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Telluroether adducts of tin(IV) halides: synthesis, spectroscopy and structures

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The extremely moisture-sensitive [$SnX_4(Me_2Te)_2$] and [SnX_4(ditelluroether)] [X = Cl or Br; ditelluroether = $C_6H_4(TeMe)_2$-*o*, $MeTe(CH_2)_3TeMe$ or $PhTe(CH_2)_3TePh$] have been prepared from SnX_4 and the tellurium compound in anhydrous dichloromethane. The crystal structures of [$SnCl_4\{C_6H_4(TeMe)_2$-*o*$\}$] and [$SnBr_4\{C_6H_4(TeMe)_2$-*o*$\}$] have been determined; both show distorted-octahedral tin(IV) with the chelating ditelluroether ligand adopting the *meso* conformation. Variable-temperature ^1H, ^{125}Te-$\{^1H\}$ and ^{119}Sn-$\{^1H\}$ NMR studies showed that the complexes undergo rapid ligand exchange in solution. The structures and properties are compared with those of previously described thio- and seleno-ether analogues. Multinuclear NMR spectroscopic studies of mixtures of $SiCl_4$ or $GeCl_4$ and various Group 16 donor ligands in CH_2Cl_2 solution provided no evidence of adduct formation.

Although there has been much recent interest in the study of polytelluride (Te_n^{2-})[1] and tellurolate (RTe^-)[2] ligands, metal complexes containing telluroether (R_2Te) ligands have been neglected in comparison with thio- and seleno-analogues.[3] Chelating bi- and poly-dentate telluroethers were first reported about 10 years ago,[4,5] and subsequently complexes with various transition metals including Pd^{II}, Pt^{II},[6] Co^{III},[7] Cu^I and Ag^I[8,9] were characterised. In contrast to Group 15 donor ligands, relatively little attention has been devoted to the study of the metal–Group 16 donor element bond (ref. 10 is a significant exception to this statement), and with a view to exploring some of the factors involved we have initiated a study of the complexes of thio-, seleno- and telluro-ethers with main-group acceptors. We have reported elsewhere[11,12] the synthesis, spectroscopic properties and structures of complexes of thio- and seleno-ethers with the hard Lewis acid tin(IV) halides, and we describe here studies of the reactions of SnX_4 (X = Cl, Br or I) with mono- and di-telluroether ligands. No tin telluroethers appear in the literature, although RTe–Sn bonds are established.[13] Attempts to prepare Group 16 donor ligand complexes of $SiCl_4$ and $GeCl_4$ are also described.

Experimental

Physical measurements were made as described previously.[4,11] Variable-temperature ^1H NMR spectra were recorded using a Bruker AM360 spectrometer operating at 360 MHz and are referenced to $SiMe_4$ (δ 0), ^{119}Sn-$\{^1H\}$ NMR spectra in 10 mm NMR tubes containing 10–15% deuteriated solvent using a Bruker AM360 spectrometer operating at 134.2 MHz and referenced to neat external $SnMe_4$ (^{119}Sn, δ 0), ^{125}Te-$\{^1H\}$ (113.6 MHz) referenced to neat external Me_2Te, ^{77}Se-$\{^1H\}$ (68.68 MHz) referenced to neat external Me_2Se, and ^{73}Ge-$\{^1H\}$ (12.6 MHz) referenced to $GeMe_4$. The compound [$Cr(acac)_3$] (acac = acetylacetonate) was added to the NMR solutions as a relaxation agent prior to recording ^{119}Sn-$\{^1H\}$ and ^{73}Ge-$\{^1H\}$ spectra, to avoid signal diminution *via* the nuclear Overhauser effect (NOE) resulting from the negative magnetogyric moments of the nuclei. Tellurium ligands were made by literature methods.[4,5]

Syntheses

The complexes [SnX_4L_2] (X = Cl or Br, L = Me_2Te) and [SnX_4(L–L)] [L–L = $MeTe(CH_2)_3TeMe$, $PhTe(CH_2)_3TePh$ or $C_6H_4(TeMe)_2$-*o*] were all made by the same general method. The complexes are extremely moisture sensitive and the free tellurium compounds slowly air-oxidise, so all reactions were carried out under an atmosphere of dry dinitrogen in rigorously dry solvents, using standard Schlenk, vacuum-line and dry-box techniques. The complexes slowly decompose over a period of weeks even in the dry-box.

[$SnCl_4(Me_2Te)_2$]. Tin(IV) chloride (0.26 g, 1 mmol) was added to a solution of Me_2Te (0.32 g, 2 mmol) in anhydrous dichloromethane (10 cm^3). The complex formed immediately as a yellow precipitate which was filtered off and dried *in vacuo* (Found: C, 8.6; H, 2.3. Calc. for $C_4H_{12}Cl_4SnTe_2$: C, 8.3; H, 2.1%). $\tilde{\nu}/cm^{-1}$ (Sn–Cl) 312. ^1H NMR (CD_2Cl_2): δ 3.0 (s) (300 K); 3.04, 3.06 (180 K).

[$SnBr_4(Me_2Te)_2$]. A saturated solution of tin(IV) bromide (0.44 g, 1 mmol) in dichloromethane (5 cm^3) was added dropwise to a solution of Me_2Te (0.32 g, 2 mmol) in anhydrous dichloromethane (5 cm^3). The complex formed as a fawn powder which was filtered off and dried *in vacuo* (Found: C, 6.7; H, 1.7. Calc. for $C_4H_{12}Br_4SnTe_2$: C, 6.4; H, 1.6%). $\tilde{\nu}/cm^{-1}$ (Sn–Br) 220. ^1H NMR (300 K, CD_2Cl_2): δ 2.8 (s).

[$SnCl_4\{MeTe(CH_2)_3TeMe\}$]. Tin(IV) chloride (0.26 g, 1 mmol) was added to a solution of $MeTe(CH_2)_3TeMe$ (0.32 g, 1 mmol) in anhydrous dichloromethane (10 cm^3). The complex precipitated as a yellow powder which was filtered off and dried *in vacuo* (Found: C, 9.9; H, 2.0. Calc. for $C_5H_{12}Cl_4SnTe_2$: C, 10.2; H, 2.0%). $\tilde{\nu}/cm^{-1}$ (Sn–Cl) 313, 309 and 305.

[$SnCl_4\{PhTe(CH_2)_3TePh\}$]. Red-brown precipitate (Found: C, 25.7; H, 2.5. Calc. for $C_{15}H_{16}Cl_4SnTe_2$: C, 25.5; H, 2.3%). $\tilde{\nu}/cm^{-1}$ (Sn–Cl) 332, 321 and 314.

[$SnCl_4\{C_6H_4(TeMe)_2$-*o*$\}$]. White crystalline precipitate (Found: C, 15.4; H, 1.7. Calc. for $C_8H_{10}Cl_4SnTe_2$: C, 15.4; H, 1.6%). $\tilde{\nu}/cm^{-1}$ (Sn–Cl) 315, 304 and 284. ^1H NMR (CD_2Cl_2): δ 2.45 (s, 3 H), 7.3, 7.7 (2 H) (300 K); 2.61, 2.71, 7.0–7.7 (180 K).

[$SnBr_4\{MeTe(CH_2)_3TeMe\}$]. A saturated solution of tin(IV) bromide (0.44 g, 1 mmol) in anhydrous dichloromethane (5 cm^3) was added dropwise to a solution of $MeTe(CH_2)_3TeMe$ (0.32 g, 1 mmol) in anhydrous dichloromethane (5 cm^3). A yellow precipitate formed immediately which was filtered off and dried *in vacuo* (Found: C, 8.1; H, 2.2; Br, 42.1. Calc. for $C_5H_{12}Br_4SnTe_2$: C, 7.9; H, 1.6; Br, 41.7%). $\tilde{\nu}/cm^{-1}$ (Sn–Br) 219, 217, 212 and 210.

[$SnBr_4${PhTe(CH_2)$_3$TePh}]. Brown precipitate (Found: C, 19.9; H, 1.9; Br, 37.2. Calc. for $C_{15}H_{16}Br_4SnTe_2$: C, 20.4; H, 1.8; Br, 36.0%). ṽ/cm^{-1} (Sn–Br) 218, 215, 213 and 207.

[$SnBr_4${C_6H_4(TeMe)$_2$-*o*}]. Dark brown crystalline precipitate (Found: C, 12.3; H, 1.5; Br, 40.3. Calc. for $C_8H_{10}Br_4SnTe_2$: C, 12.3; H, 1.3; Br, 39.9%). ṽ/cm^{-1} (Sn–Br) 218, 216, 214 and 207. ^{1}H NMR (CD_2Cl_2): δ 2.4 (13 H), 7.3, 7.7 (2 H) (300 K); 2.6, 7.5, 7.65 (180 K).

X-Ray crystallography

Single crystals of [$SnCl_4${C_6H_4(TeMe)$_2$-*o*}] and [$SnBr_4${C_6H_4(TeMe)$_2$-*o*}] were obtained from a solution of the appropriate complex in CH_2Cl_2. For each compound the selected crystal was coated with mineral oil, mounted on a glass fibre using silicone grease as adhesive, and immediately placed in a stream of cold nitrogen gas and cooled to 150 K to prevent hydrolysis and/or solvent loss. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Cryostreams low-temperature attachment and graphite-monochromated Mo-Kα X-radiation (λ 0.71073 Å). The intensities of three standard reflections were monitored every 150. No significant crystal decay or movement was observed. As there were no identifiable faces for [$SnCl_4${C_6H_4(TeMe)$_2$-*o*}] the raw data were corrected for absorption using ψ scans. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses in each case. Crystallographic data are presented in Table 1.

The structures were solved by direct methods,[14] and then developed by iterative cycles of full-matrix least-squares refinement and Fourier-difference syntheses which located all non-H atoms in the asymmetric unit.[15] For [$SnBr_4${C_6H_4(TeMe)$_2$-*o*}] ψ scans did not provide a satisfactory absorption correction, and hence an empirical absorption correction using DIFABS[16] was applied to the raw data with the model at isotropic convergence. All non-H atoms in the structures were refined anisotropically (with the exception of [$SnBr_4${C_6H_4(TeMe)$_2$-*o*}] for which C(4) was refined isotropically since anisotropic refinement resulted in this atom becoming non-positive definite, probably a result of an imperfect absorption correction), and H-atoms were placed in fixed, calculated positions with *d*(C–H) = 0.96 Å. Selected bond lengths and angles are given in Tables 2 and 3.

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Results and Discussion

The reaction of $SnCl_4$ with Me_2Te in anhydrous CH_2Cl_2 precipitated a yellow solid, identified as [$SnCl_4(Me_2Te)_2$] by analysis. The solid is extremely easily hydrolysed, even the briefest exposure to the laboratory atmosphere causes it to turn orange-red due to liberation of Me_2Te. The far-IR spectrum shows a strong ν(Sn–Cl) vibration at 312 cm^{-1}, consistent with a *trans* geometry {compare *trans*-[$SnCl_4(Me_2Se)_2$] 312 cm^{-1}}.[12] The ^{1}H NMR spectrum in CD_2Cl_2 at 300 K consists of a single line at δ 3.0 which is little changed on cooling the solution to 200 K, but on further cooling broadens, and at 180 K the resonance has split into two (δ 3.04, 3.06 relative intensity 1 : 2, tentatively attributed to *cis* and *trans* isomers). Even at the lowest temperature obtainable in this solvent (*ca.* 175 K) no $^{117/119}$Sn satellites were observed. Addition of Me_2Te to this solution produces only a single resonance over the range 300–180 K consistent with fast exchange between free and co-ordinated telluroether. This behaviour can be compared with that[12] of [$SnCl_4(Me_2Se)_2$] which shows a single resonance at 300 K, but this splits into two below about 250 K and at 180 K two sharp resonances with $^{117/119}$Sn satellites are present assignable to *cis* and *trans* isomers. Attempts to observe ^{119}Sn-{^{1}H} or ^{125}Te-{^{1}H} spectra from CH_2Cl_2 solutions of [$SnCl_4(Me_2Te)_2$] were unsuccessful over the temperature range 300–180 K, and significantly a solution containing an excess (*ca.* two-fold) of Me_2Te did not exhibit a ^{125}Te-{^{1}H} resonance either, confirming fast exchange. In contrast, solutions of [$SnCl_4(Me_2Se)_2$] in CH_2Cl_2 exhibit single ^{77}Se-{^{1}H} and ^{119}Sn-{^{1}H} resonances at 300 K, and on cooling to <250 K separate resonances attributable to *cis* and *trans* isomers were resolved. The reaction of $SnBr_4$ with Me_2Te in CH_2Cl_2 afforded fawn [$SnBr_4(Me_2Te)_2$], which decomposed in a few days even in the solid state, turning black. The ^{1}H NMR spectra of the freshly prepared bromide in CH_2Cl_2 were similar to that of the chloride. Owing to the instability of the Me_2Te complexes, attempts to obtain crystals suitable for an X-ray study failed.

The reaction of SnX_4 (X = Cl or Br) with the ditelluroethers RTe(CH_2)$_3$TeR (R = Me or Ph) or C_6H_4(TeMe)$_2$-*o* in dry dichloromethane resulted in the precipitation of yellow or brown solids [SnX_4(L–L)]. In previous studies of dithioether and diselenoether complexes we isolated [SnX_4(L–L)] [X = Cl or Br, L–L = MeE(CH_2)$_n$EMe (*n* = 2 or 3), or C_6H_4(EMe)-*o*; X = Cl, L–L = PhE(CH_2)$_n$EPh, E = S or Se]. For the ditelluroether studies a more restricted range of ligands was available since RTe(CH_2)$_2$TeR are not known.[4] The [SnX_4(ditelluroether)] are much less soluble in chlorinated solvents than the complexes with selenium or sulfur analogues, and this probably accounts for the successful preparation of [$SnBr_4${PhTe(CH_2)$_3$TePh}], whereas $SnBr_4$ complexes of PhE(CH_2)$_3$EPh (E = S or Se) were not isolated, although they were observed in solution by NMR spectroscopy. The addition of a solution of MeTe(CH_2)$_3$TeMe or C_6H_4(TeMe)$_2$-*o* to SnI_4 in CH_2Cl_2 immediately precipitated dark brown solids, with compositions approximating to [SnI_4(ditelluroether)] (no SnI_4 complexes with dithio- or diseleno-ethers have been obtained).[11,12] However the solids appeared to be inhomogenous from careful examination by optical microscopy and energy dispersive X-ray spectroscopy (EDX), and they proved too unstable to purify. The [SnX_4(ditelluroether)] appear to be stable in the solid state in a dry-box for several weeks, but darken and become sticky on longer storage. The [SnX_4{C_6H_4(TeMe)$_2$-*o*}] dissolve in chlorocarbons, but [SnX_4{RTe(CH_2)$_3$TeR}], especially when R = Me, are almost insoluble in chlorocarbons, continuing a trend of decreasing solubility for [SnX_4{MeE(CH_2)$_3$EMe}] (S > Se) noted previously.[11,12] Solubility is higher in dry acetone or tetrahydrofuran, but it is likely that the O-donor solvent partially displaces the tellurium ligand, since the ^{1}H NMR spectra of such solutions reveal several species to be present.

The far-IR spectra of the complexes show several bands (Experimental section) typical of *cis*-SnX_4 groups, and the expected structures with chelating ditelluroether ligands were confirmed in two cases by single-crystal X-ray studies (below). The very poor solubility of the complexes in chlorinated solvents, especially at low temperatures, restricted NMR spectroscopic studies, and no useful data were obtained from the complexes of the RTe(CH_2)$_3$TeR ligands. For [$SnCl_4${C_6H_4(TeMe)$_2$-*o*}] in CD_2Cl_2 at 300 K the ^{1}H NMR spectrum showed a single δ(Me) at 2.45 which broadened on cooling and at 180 K two resonances δ 2.61 and 2.71 (ratio *ca.* 1 : 3) were present, attributable to *meso* and DL diastereoisomers, showing that reversible ring opening and pyramidal inversion were slow at this temperature. Owing to very poor solubility at 180 K the signal-to-noise ratio was relatively poor and $^{117/119}$Sn satellites not observed. The ^{1}H NMR spectra of [$SnBr_4${C_6H_4(TeMe)$_2$-*o*}] showed only a singlet δ(Me) resonance over the range 300–180 K. The compounds [SnX_4{C_6H_4(TeMe)$_2$-*o*}] exhibited neither ^{125}Te-{^{1}H} nor ^{119}Sn-{^{1}H} NMR resonances even at 180 K. Whilst the poor solubility of the complexes would make observation of these nuclei difficult, separate experiments in which mixtures of [$SnCl_4${C_6H_4(TeMe)$_2$-*o*}] and C_6H_4(TeMe)$_2$-*o* were studied also failed to show any ^{125}Te-{^{1}H} resonance, even for the readily soluble free ditelluroether, demonstrating that fast exchange on the NMR time-scale is making the resonances unobservably broad. Although similar exchange occurs in the SnX_4–dithioether or –diselenoether systems at room temperature,[11,12] the exchange slows on cooling and $^{117/119}$Sn-{^{1}H} or ^{77}Se-{^{1}H} resonances are easily observed at low temperatures. The results from the telluroether complexes are consistent with more extensive dissociation in these latter systems, not unexpected given the combination of hard Lewis acid (SnX_4) and soft donor tellurium centres. Indeed it seems likely that our ability to isolate solid [SnX_4(ditelluroether)] complexes owes more to their insolubility in chlorocarbons than to their inherent stability.

In view of the fact that there are no structurally characterised tin–telluroether species in the literature, and to provide a comparison with the tin thio- and seleno-ether species which we have already reported,[11,12] single-crystal X-ray determinations were undertaken on [$SnX_4\{C_6H_4(TeMe)_2$-*o*}] (X = Cl or Br). In each case the structure shows (Fig. 1 and 2, Tables 2 and 3) a discrete tin(IV) species involving a chelating $C_6H_4(TeMe)_2$-*o* ligand, giving a distorted octahedral molecule: X = Cl, Sn–Te 2.908(1), 2.9222(8), Sn–Cl 2.384(2), 2.390(2), 2.433(2), 2.457(2); X = Br, Sn–Te 2.981(2), Sn–Br 2.526(2), 2.567(2), 2.622(2) Å. In both compounds the ditelluroether ligand adopts a *meso* arrangement, with both methyl substituents directed to the same side of the SnX_2Te_2 plane. The Te–Sn–Te angles involving the chelate ring are 81.67(2) and 74.99(7)° for the chloro and bromo species respectively. Thus, the shorter Sn–Te distances in the chloro species permit a less strained arrangement within the five-membered chelate ring compared to the bromo species, and hence a smaller distortion from 90°. In both compounds the other angles subtended at Sn also show a significant deviation from the 90 or 180° expected for a regular octahedron. This *meso* configuration was also observed for the analogous tin(IV) thio- and seleno-ether compounds. The Sn-Te bond lengths in the chloro adduct are noticeably shorter than in the bromo species, probably reflecting the greater Lewis acidity of the former. Also consistent with our observations in the thioether and selenoether analogues is the variation in *d*(Sn–X) distance to the *trans* ligand, with that *trans* to Te being consistently shorter than that *trans* to X. This leads to the conclusion that in

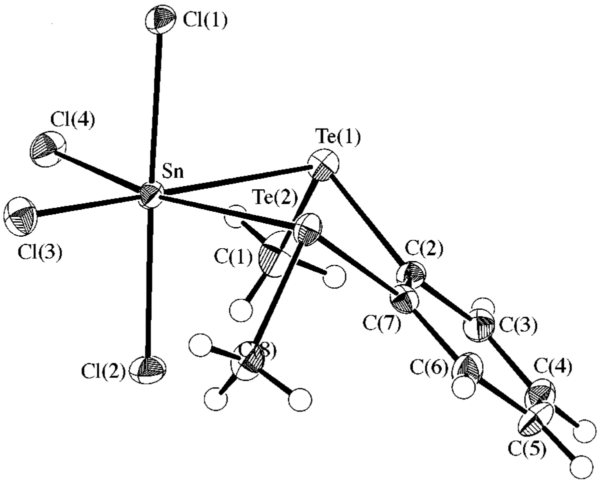

Fig. 1 View of the structure of [$SnCl_4\{C_6H_4(TeMe)$-*o*}] with the numbering scheme adopted. Ellipsoids are shown at 40% probability

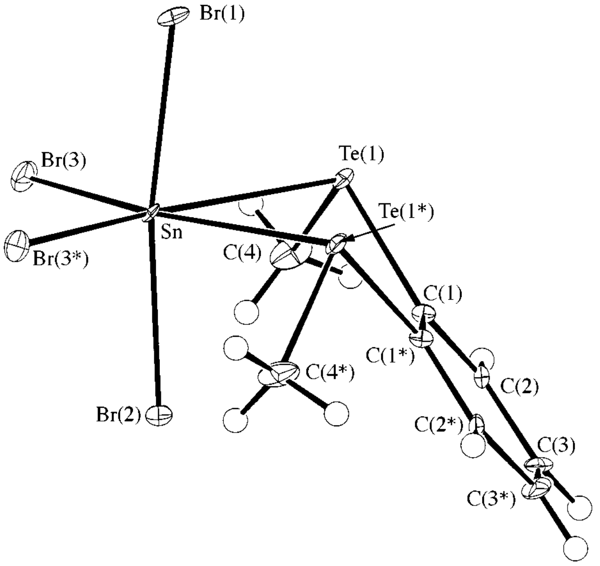

Fig. 2 View of the structure of [$SnBr_4\{C_6H_4(TeMe)$-*o*}] with the numbering scheme adopted. Ellipsoids are shown at 40% probability and atoms marked with an asterisk are related by a crystallographic mirror plane

Table 1 Crystallographic data *

Complex	[$SnCl_4\{C_6H_4(TeMe)_2$-*o*}]	[$SnBr_4\{C_6H_4(TeMe)_2$-*o*}]
Formula	$C_8H_{10}Cl_4SnTe_2$	$C_8H_{10}Br_4SnTe_2$
M	621.87	799.67
Colour, morphology	Yellow, column	Red-brown, block
Crystal dimensions/mm	0.40 × 0.15 × 0.10	0.30 × 0.20 × 0.20
Space group	$P2_1/n$	$P2_1/m$
a/Å	8.064(3)	6.829(9)
b/Å	14.362(2)	11.50(1)
c/Å	13.549(2)	10.23(1)
β/°	102.10(1)	100.5(1)
U/Å^3	1534.3(6)	790(1)
Z	4	2
F(000)	1120	704
D_c/g cm^{-3}	2.692	3.361
μ(Mo-Kα)/cm^{-1}	60.88	153.52
Transmission factors (maximum, minimum)	1.000, 0.886	1.000, 0.410
Unique observed reflections	2834	1482
R_{int} (based on F^2)	0.028	0.051
Unique observed reflections with [$I_o > 2.5\sigma(I_o)$]	2120	1234
No. refined parameters	136	68
Goodness of fit	1.33	2.67
R (based on *F*)	0.031	0.039
R' (based on *F*)	0.035	0.043
Maximum, minimum residual peaks/e Å^{-3}	1.60, −0.84	1.70, −1.90

* Details in common: monoclinic; $2\theta_{max}$ 50°; ω–2θ scans; final Δ/σ 0.00; $R = \Sigma(|F_o|_i - |F_c|_i)/\Sigma|F_o|_i$; $R' = [\Sigma w_i(|F_o|_i - |F_c|_i)^2/\Sigma w_i|F_o|_i^2]^{\frac{1}{2}}$; goodness of fit = $[\Sigma(|F_o|_i - |F_c|_i)/\sigma_i]/(n - m) \approx 1$.

these hard SnX$_4$ adducts the halogen ligands exert a greater *trans* influence than do the telluroether donors, contrasting with the trend usually observed in transition-metal complexes involving these ligands where the telluroether function exerts a greater *trans* influence than halogen.[3]

Since we now have structural data on five [SnX$_4${*meso*-C$_6$H$_4$(EMe)$_2$-*o*}] (X = Cl, E = S, Se or Te; X = Br, E = Se or Te), it is useful to compare the structural trends along the series and relevant data are listed in Table 4. Some structural features are common to all examples: (*a*) the *cis* X–Sn–X angles are all >90° with the largest X–Sn–X angle in plane (*i.e. trans* to the bidentate ligand); (*b*) the axial X groups bend towards the neutral ligand with X–Sn–X typically *ca.* 170°; (*c*) the E–Sn–E angles are <90°; (*d*) *d*(Sn–X) *trans*-X > *d*(Sn–X) *trans*-E; (*e*) the *d*(Sn–X) of the axial X groups within each complex are surprisingly different ($\geqslant 7\sigma$). If we look at the same data for several [SnX$_4$(dithioalkane)] complexes[11] all of which contain DL forms of the dithioalkane we find the same trends as in (*a*)–(*d*) although the differences are smaller, whilst effect (*e*) is not present. This suggests that, whilst some of the distortion of the octahedron about tin may be caused by attempts to minimise X···X repulsions, the largest distortions are caused by the poor match of the chelate bites of the rigid *o*-phenylene ligands to the tin, an effect exacerbated by the *meso* configuration of the ligands which presumably is responsible for (*e*). Indeed a similar difference (7σ) in the two axial *d*(Pt–Cl) is observed in [PtCl$_4${*meso*-C$_6$H$_4$(SeMe)$_2$-*o*}].[17] Examination of the packing diagrams shows no short intermolecular contacts involving the axial X groups which could account for the different axial Sn–X bond lengths. In the [SnX$_4$(dithioalkane)] complexes the two axial *d*(Sn–X) distances in each complex are the same, indeed in the majority of cases this is a requirement of the crystallographic symmetry.

We were also interested in how the binding of these ligands to a hard Lewis acid might differ from co-ordination to a transition metal. Comparable structural data on closely related complexes are limited, particularly by the few structurally characterised telluroether complexes.[3] However, from recent studies we have data on pseudo-tetrahedral complexes of type [ME$_4$]$^+$ (E = S, Se or Te) containing the soft d^{10} transition metals Cu^{I} and Ag^{I}.[9] Comparisons of the *d*(Cu–E) and *d*(Ag–E) bond lengths shows an increase of *ca.* 0.1 Å between E = S and Se, and a further 0.15 Å from E = Se to Te. Comparing the data in Table 4 we see the same increases along the series, *i.e.* within the limits of the precision of the X-ray data the same changes in bond length on changing the ligand donor from S to Se to Te occur for a soft transition-metal acceptor and for the hard tin(IV), arguing for similar relative effects in the bonding.* Since the weaker Lewis acidity of SnBr$_4$ *versus* SnCl$_4$ results in a small increase of Sn–E bond lengths in the bromides for comparable complexes, it is clear that significant changes in donor–acceptor bonds are reflected in the X-ray structural data. A similar effect attributed to weaker Lewis acidity has been observed in a series of mercury(II) halide–selenoether complexes.[18]

Silicon and germanium halides

An obvious extension of these studies of tin(IV) complexes is to examine complexation of silicon(IV) or germanium(IV) halides by Group 16 donor ligands. No examples of such complexes were found in the literature, although a limited number of complexes with N-, O- and sometimes P-donor ligands have been described.[19] Previous work has established that for all the Group 14 acceptors the Lewis acidity is MCl$_4$ > MBr$_4$ > MI$_4$ for fixed M, and hence we examined the reactions with SiCl$_4$ and GeCl$_4$. There was no visually evident reaction on mixing

Table 2 Selected bond lengths (Å) and angles (°) for [SnCl$_4${C$_6$H$_4$(TeMe)$_2$-*o*}]

Te(1)–Sn	2.908(1)	Te(1)–C(1)	2.131(8)
Te(1)–C(2)	2.128(8)	Te(2)–Sn	2.9222(8)
Te(2)–C(7)	2.117(7)	Te(2)–C(8)	2.122(8)
Sn–Cl(1)	2.457(2)	Sn–Cl(2)	2.433(2)
Sn–Cl(3)	2.384(2)	Sn–Cl(4)	2.390(2)
C(2)–C(3)	1.40(1)	C(2)–C(7)	1.40(1)
C(3)–C(4)	1.38(1)	C(4)–C(5)	1.38(1)
C(5)–C(6)	1.38(1)	C(6)–C(7)	1.39(1)
Sn–Te(1)–C(1)	99.1(3)	Sn–Te(1)–C(2)	94.1(2)
C(1)–Te(1)–C(2)	96.4(3)	Sn–Te(2)–C(7)	93.7(2)
Sn–Te(2)–C(8)	97.3(3)	C(7)–Te(2)–C(8)	96.9(3)
Te(1)–Sn–Te(2)	81.67(2)	Te(1)–Sn–Cl(1)	88.55(5)
Te(1)–Sn–Cl(2)	90.53(5)	Te(1)–Sn–Cl(3)	174.10(6)
Te(1)–Sn–Cl(4)	87.51(6)	Te(2)–Sn–Cl(1)	86.54(5)
Te(2)–Sn–Cl(2)	91.30(5)	Te(2)–Sn–Cl(3)	92.73(6)
Te(2)–Sn–Cl(4)	168.44(6)	Cl(1)–Sn–Cl(2)	177.75(7)
Cl(1)–Sn–Cl(3)	89.25(7)	Cl(1)–Sn–Cl(4)	89.13(7)
Cl(2)–Sn–Cl(3)	91.47(8)	Cl(2)–Sn–Cl(4)	92.88(7)
Cl(3)–Sn–Cl(4)	97.93(8)		

Table 3 Selected bond lengths (Å) and angles (°) for [SnBr$_4${C$_6$H$_4$(TeMe)$_2$-*o*}]

Te(1)–Sn	2.981(2)	Te(1)–C(1)	2.13(1)
Te(1)–C(4)	2.13(1)	Sn–Br(1)	2.567(2)
Sn–Br(2)	2.622(2)	Sn–Br(3)	2.526(2)
C(1)–C(2)	1.38(2)	C(1)–C(1*)	1.39(2)
C(3)–C(3*)	1.35(3)	C(2)–C(3)	1.40(2)
Sn–Te(1)–C(1)	93.1(3)	Sn–Te(1)–C(4)	99.6(3)
C(1)–Te(1)–C(4)	95.8(4)	Te(1)–Sn–Te(1*)	74.99(7)
Te(1)–Sn–Br(1)	84.36(7)	Te(1)–Sn–Br(2)	88.96(7)
Te(1)–Sn–Br(3)	92.66(7)	Br(3)–Sn–Br(3*)	99.68(9)
Te(1*)–Sn–Br(3)	167.64(4)		
Br(1)–Sn–Br(2)	171.58(7)		
Br(1)–Sn–Br(3*)	93.91(7)		
Br(2)–Sn–Br(3*)	91.51(6)		

Table 4 Comparative structural data*

	[SnCl$_4${C$_6$H$_4$(SMe)$_2$-*o*}]	[SnCl$_4${C$_6$H$_4$(SeMe)$_2$-*o*}]	[SnCl$_4${C$_6$H$_4$(TeMe)$_2$-*o*}]	[SnBr$_4${C$_6$H$_4$(SeMe)$_2$-*o*}]	[SnBr$_4${C$_6$H$_4$(TeMe)$_2$-*o*}]
d(Sn–E)/Å	2.659(2), 2.6777(2)	2.749(1), 2.787(2)	2.908(1), 2.9222(8)	2.841(2)	2.981(2)
d(Sn–X) *trans*-E/Å	2.357(2)	2.360(3), 2.364(3)	2.384(2), 2.390(2)	2.512(1)	2.526(2)
d(Sn–X) *trans*-X/Å	2.401(2), 2.382(2)	2.426(3), 2.389(3)	2.433(2), 2.457(2)	2.600(2), 2.547(2)	2.567(2), 2.622(2)
X–Sn–X					
(in plane)/°	103	102	98	102	99
(axial)/°	169	170	178	169	172
E–Sn–E/°	74	76	82	72	75

* From refs. 11, 12 and this work.

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* It could be argued that d^{10} Cu^{I} and Ag^{I} are atypical transition-metal acceptors and complexes of open-shell metal ions such as Rh^{III} or Pd^{II} would provide a better comparison. Unfortunately a suitable set of isostructural thio-, seleno-, and telluro-ether complexes has not been structurally characterised.[3]

anhydrous CH_2Cl_2 solutions of $SiCl_4$ and Me_2S, Me_2Se or $MeSCH_2CH_2SMe$, and applying high vacuum and gentle warming to the solutions removed the constituents stepwise, leaving no residue. Whilst no solid complexes were obtained these results do not rule out the formation of weak adducts in equilibrium with the starting materials: $SiCl_4 + nL \rightleftharpoons SiCl_4L_n$. Hence the solutions were also examined *in situ* using ^1H, $^{29}Si\text{-}\{^1H\}$ (and for the Me_2Se system, $^{77}Se\text{-}\{^1H\}$) NMR spectroscopy over the temperature range 300–180 K. In all cases the spectra were indistinguishable from those of the constituents in isolation, confirming no adduct formation. Similar results were found in the cases of $GeCl_4$ and the same ligands over this temperature range. The ^{73}Ge nucleus has a low resonance frequency ($\Xi = 3.488$ MHz), $I = \frac{9}{2}$, and is 7.8% abundant leading to a mediocre receptivity ($D_c = 0.617$).[20] However in the T_d environment in $GeCl_4$ the resonance is easily observed; from a 5% solution in CH_2Cl_2, δ 29.4 (lit.,[21] 30.9 ± 0.5 for the neat liquid), with a linewidth of *ca.* 5 Hz. The resonance was unshifted and the linewidth unchanged within experimental error in the presence of the Group 16 ligands. The resonance of a $GeCl_4L_n$ complex might be unobservably broad due to the rapid quadrupolar relaxation in the low-symmetry environment. However any complex formation, even a rapid equilibrium on the NMR time-scale, would be expected to result in substantial line broadening or possibly complete loss of the parent $GeCl_4$ resonance.

In summary, the affinity of Group 14 Lewis acids for Group 16 ligands falls in the orders $SR_2 > SeR_2 > TeR_2$, $SnCl_4 \geqslant GeCl_4, SiCl_4$, and $SnCl_4 > SnBr_4 > SnI_4$.

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