The first examples of germanium tetrafluoride and tin tetrafluoride complexes with soft thioether coordination—synthesis, properties and crystal structures†

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The first thioether complexes of the hard Lewis acidic GeF_4 and SnF_4 have been prepared by reaction of $[GeF_4(MeCN)_2]$ or $[SnF_4(MeCN)_2]$ respectively with the thioether ligand in rigorously anhydrous CH_2Cl_2 solution. The isolated compounds were characterised spectroscopically (IR, ^{1}H and ^{19}F{^{1}H} NMR) and by microanalyses. Crystal structures of four representative examples, $[GeF_4\{MeS(CH_2)_2SMe\}]$, $[GeF_4\{EtS(CH_2)_2SEt\}]$, $[SnF_4\{EtS(CH_2)_2SEt\}]$ and $[SnF_4\{^iPrS(CH_2)_2S^iPr\}]$, reveal distorted octahedral adducts with chelating thioethers, and weak, secondary Ge–S and Sn–S bonds. These compounds are the first reported examples of thioether complexes with any main group metal/metalloid fluoride acceptor.

Introduction

Within the main group the Lewis acidic tin(IV) chloride and bromide probably have the most extensive coordination chemistry, forming complexes with a range of different ligand types, including both hard and soft donor groups from Groups 15 and 16.[1,2] Recently we have extended this to report systematic series of donor–acceptor adducts of the much less studied SnF_4 with phosphine oxides, ethers, and the first examples with phosphine ligands.[3,4] In contrast, the coordination chemistry of germanium is sparse, despite its importance for many technological applications *e.g.* as an elemental semiconductor and in optics and ceramics.[5] This is generally attributed to the much lower Lewis acidity of the Ge(IV) halides *vs.* Sn(IV) halides. However, previous work has established that towards hard O- or N-donor ligands such as phosphine oxides, amines and diimines, the small, hard GeF_4 has a greater affinity compared to the other GeX_4 (X = Cl, Br or I) units.[6–8] Nevertheless, there are no reported examples of any Ge(IV) adducts with soft, neutral Group 16 ligands and in earlier work focusing on complexes of SnX_4 (X = Cl, Br, I) with neutral Group 16 donor ligands, we noted that neither $GeCl_4$ or $SiCl_4$ showed any interaction with Me_2S or $MeS(CH_2)_2SMe$ in CH_2Cl_2 solution by VT NMR spectroscopy.[9] $GeCl_4$ is reported to be reduced to Ge(II) by tertiary phosphines giving $[R_3PCl][GeCl_3]$.[10] Furthermore, there are no documented examples of main group metal/metalloid fluoride adducts with thioether co-ligands.

We report here the synthesis, spectroscopic characterisation and crystal structures of the first examples of Ge(IV) and Sn(IV) fluoride complexes with soft thioether coordination.

Results and discussion

Since GeF_4 is a gas (sub. 236 K) it is inconvenient as a precursor, hence we have used the soluble, molecular $[GeF_4(MeCN)_2]$.[6,11] Reaction of this with one mol. equiv. of L–L (L–L = $MeS(CH_2)_2SMe$

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or $EtS(CH_2)_2SEt$) in anhydrous CH_2Cl_2 solution, followed by slow evaporation of the solvent from a solution at ambient pressure gave the adducts as colourless crystals. The products are *extremely* moisture sensitive and hence all measurements used freshly prepared crystalline samples handled in a dry-box under N_2.

The IR and Raman spectra of the isolated solids show evidence for coordinated dithioether and broad features around 600–650 cm^{-1} due to the *cis*-GeF_4 unit of the octahedron.

Variable temperature ^{1}H NMR spectra of these compounds in rigorously dry CD_2Cl_2 showed extensive ligand dissociation at 25 °C, although cooling led initially to broadening of the resonances and then (*ca.* −50 °C) to individual resonances corresponding to the 'free' and coordinated dithioether (even at −90 °C we only observe one form of coordinated ligand—either the compounds are still undergoing rapid pyramidal inversion, hence individual resonances for the *meso* and DL diastereoisomers are not apparent, or only one form is present in observable amounts). At 25 °C the ^{19}F{^{1}H} NMR resonances are not observed but on cooling the solutions, ill-defined, broad resonances appear, which sharpen and split on cooling further, and at −50 °C give two well-defined triplets, L–L = $MeS(CH_2)_2SMe$, $\delta(^{19}F) = −123.0, −87.0$ ($^2J_{FF} = 77$ Hz); L–L = $EtS(CH_2)_2SEt$ $\delta(^{19}F) −117.9, −85.6$ (74 Hz), as expected for *cis*-$[GeF_4(L–L)]$. The ^{19}F NMR shifts are to high frequency of those for GeF_4 complexes with O- or N-donor ligands such as phosphine oxides, ethers or amines,[6,7] reflecting the more deshielded nature of the GeF_4 unit coordinated to the weaker σ-donor thioether. We also note that the F–F coupling constants in the GeF_4 thioether complexes are larger than those in the phosphine oxide, diamine or diimine complexes (*ca.* 55–65 Hz).

The identities of the products as $[GeF_4\{RS(CH_2)_2SR\}]$ (R = Me or Et) have been authenticated by crystal structure determinations (Fig. 1 and 2, Tables 1 and 2) each of which reveals a distorted octahedral environment at Ge through coordination to four F ligands and two S atoms from a chelating dithioether. Both complexes adopt the DL configuration with one R group above and one below the GeF_2S_2 coordination plane. The Ge–S bond distances lie in the region 2.4334(7)–2.4903(8) Å, the rather long distances indicating weak association of the thioether donor

Table 1 Selected bond lengths (Å) and angles (°) for [GeF$_4${MeS-(CH$_2$)$_2$SMe}]

Ge1–F3	1.7487(14)	Ge1–F2	1.7592(15)
Ge1–F4	1.7734(14)	Ge1–F1	1.7764(14)
Ge1–S1	2.4334(7)	Ge1–S2	2.4728(7)
F3–Ge1–F2	95.87(7)	F3–Ge1–F4	92.89(7)
F2–Ge1–F4	93.65(7)	F3–Ge1–F1	92.07(7)
F2–Ge1–F1	93.70(7)	F4–Ge1–F1	170.67(6)
F3–Ge1–S1	175.15(5)	F2–Ge1–S1	87.93(5)
F4–Ge1–S1	89.87(5)	F1–Ge1–S1	84.66(5)
F3–Ge1–S2	89.12(5)	F2–Ge1–S2	174.15(5)
F4–Ge1–S2	83.01(5)	F1–Ge1–S2	89.17(5)
S1–Ge1–S2	87.26(2)		

Table 2 Selected bond lengths (Å) and angles (°) for [GeF$_4${EtS-(CH$_2$)$_2$SEt}]

Ge1–F2	1.7507(16)	Ge1–F3	1.7561(16)
Ge1–F1	1.7714(15)	Ge1–F4	1.7761(15)
Ge1–S1	2.4611(8)	Ge1–S2	2.4903(8)
F2–Ge1–F3	97.76(8)	F2–Ge1–F1	94.23(7)
F3–Ge1–F1	93.40(8)	F2–Ge1–F4	92.52(7)
F3–Ge1–F4	92.40(8)	F1–Ge1–F4	170.42(7)
F2–Ge1–S1	87.88(6)	F3–Ge1–S1	173.77(6)
F1–Ge1–S1	83.49(6)	F4–Ge1–S1	89.98(6)
F2–Ge1–S2	173.37(6)	F3–Ge1–S2	87.98(6)
F1–Ge1–S2	88.71(5)	F4–Ge1–S2	83.88(5)
S1–Ge1–S2	86.55(3)		
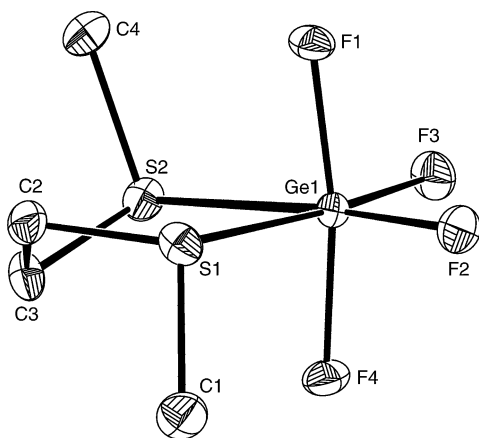
Fig. 1 View of the structure of [GeF$_4${MeS(CH$_2$)$_2$SMe}] with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Fig. 2 View of the structure of [GeF$_4${EtS(CH$_2$)$_2$SEt}] with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

atoms. The S–Ge–S chelate angles are 87.26(2) and 86.55(3)° respectively. There is a disparity between the Ge–F$_{transF}$ and Ge–F$_{transS}$ bond distances, with the former *ca.* 0.02 Å longer, consistent with the order of *trans* influence of F > S in these species. Comparison of the Ge–F bond lengths with those in O- or N-donor ligand complexes shows little difference, confirming the Ge–F as the dominant interactions with much weaker secondary bonding to the sulfur.

No solid was isolated from treatment of [GeF$_4$(MeCN)$_2$] with two mol. equivs. of Me$_2$S in CH$_2$Cl$_2$ solution, and attempts to remove the solvent *in vacuo* led to evaporation of all of the constituents, suggesting that any adduct(s) are only very

weakly associated. A broad singlet at $\delta = -119.5$ ppm was observed at 25 °C in the ^{19}F{^{1}H} NMR spectrum of a mixture of [GeF$_4$(MeCN)$_2$] and excess Me$_2$S. This disappeared at -50 °C, and cooling further to -90 °C revealed two triplets (δ -96.4 and -140.8 ppm, $^2J_{FF}$ = 80 Hz) and a weak singlet (δ -102.6 ppm), consistent with the presence of both the *cis* (major) and *trans* (minor) forms of [GeF$_4$(Me$_2$S)$_2$] in solution at low temperature. For comparison a solution of [GeF$_4$(MeCN)$_2$] in CH$_2$Cl$_2$ at -90 °C has two triplets at δ -101.2 and -134.2 ($^2J_{FF}$ = 55 Hz) and weak singlet at δ -108.2 due to *cis* and *trans* forms of the nitrile complex.[6]

An anhydrous CD$_2$Cl$_2$ solution of [GeF$_4$(MeCN)$_2$] containing one mol. equiv. of [9]aneS$_3$ showed no resonances in the ^{19}F{^{1}H} NMR spectrum at ambient temperatures, but on cooling below -30 °C two triplets of equal intensity appeared at δ -118.9 and -134.2 (J_{FF} = 70 Hz) which we tentatively attribute to the formation of [GeF$_4$(κ^2-[9]aneS$_3$)]; however on evaporation of the solvent the ligand crystallised out. This behaviour contrasts with the hard N-donor analogue Me$_3$[9]aneN$_3$ which forms the crystallographically authenticated *fac*-[GeF$_3$(κ^3-Me$_3$[9]aneN$_3$)]$^+$.[7] The soft donor [9]aneS$_3$ appears unable to displace a fluoride ligand from the germanium and hence binds only weakly in the κ^2-coordination mode.

Building upon the successful formation of the Ge(IV) thioether complexes we investigated similar reactions of [SnF$_4$(MeCN)$_2$][12] with the dithioethers RS(CH$_2$)$_2$SR (R = Me, Et and ^{i}Pr) in anhydrous CH$_2$Cl$_2$. For R = Et and ^{i}Pr this led to precipitation of some white solid which did not contain significant amounts of dithioether, and appears to be largely [SnF$_4$]$_n$ polymer from its IR spectrum (in contrast to the other tin(IV) halides which are tetrahedral molecules, in the solid state the structure of SnF$_4$ is based upon vertex sharing octahedra).[13] However, careful concentration of the mother liquor and cooling to *ca.* -18 °C led to formation of colourless crystals of [SnF$_4${RS(CH$_2$)$_2$SR}]. Using MeS(CH$_2$)$_2$SMe and [SnF$_4$(MeCN)$_2$] gives [SnF$_4${MeS(CH$_2$)$_2$SMe}] as a white powder, which is less soluble in chlorocarbons. The NMR evidence described below shows that the [SnF$_4${RS(CH$_2$)$_2$SR}] are extensively dissociated in solution at room temperature, and it seems that some of the "SnF$_4$" formed in this dissociation, then

oligomerises to $[SnF_4]_n$. IR spectroscopy shows features in the range 560–600 cm^{-1} due to the *cis*-SnF_4 fragment as expected for these complexes,[4] and together with microanalyses confirm the formulations $[SnF_4\{RS(CH_2)_2SR\}]$. The solubility of the complexes (R = Me or Et) in anhydrous chlorocarbons is modest, hence the VT NMR studies were focused upon the much more soluble ^iPr complex. The ^1H NMR spectrum of this complex in CD_2Cl_2 at 25 °C is simple showing single resonances for CH_2, CH and Me protons only slightly shifted to high frequency from those in the ligand, and consistent with fast exchange/dissociation. On cooling the exchange between free and coordinated ligand slows and at −50 °C in addition to resonances of the "free" ligand, two doublet δ(Me) resonances ($^3J_{HH}$ *ca.* 8 Hz) of approximately equal intensities and associated overlapping CH_2 and CH multiplets are seen due to DL and *meso* forms of the coordinated dithioether (see Experimental). No $^{19}F\{^1H\}$ NMR spectrum of this complex in CD_2Cl_2 was observed at ambient temperatures, but on cooling two broad resonances appear and at −50 °C these have resolved into two triplets $^2J_{FF}$ = 52 Hz with associated ^{119}Sn and ^{117}Sn satellites. The $^{119/117}Sn$–^{19}F coupling constants are rather larger for the Sn–F$_{transF}$ than Sn–F$_{transS}$, are similar in magnitude to those observed in tin(IV) fluoride complexes with diphosphine ligands,[4] and larger than those in complexes of diamines, ethers or phosphine oxides.[3,4] Attempts to observe a ^{119}Sn NMR spectrum of this complex even at low temperatures were unsuccessful; it may be that the complex is still undergoing some dynamic processes on the tin NMR timescale, but it seems more likely the failure is due a combination of the modest sensitivity of the ^{119}Sn nucleus (D_c = 25), the multiplet splitting expected (t,t) and the rather poor solubility of the complex at low temperatures. The ^1H and $^{19}F\{^1H\}$ NMR spectra of $[SnF_4\{RS(CH_2)_2SR\}]$ (R = Me or Et) were analogous to those of $[SnF_4\{^iPrS(CH_2)_2S^iPr\}]$, but the poor solubility hindered low temperature studies, and the invertomers were not identified.

Confirmation of the formulations follows from X-ray crystal structure determinations for $[SnF_4\{RS(CH_2)_2SR\}]$ (R = Et and ^iPr). The $[SnF_4\{EtS(CH_2)_2SEt\}]$ is isomorphous with its Ge analogue (*vide supra*) and shows (Fig. 3, Table 3) a distorted octahedral coordination environment at Sn, giving the DL isomer, with similar trends in bond distances and angles, and d(Sn–S) *ca.*

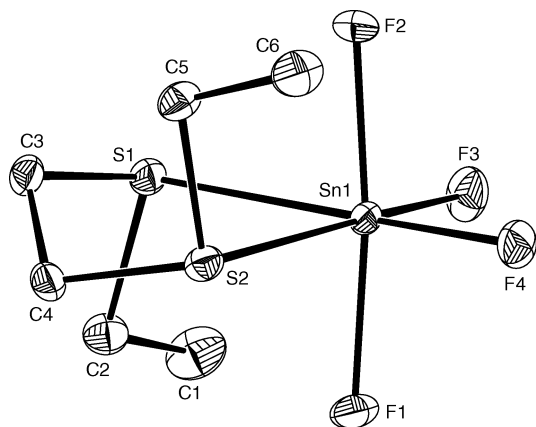**Table 3** Selected bond lengths (Å) and angles (°) for $[SnF_4\{EtS-(CH_2)_2SEt\}]$

Sn1–F1	1.9540(12)	Sn1–F2	1.9490(12)
Sn1–F3	1.9298(13)	Sn1–F4	1.9352(12)
Sn1–S1	2.5849(6)	Sn1–S2	2.6028(6)
F3–Sn1–F4	97.48(6)	F3–Sn1–F2	93.83(5)
F4–Sn1–F2	93.00(5)	F3–Sn1–F1	90.46(5)
F4–Sn1–F1	91.12(5)	F2–Sn1–F1	173.62(5)
F3–Sn1–S1	88.82(4)	F4–Sn1–S1	173.31(4)
F2–Sn1–S1	84.33(4)	F1–Sn1–S1	91.04(4)
F3–Sn1–S2	172.42(4)	F4–Sn1–S2	89.12(4)
F2–Sn1–S2	89.51(4)	F1–Sn1–S2	85.69(4)
S1–Sn1–S2	84.73(2)		

0.15 Å longer than d(Ge–S), consistent with the increased radius of Sn(IV) over Ge(IV), and the S–Sn–S chelate angle is 84.73(2)°. The structure of $[SnF_4\{^iPrS(CH_2)_2S^iPr\}]$ (Fig. 4, Table 4) is similar, with d(Sn–S) = 2.5844(7) Å.

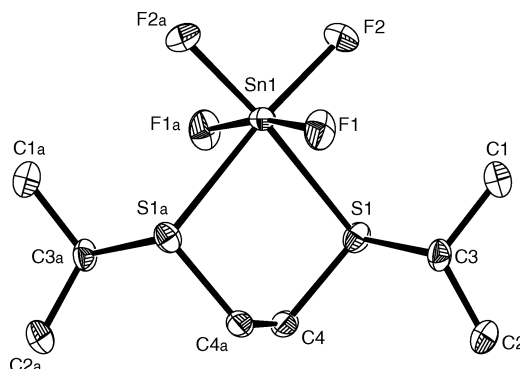**Fig. 4** View of the structure of $[SnF_4\{^iPrS(CH_2)_2S^iPr\}]$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: a = −x, y, 3/2 − z.

Attempts to prepare a complex of [9]aneS$_3$ with tin(IV) fluoride were unsuccessful. A solution of $[SnF_4(MeCN)_2]$ in CH_2Cl_2 treated with [9]aneS$_3$, initially precipitated "$[SnF_4]_n$", and on concentration of the mother liquor, [9]aneS$_3$ crystallised out. No convincing $^{19}F\{^1H\}$ resonances were seen from the mother liquor even at low temperatures. This behaviour contrasts with that of SnCl$_4$ which forms the structurally characterised $[SnCl_3\{[9]aneS_3\}]_2SnCl_6$.[14]

The addition of excess Me_2S to a solution of $[SnF_4(MeCN)_2]$ in CH_2Cl_2 gave a clear solution which did not exhibit a $^{19}F\{^1H\}$ NMR spectrum at room temperature, but at 0 °C three broad singlets

Table 4 Selected bond lengths (Å) and angles (°) for $[SnF_4\{^iPrS-(CH_2)_2S^iPr\}]^a$

Sn1–F2	1.9341(13)	Sn1–F1	1.9464(13)
Sn1–S1	2.5844(7)		
F2–Sn1–F2a	96.04(9)	F2–Sn1–F1a	93.12(6)
F2–Sn1–F1	93.82(6)	F2–Sn1–S1a	174.71(4)
F1–Sn1–F1a	169.63(8)	F2–Sn1–S1	88.83(5)
F1–Sn1–S1	88.58(4)	F2–Sn1–S1a	83.86(4)
S1–Sn1–S1a	86.37(3)		

^{a} Symmetry operation: a = −x, y, 3/2 − z.

Fig. 3 View of the structure of $[SnF_4\{EtS(CH_2)_2SEt\}]$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

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appeared, and on further cooling to −60 °C these resolved into two triplets and a singlet each with $^{119/117}$Sn satellites [$\delta = -138.5$ (t, $^2J_{FF} = 55$ Hz, ^{119}Sn–^{19}F = 2703, ^{117}Sn–^{19}F = 2583 Hz); $\delta = -174.3$ (t, ^{119}Sn–^{19}F = 2263, ^{117}Sn–^{19}F = 2162 Hz); $\delta = -145.8$ (s, ^{119}Sn–^{19}F = 2547, ^{117}Sn–^{19}F = 2437 Hz)] consistent with [SnF$_4$(Me$_2$S)$_2$], with an approximate *cis : trans* ratio of 6 : 1. Evaporation of this solution under reduced pressure resulted in precipitation of a white, largely ligand-free, solid, and the complex has not been isolated. This contrasts with [SnX$_4$(Me$_2$S)$_2$] (X = Cl or Br) which are readily isolated and are fully characterised both structurally and spectroscopically.[15,16]

The germanium fluoride complexes described here are the only thioether examples, so no further comparisons are possible, but a range of thioether adducts of SnCl$_4$ and SnBr$_4$ are known[15,16] (the only isolated SnI$_4$ example is the purple insoluble [SnI$_4${[9]aneS$_3$}], although [SnI$_4${MeS(CH$_2$)$_n$SMe}] have been detected in solution at low temperatures by ^{119}Sn NMR spectroscopy).[16,17] Comparison of X-ray structural data on [SnX$_4${RS(CH$_2$)$_n$SR}] (X = F, Cl or Br; n = 2 or 3) shows a small increase in d(Sn–S) as the halogen changes F (2.584(1)–2.603(1) Å) → Cl (2.619(2)–2.677(2) Å) → Br (2.700(7) Å), the same trend seen in complexes with hard N- or O-donor ligands and softer phosphines,[3,4] consistent with the fluoride being the strongest Lewis acid towards the dithioethers. Comparing the solution NMR data is less secure mainly due to the tendency of the fluoride adducts to deposit SnF$_4$ polymer. It is clear that the [SnX$_4${RS(CH$_2$)$_n$SR}] (X = Cl or Br) are also undergoing rapid exchange in solution at ambient temperatures and on cooling the resonances sharpen and split as exchange slows and invertomers are seen.[16] However, in these cases dissociation produces the tetrahedral molecular SnX$_4$ which remains in solution. The VT NMR results suggest that the binding of the dithioethers in solution is SnF$_4$ ∼ SnCl$_4$ > SnBr$_4$ >> SnI$_4$.

Conclusions

The compounds described here represent the first authenticated examples of main group metal/metalloid fluoride complexes containing soft thioether ligands and also the first thioether adducts of Ge. The results demonstrate that the molecular [GeF$_4$(MeCN)$_2$] is a useful synthon to allow entry into these extremely unusual soft/hard donor/acceptor adducts. The absence of any evidence for adduct formation using GeCl$_4$ with similar thioether ligands[9] shows that GeF$_4$ is a significantly better Lewis acid even towards soft donor ligands, and will provide a starting point for development of a substantial new coordination chemistry for germanium(IV).

Experimental

GeF$_4$ was obtained from Aldrich and converted into [GeF$_4$(MeCN)$_2$],[6,11] and [SnF$_4$(MeCN)$_2$] made as described.[12] MeCN and CH$_2$Cl$_2$ were dried by distillation from CaH$_2$. Me$_2$S (Aldrich) was dried over 4A molecular sieves. The dithioethers were made as described[18] and stored over molecular sieves. All reactions were conducted using Schlenk, vacuum line and glove-box techniques and under a dry dinitrogen atmosphere.

Infra-red spectra were recorded as Nujol mulls on a Perkin Elmer PE 983G spectrometer. Raman spectra used a Perkin Elmer FT-Raman 2000R with a Nd:YAG laser. ^{1}H and ^{19}F{^{1}H}

NMR spectra were recorded from CD$_2$Cl$_2$ solutions on a Bruker DPX400, and referenced to residual H resonances of the solvent or CFCl$_3$ respectively. Microanalytical measurements were performed by the microanalytical service at Strathclyde University.

Preparations

[GeF$_4${EtS(CH$_2$)$_2$SEt}]

The ligand EtS(CH$_2$)$_2$SEt (0.018 g, 0.12 mmol) was added to a solution of [GeF$_4$(CH$_3$CN)$_2$] (0.023 g, 0.10 mmol) in CH$_2$Cl$_2$ (15 mL) at room temperature. After stirring for 10 min, the solution was concentrated slowly by evaporation which gave colourless crystalline solid which was isolated by filtration. Yield: >60%. C$_6$H$_{14}$F$_4$GeS$_2$·CH$_2$Cl$_2$ (383.84): calcd. C 21.9, H 4.2; found C 22.4, H 4.5. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 2.98$ (s, 4H, CH$_2$), 2.77 (q, 4H, CH$_2$), 1.35 (t, 6H, Me); (−70 °C): $\delta = 3.36$ (br m, CH$_2$, coordinated L–L), 2.94 (q, CH$_2$, coordinated L–L), 2.64 (s, CH$_2$, uncoordinated L–L), 2.52 (q, CH$_2$, uncoordinated L–L), 1.34 (t, Me, coordinated L–L), 1.16 (t, Me, uncoordinated L–L). ^{19}F{^{1}H} NMR (CD$_2$Cl$_2$, −50 °C): $\delta = -117.9$ (t), −85.6 (t, $^2J_{FF} = 74$ Hz). IR (Nujol): 649, 635, 620, 605 sh ν(GeF) cm^{-1}. Raman: 652, 633, 620, 598 ν(GeF) cm^{-1}.

[GeF$_4${MeS(CH$_2$)$_2$SMe}]

[GeF$_4${MeS(CH$_2$)$_2$SMe}] was made analogously to the EtS(CH$_2$)$_2$SEt complex above, but using more CH$_2$Cl$_2$ due to the lower solubility of the target complex. 2,5-Dithiahexane (0.015 g, 0.12 mmol) was added to a solution of [GeF$_4$(CH$_3$CN)$_2$] (0.023 g, 0.10 mmol) in CH$_2$Cl$_2$ (40 mL) at room temperature. After stirring for 10 min, the solution was concentrated slowly by evaporation to give a colourless crystalline solid which was collected by filtration. Yield >60%. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 2.72$ (s, 4H, CH$_2$), 2.15 (s, 6H, Me). ^{19}F{^{1}H} NMR (CD$_2$Cl$_2$, −50 °C): $\delta = -123.0$ (t), −87.0 (t, $^2J_{FF} = 77$ Hz). IR (Nujol): 645 sh, 629, 614, 590 sh ν(GeF) cm^{-1}. Raman: 651, 642, 615, 589 ν(GeF) cm^{-1}.

[SnF$_4${MeS(CH$_2$)$_2$SMe}]

MeS(CH$_2$)$_2$SMe (0.12 g, 1.00 mmol) was added dropwise to a solution of [SnF$_4$(MeCN)$_2$] (0.278 g, 1.00 mmol) in CH$_2$Cl$_2$ (10 mL) and stirred for 0.5 h. Some white precipitate formed; the solution was decanted off, and was left in the freezer for one week, when it deposited a white powder, which was collected by filtration and dried *in vacuo*. Yield 0.22 g, 69%. C$_4$H$_{10}$F$_4$S$_2$Sn (316.94): calcd. C 15.2, H 3.2; found C 14.9, H 2.4. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 2.69$ (s, 4H, CH$_2$), 2.11 (s, 6H, Me). ^{19}F{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$, −70 °C): $\delta = -133.1$ (t, $^1J(^{119}$SnF) = 2662, $^1J(^{117}$SnF) = 2452 Hz), −159.5 (t, $^1J(^{119}$SnF) = 2221, $^1J(^{117}$SnF) ∼2070 or not resolved, $^2J_{FF} = 53$ Hz). IR (Nujol): 556 sh, 567 s, br, 588 sh ν(SnF) cm^{-1}.

[SnF$_4${EtS(CH$_2$)$_2$SEt}]

[SnF$_4$(MeCN)$_2$] (0.278 g, 1.00 mmol) was added to a solution of EtS(CH$_2$)$_2$SEt (0.34 g, 2.30 mmol) in CH$_2$Cl$_2$ (10 mL) and stirred for 1 h. A small amount of white precipitate occurred and the reaction mixture was left in the freezer for 2 weeks where a few colourless crystals grew on the walls of the Schlenk tube which

Table 5 Crystallographic parameters

Complex	[GeF$_4$\{MeS(CH$_2$)$_2$SMe\}]	[GeF$_4$\{EtS(CH$_2$)$_2$SEt\}]	[SnF$_4$\{EtS(CH$_2$)$_2$SEt\}]	[SnF$_4$\{^{i}PrS(CH$_2$)$_2$S^{i}Pr\}]
Formula	C$_4$H$_{10}$F$_4$GeS$_2$	C$_6$H$_{14}$F$_4$GeS$_2$	C$_6$H$_{14}$F$_4$S$_2$Sn	C$_8$H$_{18}$F$_4$S$_2$Sn
M	270.83	298.88	344.98	373.03
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
a/Å	7.1148(10)	10.9011(15)	11.093(2)	10.540(3)
b/Å	11.1822(15)	8.5151(15)	8.4148(15)	7.573(2)
c/Å	10.9875(15)	11.935(3)	12.276(2)	17.642(5)
α/°	90	90	90	90
β/°	98.884(10)	101.202(10)	100.627(7)	97.456(10)
γ/°	90	90	90	90
U/Å^3	863.7(2)	1086.7(3)	1126.2(3)	1396.2(6)
Z	4	4	4	4
μ(Mo-Kα)/mm^{-1}	4.030	3.212	2.649	2.144
Total reflns.	10496	13998	11875	7267
Unique reflns.	1981	2474	2579	1598
R$_{int}$	0.027	0.053	0.024	0.025
No. of params.	100	118	120	69
$R1$ [$I_o > 2\sigma(I_o)$]	0.026	0.031	0.018	0.019
$wR2$ [$I_o > 2\sigma(I_o)$]	0.065	0.077	0.036	0.038
$R1$ [all data]^a	0.031	0.041	0.020	0.022
$wR2$ [all data]^a	0.069	0.082	0.038	0.039

^{a} $R1 = \sum ||F_o| - |F_c||/\sum |F_o|$; $wR2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4]^{1/2}$.

were removed for crystal structure analysis. The solution was then decanted off and the solvent was concentrated *in vacuo* to give a white solid which was collected by filtration and dried *in vacuo*. Yield 0.18 g, 52%. C$_6$H$_{14}$F$_4$S$_2$Sn (344.99): calcd. C 20.9, H 4.1; found C 20.1, H 4.5. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 2.68 (s, 4H, CH$_2$), 2.53 (q, 4H, CH$_2$), 1.21 (t, 6H, Me). ^{19}F\{^{1}H\} NMR (CD$_2$Cl$_2$, −70 °C): δ = −131.6 (t, $^1J(^{119}$SnF) = 2652, $^1J(^{117}$SnF) = 2533 Hz), −154.2 (t, $^1J(^{119}$SnF) = 2239, $^1J(^{117}$SnF) = 2143, $^2J_{FF}$ = 53 Hz). IR (Nujol): 579, 564 br ν(SnF) cm^{-1}.

[SnF$_4$\{^{i}PrS(CH$_2$)$_2$S^{i}Pr\}]

^{i}PrS(CH$_2$)$_2$S^{i}Pr (0.16 g, 0.90 mmol) was added dropwise to a solution of [SnF$_4$(MeCN)$_2$] (0.25 g, 0.90 mmol) in CH$_2$Cl$_2$ (10 mL) and stirred for 0.5 h. A small amount of white precipitate was present; the solution was left in the freezer for 1 week. Some crystals grew on the walls of the Schlenk tube (collected for structure determination). The solution was then decanted off and reduced *in vacuo* to give a white solid. Yield 0.22 g, 64%. C$_8$H$_{18}$F$_4$S$_2$Sn·2CH$_2$Cl$_2$ (542.94): calcd. C 22.1, H 4.1; found C 21.6, H 4.3. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C): δ = 2.93 (*quin*, 2H, CH), 2.69 (s, 4H, CH$_2$), 1.24 (d, 12H, Me); (−70 °C): δ = 3.70–3.52 (m, CH, coordinated L–L), 3.0 (m, CH$_2$, coordinated L–L), 2.99 (m, CH, free L–L), 2.63 (s, CH$_2$, free L–L), 1.49 (d, Me, coordinated L–L), 1.36 (d, Me, coordinated L–L), 1.25 (d, Me, free L–L). ^{19}F\{^{1}H\} NMR (CD$_2$Cl$_2$, −50 °C): δ = −129.1 (t, $^1J(^{119}$SnF) = 2648, $^1J(^{117}$SnF) = 2564 Hz), −150.4 (t, $^1J(^{119}$SnF) = 2246, $^1J(^{117}$SnF) = 2148, $^2J_{FF}$ = 52 Hz). IR (Nujol): 571 s, vbr ν(SnF) cm^{-1}. Raman: 608, 576 cm^{-1}.

X-Ray crystallography

Crystals were obtained as described in the text. Data collection used a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα X-radiation (λ = 0.71073 Å) and with the crystal held at 120 K in a cooled nitrogen gas stream. Structure solution was straightforward[19,20] with H atoms introduced into the model in calculated positions. Selected bond lengths and angles are given in Tables 1–4 with crystallographic data in Table 5.

CCDC reference numbers 652440–652442 and 658599.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713316b

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