] and angles (°) for [$GeBr_4$($Me_2NCH_2CH_2NMe_2$)].

Ge1–Br1	2.4388(10)	Ge1–Br2	2.4587(10)
Ge1–Br3	2.4372(10)	Ge1–Br4	2.4506(11)
Ge1–N1	2.188(5)	Ge1–N2	2.193(5)
Br1–Ge1–Br2	89.72(3)	Br1–Ge1–Br3	95.35(4)
Br1–Ge1–Br4	88.53(4)	Br2–Ge1–Br3	88.89(4)
Br2–Ge1–Br4	177.28(4)	Br3–Ge1–Br4	89.21(4)
N1–Ge1–Br1	90.45(14)	N1–Ge1–Br2	90.19(15)
N1–Ge1–Br4	91.89(15)	N2–Ge1–Br2	92.81(13)
N2–Ge1–Br3	91.99(15)	N2–Ge1–Br4	89.20(13)
N1–Ge1–N2	82.3(2)	N1–C3–C4–N2	–61.7(8)

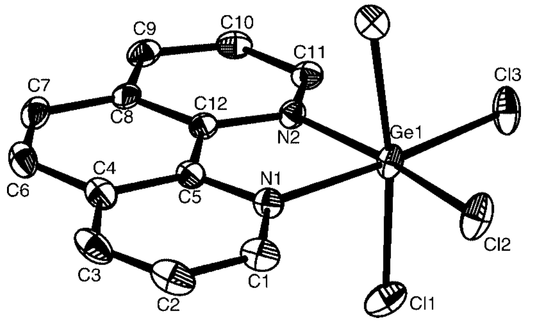

Figure 4. Structure of [$GeCl_4$(1,10-phenanthroline)]·0.5MeCN showing the atom labelling scheme. There are two molecules in the asymmetric unit and the second molecule is very similar. The solvate and the H atoms have been omitted for clarity and the atom displacement ellipsoids are drawn at the 50% probability level.

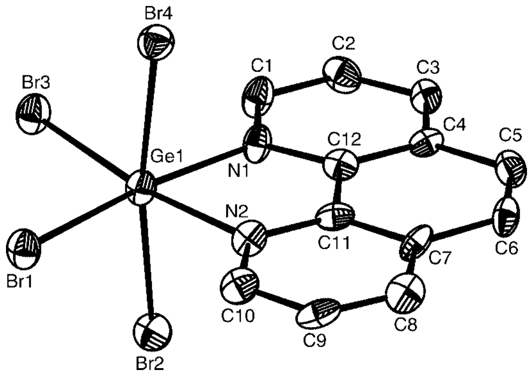

Figure 5. Structure of [$GeBr_4$(1,10-phenanthroline)]·0.4CH_2Cl_2 showing the atom labelling scheme. The solvate and the H atoms have been omitted for clarity and the atom displacement ellipsoids are drawn at the 50% probability level.

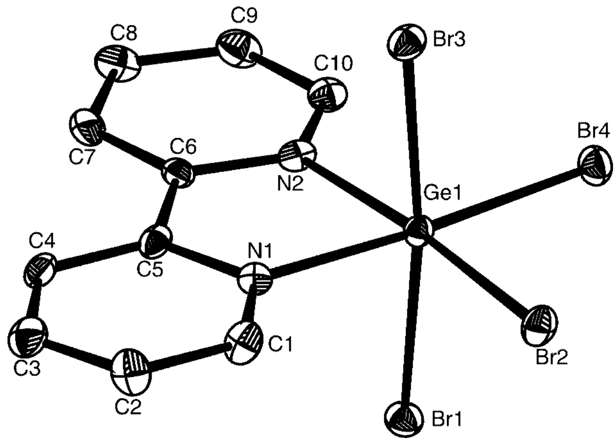

Figure 6. Structure of [$GeBr_4$(2,2′-bipy)] showing the atom labelling scheme. The H atoms have been omitted for clarity and the atom displacement ellipsoids are drawn at the 50% probability level.

Table 6. Comparison of Ge–N and Ge–X bond lengths (Å).

Complex	Ge–N	Ge–X_{transX}	Ge–X_{transN}	N···N	Ref.
[GeF_4(1,10-phenanthroline)]	2.046(3)	1.781(2)	1.753(2)	2.629(6)	this work
[$GeCl_4$(1,10-phenanthroline)]	2.076(2), 2.072(2)	2.262(1), 2.280(1)	2.223(1), 2.224(1)	2.652(2)	this work
[a]	2.074(2), 2.093(2)	2.237(1), 2.245(1)	2.227(1), 2.249(1)	2.656(2)	
[$GeBr_4$(1,10-phenanthroline)]	2.069(7), 2.078(7)	2.492(2), 2.472(2)	2.390(2), 2.379(2)	2.632(10)	this work
[GeF_4(2,2′-bipy)]	2.023(4), 2.029(4)	1.777(2)	1.757(3), 1.761(3)	2.585(5)	[9]
[$GeCl_4$(2,2′-bipy)]	2.062(4), 2.068(4)	2.272(1), 2.262(1)	2.241(1), 2.246(1)	2.629(–)	[12]
[$GeBr_4$(2,2′-bipy)]	2.070(3), 2.073(4)	2.428(1), 2.444(1)	2.416(1), 2.420(1)	2.634(5)	this work
[$GeF_4(Me_2NCH_2CH_2NMe_2)$]	2.073(6), 2.090(4)	1.766(4), 1.782(4)	1.766(2), 1.750(4)	2.815(7)	this work
[$GeCl_4(Me_2NCH_2CH_2NMe_2)$]	2.148(12), 2.156(10)	2.253(5), 2.248(4)	2.247(3), 2.236(4)	2.908(–)	[8]
[$GeBr_4(Me_2NCH_2CH_2NMe_2)$]	2.188(5), 2.193(5)	2.451(1), 2.459(1)	2.437(1), 2.439(1)	2.881(8)	this work

[a] There are two molecules in the asymmetric unit. The first line refers to the Ge1 centred molecule.

and the reorganisation energy necessary to convert the tetrahedral GeX_4 to the four-coordinate fragment of the octahedron produced on bonding the Lewis base. For comparison the key bond lengths are summarised in Table 6.

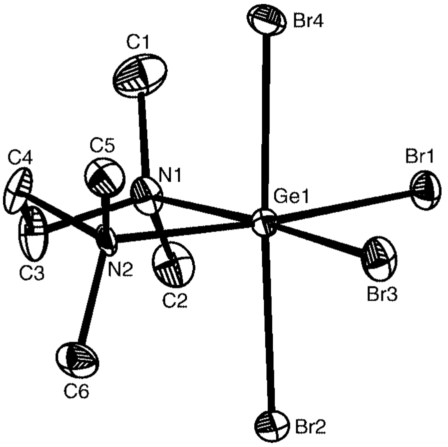

Figure 7. Structure of [$GeBr_4(Me_2NCH_2CH_2NMe_2)$] showing the atom labelling scheme. The H atoms have been omitted for clarity and the atom displacement ellipsoids are drawn at the 40% probability level.

The Ge–X bonds are all longer than in the parent (tetrahedral) GeX_4 {X = F, 1.661(1) Å at 133 K; X = Cl, 2.082(7) Å; X = Br, 2.262(2), 2.269(1) Å}[15–17] reflecting the increased coordination number. Looking at the [$GeX_4(Me_2NCH_2CH_2NMe_2)$] series there is a very clear lengthening of Ge–N as the halide changes F → Cl → Br, showing reduced Lewis acidity in this order. There is a corresponding small decrease in the N–Ge–N angle along the series. For the diimine series the Ge–N are markedly shorter in the fluorido complexes, but the differences are small between the chlorides and bromides (although marginally longer in the latter), possibly reflecting the effects of the rigid ligand skeleton in 1,10-phenanthroline and to a lesser extent 2,2′-bipyridyl (the two rings are essentially co-planar in the bipy complexes and the angles N–Ge–N change by ≤ 1° between the three complexes in each series). The two independent molecules in the unit cell of [$GeCl_4$(1,10-phenanthroline)] show small but significant differences and this is presumably attributable to packing,[18] and effects of a similar magnitude in other cases could mask trends in Ge–N distances with changing halogen co-ligands. The decreasingly strong binding of the nitrogen ligands as the halide becomes heavier is also reflected in the solution properties. Thus, whilst the fluorides show simple spectra due to coordinated ligand with high frequency shifts for the resonances in the ^1H NMR spectra at 295 K in $CDCl_3$ or CD_3CN, the diimine bromide complexes show evidence for both coordinated and "free" ligand, indicative of partial dissociation in solution at ambient temperatures. The ^1H NMR spectrum of [$GeBr_4(Me_2NCH_2CH_2NMe_2)$] at 295 K shows broad features consistent with fast exchange, whilst at low temperatures separate resonances are seen for coordinated and "free" diamine as exchange slows. The chlorides are intermediate in properties with the [$GeCl_4$(1,10-phenanthroline)] showing sharp resonances for the coordinated ligand only, but [$GeCl_4$(2,2′-bipy)] shows both "free" and coordinated ligand resonances.

The older literature contains a few reports of brown or red complexes derived from GeI_4 and nitrogen donor ligands[19] mostly characterised only by (partial) microanalytical data. We have obtained similar products in a number of cases. The IR spectra show the presence of the nitrogen ligand (protonated in some examples) and a strong band at 250 ± 5 cm^{-1} which corresponds to the t_2 vibration of tetrahedral GeI_4, but are otherwise uninformative, and since extensive dissociation is expected in solution, NMR spectroscopic data are of little help. For the 1,10-phenanthroline/GeI_4 system in CH_2Cl_2, a few good quality crystals were obtained, the structure revealed the composition to be GeI_4·(1,10-phenH)$_3$·I_3, presumably formed by trace hydrolysis (Table 7). This contained tetrahedral GeI_4, 1,10-phenanthrolinium cations, and iodide ions. Two of the three protonated 1,10-phenanthrolines were involved in N–H···I H-bonding and one I^- (I5) showed a weak interaction to an iodine atom of GeI_4 (3.483 Å), rather shorter than that found in $Et_4NI·2GeI_4$ (3.660–3.792 Å).[20] The unit cell is

Table 7. Selected bond lengths [Å] and angles (°) for GeI_4·3[$C_{12}H_9N_2$]·3I.

Ge1–I1	2.5388(6)	Ge1–I3	2.5281(6)
Ge1–I2	2.5332(6)	Ge1–I4	2.5339(6)
I4···I5	3.4832(5)		
I1–Ge1–I2	111.54(2)	I2–Ge1–I3	107.17(2)
I1–Ge1–I3	112.35(2)	I2–Ge1–I4	108.00(2)
I1–Ge1–I4	107.46(2)	I3–Ge1–I4	110.27(2)

shown in Figure 8. In our work on the GeI_4/R_3PO systems[14] we also obtained crystals of GeI_4 and $R_3POH^+ I_3^-$, but no adducts from reactions of GeI_4 with the ligands, and there appear to be no structurally authenticated examples of GeI_4 complexes with neutral ligands.

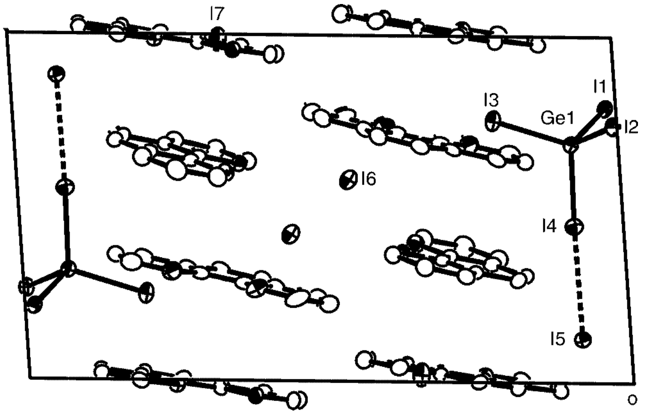

Figure 8. Unit cell packing diagram of $GeI_4{\cdot}3[C_{12}H_9N_2]{\cdot}3I$ viewed along the *a* direction. The H atoms have been omitted for clarity, only Ge and I are labelled with C drawn as boundary ellipsoids, and the atom displacement ellipsoids are drawn at the 50% probability level. The weak I···I interaction is shown as a dotted bond. I6 and I7 are involved in N–H···I H-bonds (not shown). The origin is in the lower right corner with *c* along the horizontal direction and *b* near vertical. The packing consists of nearly parallel 1,10-phenanthrolinium cations ($C_{12}H_9N_2$) lying in the *ac* plane. The cations stack to form a sheet in the *ab* plane $\{[(C_{12}H_9N_2)_3I_2]^+\}$ interleaved with a sheet of composition $[(GeI_4){\cdot}I]^-$.

Polydentate and Macrocyclic N-Ligands

Polydentate N-donor macrocycles displace halide from the appropriate GeX_4 (X = Cl or Br) in forming $[GeCl_3\{Me_3[9]aneN_3\}]^+$ and $[GeBr_3(1,3,5\text{-trimethyl-}1,3,5\text{-triazacyclohexane})]^+$,[7] and it was therefore of interest to establish if it was possible to displace fluoride from GeF_4 by similar ligands. The reaction of $Me_3[9]aneN_3$ with $[GeF_4(MeCN)_2]$ in CH_2Cl_2 produced a white solid identified as $[GeF_3\{Me_3[9]aneN_3\}]_2[GeF_6]$ by microanalysis, which was insoluble in MeCN or chlorocarbons. The IR spectrum showed two strong broad features at 629 and 602 cm^{-1} attributable to the ν(Ge–F) stretching modes of the cation and anion respectively, and a strong feature at 340 cm^{-1} which is δ(Ge–F) of the anion. Unfortunately crystals of this salt could not obtained due to insolubility in common solvents, but a few crystals were isolated by slow evaporation of an MeCN extract of the white solid from the preparation and were found to be (Figure 9, Table 8) $[GeF_3\{Me_3[9]aneN_3\}]Cl$. The adventitious chloride anion is believed to arise from the displaced fluoride ion reacting with the chlorocarbon solvent.[21] The structure shows the expected facial geometry for the cation with Ge–N 2.043(3) Å which may be compared with 2.106(2)–2.125(2) Å in the chloride analogue $[GeCl_3\{Me_3[9]aneN_3\}]^+$.[7] The N–Ge–N angle in the former is 85.53(13)° compared to 82.59(8)–83.17(8)° in the latter. The Ge–F distance in the cation is 1.767(2) Å not significantly different from that in the $[GeF_4(\text{diimine})]$ complexes despite the cation charge. This complex is the first example in which fluoride has been displaced from GeF_4 by a neutral ligand.

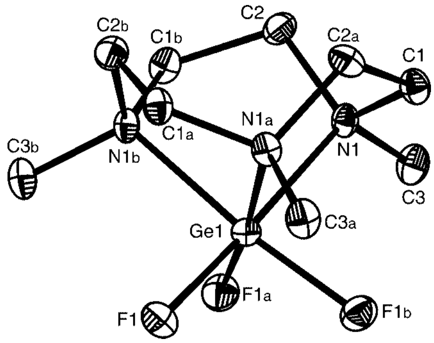

Figure 9. Structure of the cation of $[GeF_3(Me_3[9]aneN_3)]Cl$ showing the atom labelling scheme. The H atoms have been omitted for clarity and the atom displacement ellipsoids are drawn at the 50% probability level. The cation has threefold crystallographic symmetry. Symmetry operations: *a* = 1 – *y*, *x* – *y*, *z*; *b* = 1 – *x* + *y*, 1 – *x*, *z*.

Table 8. Selected bond lengths [Å] and angles (°) for $[GeF_3(Me_3[9]aneN_3)]Cl$.[a]

Ge1–F1	1.767(2)	Ge1–N1	2.043(3)
F1–Ge1–F1a	92.86(10)	N1–Ge1–N1a	85.53(13)
F1–Ge1–N1a	88.77(12)	F1–Ge1–N1b	92.68(11)

[a] Symmetry operations: *a* = 1 –*y*, *x* – *y*, *z*; *b* = 1 – *x* + *y*, 1 – *x*, *z*.

The reactions of cyclam (1,4,8,11-tetra-azacyclotetradecane) and Me_4-cyclam (1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) with $[GeF_4(MeCN)_2]$ in CH_2Cl_2 in either a 1:1 or 1:2 molar ratio, precipitated white powders which were identified by microanalysis as $[(GeF_4)_2(\text{azamacrocycle})]$. The solids are air-stable and the IR spectra reveal the presence of the macrocycle and terminal Ge–F modes. The isolated solids are insoluble in chlorocarbons and MeCN, precluding NMR studies, but the $^{19}F\{^1H\}$ NMR spectra of the reaction mixtures (in situ) show a number of resonances in the regions expected for $\delta\ F_{trans\mathrm{F}}$ and $\delta\ F_{trans\mathrm{N}}$ and on cooling the solutions these show t or d,t patterns consistent with *cis* octahedral-GeF_4 units with κ^2 coordination to the macrocycles (depending upon the rate of pyramidal inversion at N or reversible dissociation, resonances due to the presence of *meso* and DL forms of the κ^2 coordinated macrocycle may be expected). Notably absent were any features attributable to $[GeF_6]^{2-}$ $\{\delta(^{19}F) = -139\}$ or significant amounts of F^-, which would be present if fluoride had been displaced from the germanium centre. Confirmation of the κ^2-bonding mode came from the crystal structure of $[GeF_4(Me_4\text{-cyclam})]$, a few crystals of which were obtained from the filtrate of the 1:1 reaction mixture after removal of the precipitated 2:1 complex. The crystals were very small and the data quality modest, but the structure (Figure 10, Table 9) shows $[GeF_4(\kappa^2\text{-}Me_4\text{-cyclam})]$ with the *meso* conformation at the coordinated nitrogens, and the other two N-donors bent away from and not interacting with the germanium. The failure of the cyclam type ligands to form cationic complexes is rationalised in that they are not well suited to κ^3 coordination (in contrast to Me_3[9]-aneN_3), and the displacement of two fluorides to form [GeF_2(κ^4-cyclam)]$^{2+}$ is probably energetically unfavourable. Reaction of 2,2′,6′,2′′-terpyridyl with [GeF_4(MeCN)$_2$] in CH_2Cl_2 gave a white solid of composition [(GeF_4)$_3$-(2,2′,6′,2′′-terpy)$_2$] which was insoluble in MeCN or chlorocarbons. The IR spectrum showed terpy and terminal Ge–F stretches at similar frequencies to the [GeF_4(diimine)] complexes. The insolubility prevented further study, but it seems likely that the terpy is κ^2 coordinated to one GeF_4 residue and κ^1 to a second GeF_4, producing oligomers with six-coordinate germanium centres (F_4N_2 coordinated).

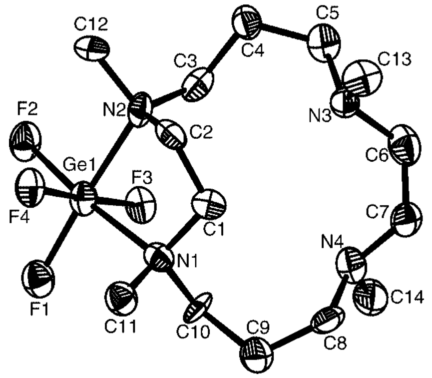

Figure 10. Structure of [GeF_4(κ^2-Me_4-cyclam)] showing the atom labelling scheme. The H atoms have been omitted for clarity and the atom displacement ellipsoids are drawn at the 50% probability level.

Table 9. Selected bond lengths [Å] and angles (°) for [GeF_4(κ^2-Me_4-cyclam)].

Ge1–F1	1.771(7)	Ge1–F2	1.775(6)
Ge1–F3	1.779(5)	Ge1–F4	1.775(5)
Ge1–N1	2.121(8)	Ge1–N2	2.086(9)
F1–Ge1–F2	95.7(3)	F2–Ge1–F3	89.8(3)
F1–Ge1–F3	92.5(3)	F2–Ge1–F4	90.5(3)
F1–Ge1–F4	91.2(3)	F3–Ge1–F4	176.2(3)
F1–Ge1–N1	90.3(3)	F1–Ge1–N2	173.2(3)
F2–Ge1–N1	174.0(3)	F2–Ge1–N2	90.1(3)
F3–Ge1–N1	90.0(3)	F3–Ge1–N2	90.8(3)
F4–Ge1–N1	89.4(3)	F4–Ge1–N2	85.4(3)
N1–Ge1–N2	83.9(3)		

Conclusions

This study has shown that GeF_4 forms robust complexes with a variety of neutral nitrogen donor ligands, all but one example containing six-coordinate germanium with F_4N_2 donor sets. The exception, [GeF_3{Me_3[9]aneN_3}]$^+$ reflects the strong pre-organisation in the macrocycle for κ^3 coordination which in this case achieves the displacement of one fluorido ligand. The complexes are generally only slightly moisture sensitive, whereas the corresponding complexes with GeX_4 (X = Cl or Br) are very sensitive to moisture, and often partially dissociated in solution. Structural studies confirm that Lewis acidity decreases along the series GeF_4 >> $GeCl_4$ > $GeBr_4$. There is no evidence that simple N-donor complexes form with GeI_4. The much stronger acceptor ability of GeF_4 may well mean that an extensive coordination chemistry is accessible, including complexes with other neutral donor types, e.g. tertiary phosphanes, thio- or seleno-ethers (none of which form simple adducts with $GeCl_4$)[10,22] and work is underway in our laboratory to explore this possibility.

Experimental Section

The germanium(IV) halides GeF_4, $GeBr_4$ and GeI_4 were obtained from Aldrich and used as received. $GeCl_4$ (Aldrich) was distilled from a mixture of $CaCl_2$/Na_2CO_3, which removes traces of water and HCl. MeCN and CH_2Cl_2 were dried by distillation from CaH_2. All reactions were conducted using Schlenk, vacuum line and glove-box techniques and under a dry dinitrogen atmosphere. Me_3[9]aneN_3 was made as described.[23] 2,2′-Bipyridyl, 1,10-phenanthroline, 2,2′,6′2′′-terpyridyl and cyclam and Me_4-cyclam were dried by heating in vacuo. Pyridine was dried by distillation from potassium, and $Me_2N(CH_2)_2NMe_2$ and NEt_3 by distillation from BaO. [GeF_4(MeCN)$_2$] was made as described.[14]

Infrared spectra were recorded as Nujol mulls on a Perkin–Elmer PE 983G spectrometer, ^{1}H NMR spectra in $CDCl_3$, CD_2Cl_2 or CD_3NO_2 solutions on a Bruker AV300, ^{19}F{^{1}H} NMR spectra on a Bruker DPX400 and referenced to $CFCl_3$. Microanalytical measurements on new complexes were performed by the microanalytical service at Strathclyde University. Representative syntheses of the complexes are given below.

Yields of the complexes were at least 80% based upon germanium.

[GeF_4(2,2′-bipy)]: 2,2′-Bipyridyl (0.04 g, 0.25 mmol) was added to a solution of [GeF_4(MeCN)$_2$] (0.057 g, 0.25 mmol) in MeCN (10 mL) at room temperature with stirring, which led to the slow formation of a white precipitate. After stirring for 20 min, the solvent was removed in vacuo to leave a white solid. Air-stable colourless crystals were obtained by vapour diffusion of diethyl ether into solution of the compound in MeCN. $C_{10}H_8F_4GeN_2$ (304.8): calcd. C 39.4, H 2.7, N 9.2; found C 39.6, H 2.6, N 9.2. ^{1}H NMR (CD_3CN, 295 K): δ = 9.03 (d, 2 H), 8.52 (m, 2 H), 8.37 (m, 2 H), 7.89 (m, 2 H) ppm. ^{19}F{^{1}H} NMR ($CDCl_3$, 295 K): δ = –116.2 (t, $^2J_{F,F}$ = 58 Hz, 2 F), –151.2 (t, 2 F) ppm. IR (Nujol): $\tilde{\nu}$ = 635 (sh), 618 (s), 605 (sh) ν(Ge–F) cm^{-1}.

[GeF_4(1,10-phenanthroline)]: Was made analogously to the 2,2′-bipyridyl complex. $C_{12}H_8F_4GeN_2$·0.5MeCN (350.8): calcd. C 44.5, H 3.2, N 10.0; found C 44.5, H 2.7, N 10.0. ^{1}H NMR (CD_3CN, 295 K): δ = 9.26 (d 2 H), 8.89 (d,d 2 H), 8.24 (s, 2 H), 8.15 (m 2 H) ppm. ^{19}F{^{1}H} NMR ($CDCl_3$, 295 K): δ = –115.7 (t, $^2J_{F,F}$ = 62 Hz, 2 F), –150.1 (t, 2 F) ppm. IR (Nujol): $\tilde{\nu}$ = 664 (s), 618 (s), 597 (s) ν(Ge–F) cm^{-1}.

[GeF_4($Me_2NCH_2CH_2NMe_2$)]: Was made similarly to the 2,2′-bipyridyl complex and the white solid obtained was washed with diethyl ether and dried in vacuo. $C_6H_{16}F_4GeN_2$ (264.8): calcd. C 27.2, H 6.1, N 10.6; found C 27.3, H 5.9, N 10.1. ^{1}H NMR ($CDCl_3$, 295 K): δ = 2.97 (m, 1 H) 2.83 (t, 3 H) ppm. ^{19}F{^{1}H} NMR ($CDCl_3$, 295 K): δ = –132.7 (t, $^2J_{F,F}$ = 60 Hz, 2 F), –150.9 (t, 2 F) ppm. IR (Nujol): $\tilde{\nu}$ = 619 (vs), 605 (s), 590 (sh) ν(Ge–F) cm^{-1}.

[GeF_4(py)$_2$]: Was made similarly to the 2,2′-bipyridyl complex using a 2:1 molar ratio of pyridine to [GeF_4(MeCN)$_2$] in CH_3CN solution. $C_{10}H_{10}F_4GeN_2$ (306.8): calcd. C 39.2, H 3.3, N 9.1; found C 39.0, H 2.7, N 9.1. ^{1}H NMR (CD_3CN, 295 K): δ = 8.89 (m, 2 H), 8.29 (m, 1 H), 7.81 (s, 2 H) ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = –125.7 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 617 (vs) ν(Ge–F) cm^{-1}.

[$GeF_4(NEt_3)_2$]: Triethylamine (0.020 g, 0.20 mmol) was added to a solution of [$GeF_4(MeCN)_2$] (0.023 g, 0.10 mmol) in CH_2Cl_2 (15 mL) at room temperature with stirring. After stirring for 10 min, the volatiles were evaporated slowly from the static solution which gave colourless crystalline solid. ^1H NMR (CD_2Cl_2, 295 K): δ = 1.2 (s, 3 H) 3.0 (s, 2 H) ppm; (253 K): δ = 1.10 (t, $^3J_{HH}$ = 6 Hz, 3 H), 1.27 (t, $^3J_{HH}$ = 6 Hz, 3 H), 2.98 (q, 2 H), 3.11 (q, 2 H). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = –129 (br); 253 K δ = –118.5 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 602 ν(Ge–F) cm^{-1}.

[$GeCl_4$(2,2′-bipy)]: $GeCl_4$ (0.22 g, 1.0 mmol) and 2,2′-bipyridyl (0.15 g, 1.0 mmol) were combined in dry dichloromethane (20 mL) producing an immediate white precipitate. The solvent was removed in vacuo and the white solid recrystallised from MeCN (20 mL). Colourless crystals were obtained by keeping the filtrate in a freezer for 3 d. $C_{10}H_8Cl_4GeN_2$ (370.6): calcd. C 32.4, H 2.2, N 7.6; found C 31.7, H 2.1, N 7.2. ^1H NMR ($CDCl_3$, 295 K): δ = 8.85 (br., H), 8.80 (br., H), 8.38 (m, H), 8.15 (m, H); (273 K): δ = 9.01 (d, J = 8 Hz, 1 H), 8.92 (m, 1 H), 8.40 (m, 1 H), 8.20 (m, 1 H) ppm. IR (Nujol): $\tilde{\nu}$ = 335, 317, 295 ν(Ge–Cl) cm^{-1}.

[$GeCl_4$(1,10-phenanthroline)]: The complex was prepared analogously to the 2,2′-bipyridyl analogue. Colourless crystals were obtained from the MeCN filtrate after several days in a freezer. $C_{12}H_8Cl_4GeN_2$ (394.6): calcd. C 36.5, H 2.0, N 7.1; found C 36.6, H 1.9, N 7.2. ^1H NMR (CD_3CN, 295 K): δ = 10.17 (d, 2 H), 9.08 (d, 2 H), 8.42 (br., 2 H), 8.36 (m, 2 H) ppm. IR (Nujol): $\tilde{\nu}$ = 357, 332, 320 (sh), 275 ν(Ge–Cl) cm^{-1}.

[$GeCl_4(Me_2NCH_2CH_2NMe_2)$]: The complex was made similarly to the 2,2′-bipyridyl analogue. $C_6H_{16}Cl_4GeN_2$ (330.6): calcd. C 21.8, H 4.9, N 8.5; found C 22.4, H 5.2, N 8.2. ^1H NMR ($CDCl_3$, 295 K): δ = 2.90 (s, 3 H), 3.05 (s, 1 H) (little change at 220 K) ppm. IR (Nujol): $\tilde{\nu}$ = 324, 303, 282 ν(Ge–Cl) cm^{-1}.

[$GeCl_4(py)_2$]: Pyridine (0.16 g, 1.0 mmol) was added to a solution of $GeCl_4$ (0.11 g, 0.5 mmol) in CH_2Cl_2 (20 mL) resulting in an immediate white precipitate, which was isolated by filtration and dried in vacuo. $C_{10}H_{10}Cl_4GeN_2$ (372.6): calcd. C 32.2, H 2.7, N 7.5; found C 31.9, H 2.5, N 7.2. ^1H NMR ($CDCl_3$, 295 K): δ = 8.71 (d, 2 H), 8.54 (m, 1 H), 8.01 (m, 2 H) ppm. IR (Nujol): $\tilde{\nu}$ = 323 (vbr) ν(Ge–Cl) cm^{-1}.

[$GeBr_4$(2,2′-bipy)]: Was made similarly to the chloride as pale yellow crystals. $C_{10}H_8Br_4GeN_2$ (548.4): calcd. C 21.9, H 1.5, N 5.1; found C 22.1, H 1.7, N 5.2. ^1H NMR ($CDCl_3$, 295 K): δ = 8.92 (m, 2 H), 8.20 (m, H), 7.69 (m, H); (253 K): δ = 9.01 (d. H), 8.90 (d, J = 8 Hz, 1 H), 8.32 (m, 1 H), 7.70 (m, 1 H) ppm. IR (Nujol): $\tilde{\nu}$ = 284 (s), 237 (s), 218 (s) ν(Ge–Br) cm^{-1}.

[$GeBr_4$(1,10-phenanthroline)]: Was made similarly to the 2,2-bipy complex. $C_{12}H_8Br_4GeN_2$ (572.4): calcd. C 25.2, H 1.4, N 4.9; found C 25.5, H 1.9, N 5.3. ^1H NMR (CD_3CN, 298 K): δ = 10.33 (d, 2 H), 9.10 (d, 2 H), 8.45 (s, 2 H), 8.40 (m, 2 H) ppm. IR (Nujol): $\tilde{\nu}$ = 247 (s), 232 (s), 203 (sh), ν(Ge–Br) cm^{-1}.

[$GeBr_4(Me_2NCH_2CH_2NMe_2)$]: The diamine (0.06 g, 0.50 mmol) was added to a solution of $GeBr_4$ (0.19 g, 0.50 mmol) in CH_2Cl_2 (10 mL) at room temperature with stirring, which lead to an immediate colour change to pale yellow and slow precipitation of a yellow solid. After stirring for 10 min the solution was filtered and the pale yellow solid was dried in vacuo. Pale yellow crystals were obtained from a concentrated solution in MeCN in the freezer. $C_6H_{16}Br_4GeN_2$ (508.4): calcd. C 14.2, H 3.2, N 5.5; found C 14.5, H 3.8, N 5.7. ^1H NMR ($CDCl_3$, 298 K): δ = 2.46 (s, 3 H), 2.75 (s, H); (235 K): δ = 2.45 (s, 1 H), 2.63 (s, 1 H), 3.00 (s, 3 H), 3.12 (s, 1 H) ppm. IR (Nujol): $\tilde{\nu}$ = 238 (sh), 216 (s), ν(Ge–Br) cm^{-1}.

[$GeBr_4(py)_2$]: Was made similarly to the chloride analogue above, as a pale yellow powder. $C_{10}H_{10}Br_4GeN_2$ (540.4): calcd. C 21.8, H 1.8, N 5.1; found C 22.0, H 2.6, N 5.2. ^1H NMR ($CDCl_3$, 295 K): δ = 8.71 (d, 2 H), 8.33 (m, 1 H), 7.83 (m, 2 H) ppm. IR (Nujol): $\tilde{\nu}$ = 237 (vbr) ν(Ge–Br) cm^{-1}.

[$(GeF_4)_3$(2,2′,6′,2′′-terpy)$_2$]: Was made analogously to the 2,2′-bipyridyl complex, using $MeCN/CH_2Cl_2$ solvent mixture. $C_{30}H_{22}F_{12}Ge_3N_6{\cdot}0.5CH_2Cl_2$ (954.7): calcd. C 38.4, H 2.4, N 8.8; found C 38.2, H 2.3, N 9.1. IR (Nujol): $\tilde{\nu}$ = 645 (br., s), 580 (s) ν(Ge–F) cm^{-1}.

[$(GeF_4)_2(Me_4$-cyclam)]: Me_4-cyclam (0.025 g, 0.10 mmol) was added to a solution of [$GeF_4(MeCN)_2$] (0.046 g, 0.20 mmol) in CH_2Cl_2 (20 mL) at room temperature with stirring, which led to slow precipitation of a white solid. After stirring for 15 min the white precipitate was separated by filtration and dried in vacuo. $C_{14}H_{32}F_8Ge_2N_4{\cdot}0.5CH_2Cl_2$ (596.1): calcd. C 29.2, H 5.5, N 9.4; found C 28.4, H 5.3, N 9.2. IR (Nujol): $\tilde{\nu}$ = 615 (vbr, s), 590 (sh) ν(Ge–F) cm^{-1}. A small number of colourless crystals of [$GeF_4(Me_4$-cyclam)] were obtained by slow evaporation of the solvent from the filtrate.

[$(GeF_4)_2$(cyclam)]: Cyclam (0.020 g, 0.10 mmol) was added to a solution of [$GeF_4(MeCN)_2$] (0.046 g, 0.20 mmol) in CH_2Cl_2 (20 mL) at room temperature with stirring which lead to immediate precipitation of a white solid. After stirring for 15 min the white precipitate was separated by filtration and dried in vacuo. $C_{10}H_{24}F_8Ge_2N_4$ (497.5): calcd. C 24.1, H 4.8, N 11.3; found C 25.5, H 4.7, N 11.7. IR (Nujol): $\tilde{\nu}$ = 3100 (br) ν(N–H), 1650 (br) δ(N–H), 624 (br., s), 572 (br., s) ν(Ge–F) cm^{-1}.

[$GeF_3\{Me_3[9]aneN_3\}]_2[GeF_6]$: $Me_3[9]aneN_3$ (0.018 g, 0.10 mmol) was added to a solution of [$GeF_4(CH_3CN)_2$] (0.035 g, 0.15 mmol) in CH_2Cl_2 (20 mL) at room temperature with stirring which lead to the precipitation of a white solid. After stirring for 30 min the white precipitate was separated by filtration and washed with diethyl ether. A few crystals of [$GeF_3(Me_3[9]aneN_3)$]Cl were obtained by extracting the crude solid in CH_3CN with heating followed by filtration and slow evaporation of the filtrate at room temperature. $C_{18}H_{42}F_{12}Ge_3N_6{\cdot}CH_2Cl_2$ (873.3): calcd. C 26.1, H 5.1, N 9.6; found C 26.6, H 5.1, N 10.1. IR (Nujol): $\tilde{\nu}$ = 629 (s), 602 (s) ν(Ge–F), 340 δ(Ge–F) cm^{-1}.

X-ray Crystallography: Details of the crystallographic data collection and refinement parameters are given in Table 10. Crystals were mostly obtained directly from the preparations as described. Data collections used a Bruker-Nonius Kappa CCD diffractometer fitted with Mo-K_α radiation (λ = 0.71073 Å) and with the crystals held at 120 K in a nitrogen gas stream. Structure solution and refinement were straightforward[24–27] with H atoms introduced into the models in calculated positions using the default C–H distance.

CCDC-652869 [for F/N(phen)], -652870 [for F/N(diamine)], -652871 [for F/N(py)], -652872 (for Cl/N), -652873 [for Br/N(phen)], -652874 [for Br/N(bipy)], -652875 [for Br/N(diamine)], -652876 [for F/N(cyclam)], -652877 (*I*), and -652878 (F_3N_3) contain the supplementary crystallographic data for this paper (the atoms in parentheses indicate the species bonded to Ge in the compound). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 10. Crystal data and structure refinement details.[a]

Compound	$[GeF_4(1,10\text{-phen})]\cdot 0.5MeCN$	$[GeF_4\{Me_2N(CH_2)_2NMe_2\}]$	$[GeF_4(py)_2]$	$[GeCl_4(1,10\text{-phen})]\cdot 0.5MeCN$	$[GeBr_4(1,10\text{-phen})]\cdot 0.4CH_2Cl_2$
Formula	$C_{13}H_{9.5}F_4GeN_{2.5}$	$C_6H_{16}F_4GeN_2$	$C_{10}H_{10}F_4GeN_2$	$C_{13}H_{9.5}Cl_4GeN_{2.5}$	$C_{12.4}H_{8.8}Br_4Cl_{0.8}GeN_2$
M	349.32	264.80	306.79	415.12	606.40
Crystal system	tetragonal	monoclinic	triclinic	triclinic	orthorhombic
Space group	$I4_1/a$ (no. 88)	$P2_1$ (no. 4)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$Pbca$ (no. 61)
a (Å)	9.2446(15)	6.359(2)	6.386(3)	7.5868(10)	14.211(4)
b (Å)	9.2446(15)	10.731(4)	7.073(3)	12.4792(15)	12.454(3)
c (Å)	29.725(4)	7.693(3)	7.154(3)	16.622(3)	18.278(6)
α (°)	90	90	116.13(3)	89.688(6)	90
β (°)	90	112.99(2)	93.67(3)	88.027(10)	90
γ (°)	90	90	109.73(3)	78.982(10)	90
V (Å^3)	2540.4(7)	483.3(3)	264.3(2)	1543.8(4)	3234.9(16)
Z	8	2	1	4	8
μ(Mo-K_α) [mm^{-1}]	2.453	3.188	2.931	2.668	11.898
F(000)	1384	268	152	820	2262
Total no. of observations	9921	3942	4537	21764	28439
R_{int}	0.065	0.040	0.056	0.032	0.173
Unique observations	1445	2060	1195	7032	3181
Parameters, restraints	93, 0	123, 1	79, 0	371, 0	188, 3
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.045, 0.097	0.036, 0.070	0.045, 0.103	0.028, 0.061	0.054, 0.104
R_1, wR_2 [all data]	0.060, 0.107	0.045, 0.073	0.049, 0.105	0.033, 0.064	0.110, 0.124

Compound	$[GeBr_4(2,2'\text{-bipy})]$	$[GeBr_4\{Me_2N(CH_2)_2NMe_2\}]$	$[GeF_4(Me_4\text{-cyclam})]$	$GeI_4\cdot 3[C_{12}H_9N_2]\cdot 3I$	$[GeF_3(Me_3[9]aneN_3)]Cl$
Formula	$C_{10}H_8Br_4GeN_2$	$C_6H_{16}Br_4GeN_2$	$C_{14}H_{32}F_4GeN_4$	$C_{36}H_{27}GeI_7N_6$	$C_9H_{21}ClF_3GeN_3$
M	548.41	508.44	405.03	1504.53	336.33
Crystal system	monoclinic	orthorhombic	orthorhombic	triclinic	trigonal
Space group	Pn (no. 7)	$Pna2_1$ (no. 33)	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)	$R3c$ (no. 161)
a (Å)	8.2473(10)	14.877(4)	9.650(3)	10.6183(15)	8.8068(12)
b (Å)	6.9155(10)	7.4172(15)	12.621(4)	10.6674(10)	8.8068(12)
c (Å)	12.566(2)	11.947(4)	15.120(4)	18.606(2)	29.556(6)
α (°)	90	90	90	85.261(10)	90
β (°)	102.346(10)	90	90	85.491(5)	90
γ (°)	90	90	90	86.619(10)	120
V (Å^3)	700.11(17)	1318.3(6)	1841.6(9)	2090.9(4)	1985.2(6)
Z	2	4	4	2	6
μ(Mo-K_α) [mm^{-1}]	13.58	14.41	1.704	5.934	2.535
F(000)	508	952	848	1376	1032
Total no. of observations	9565	9995	19108	42764	3306
R_{int}	0.054	0.070	0.162	0.045	0.032
Unique observations	3124	3002	3228	9567	914
Parameters, restraints	154, 2	123, 1	208, 0	451, 0	52, 1
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.026, 0.053	0.040, 0.056	0.080, 0.141	0.032, 0.067	0.026, 0.057
R_1, wR_2 [all data]	0.027, 0.054	0.071, 0.062	0.133, 0.165	0.044, 0.072	0.031, 0.062

[a] Common items: temperature = 120 K; wavelength (Mo-K_α) = 0.71073 Å; θ(max) = 27.5°. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma\, wF_o^4]^{1/2}$.

Acknowledgments

We thank Research Councils U.K. (EP/C006763/1) and the Engineering and Physical Sciences Research Council (GR/T09613/01) for support. A. L. H. thanks the Royal Society for a University Research Fellowship.

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Received: July 10, 2007