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Cite this: DOI: 10.1039/c2dt30968h

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PAPER

TeX_4 (X = F, Cl, Br) as Lewis acids – complexes with soft thio- and seleno-ether ligands†‡

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Received 3rd May 2012, Accepted 25th June 2012
DOI: 10.1039/c2dt30968h

TeF_4 reacts with OPR_3 (R = Me or Ph) in anhydrous CH_2Cl_2 to give the colourless, square based pyramidal 1 : 1 complexes $[TeF_4(OPR_3)]$ only, in which the OPR_3 is coordinated basally in the solid state, (R = Me: d(Te–O) = 2.122(2) Å; R = Ph: d(Te–O) = 2.1849(14) Å). Variable temperature $^{19}F\{^1H\}$, $^{31}P\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectroscopic studies strongly suggest this is the low temperature structure in solution, although the systems are dynamic. The much softer donor ligands SMe_2 and $SeMe_2$ show a lower affinity for TeF_4, although unstable, yellow products with spectroscopic features consistent with $[TeF_4(EMe_2)]$ are obtained by the reaction of TeF_4 in neat SMe_2 or *via* reaction in CH_2Cl_2 with $SeMe_2$. TeX_4 (X = F, Cl or Br) causes oxidation and halogenation of $TeMe_2$ to form X_2TeMe_2. The Br_2TeMe_2 hydrolyses in trace moisture to form $[BrMe_2Te–O–TeMe_2Br]$, the crystal structure of which has been determined. TeX_4 (X = Cl or Br) react with the selenoethers $SeMe_2$, $MeSe(CH_2)_3SeMe$ or o-$C_6H_4(SeMe)_2$ (X = Cl) in anhydrous CH_2Cl_2 to give the distorted octahedral monomers *trans*-$[TeX_4(SeMe_2)_2]$, *cis*-$[TeX_4\{MeSe(CH_2)_3SeMe\}]$ and *cis*-$[TeCl_4\{o\text{-}C_6H_4(SeMe)_2\}]$, which have been characterised by IR, Raman and multinuclear NMR (^1H, $^{77}Se\{^1H\}$ and $^{125}Te\{^1H\}$) spectroscopy, and *via* X-ray structure determinations of representative examples. Tetrahydrothiophene (tht) can form both 1 : 1 and 1 : 2 Te : L complexes. For X = Br, the former has been shown to be a Br-bridged dimer, $[Br_3(tht)Te(\mu\text{-}Br)_2TeBr_3(tht)]$, by crystallography with the tht ligands *anti*, whereas the latter are *trans*-octahedral monomers. Like its selenoether analogue, $MeS(CH_2)_3SMe$ forms distorted octahedral *cis*-chelates, $[TeX_4\{MeS(CH_2)_3SMe\}]$, whereas the more rigid o-$C_6H_4(SMe)_2$ unexpectedly forms a zig-zag chain polymer in the solid state, $[TeCl_4\{o\text{-}C_6H_4(SMe)_2\}]_n$, in which the dithioether adopts an extremely unusual bridging mode. This is in contrast to the chelating monomer, *cis*-$[TeCl_4\{o\text{-}C_6H_4(SeMe)_2\}]$, formed with the analogous selenoether and may be attributed to small differences in the ligand chelate bite angles. The wider bite angle xylyl-linked bidentates, o-$C_6H_4(CH_2EMe_2)_2$ behave differently; the thioether forms *cis*-chelated $[TeX_4\{o\text{-}C_6H_4(CH_2SMe)_2\}]$ confirmed crystallographically, whereas the selenoether undergoes C–Se cleavage and rearrangement on treatment with TeX_4, forming the cyclic selenonium salts, $[C_9H_{11}Se]_2[TeX_6]$. The tetrathiamacrocycle, [14]aneS_4 (1,4,8,11-tetrathiacyclotetradecane), does not react cleanly with $TeCl_4$, but forms the very poorly soluble $[TeCl_4([14]aneS_4)]_n$, shown by crystallography to be a zig-zag polymer with *exo*-coordinated [14]-aneS_4 units linked *via* alternate S atoms to a *cis*-$TeCl_4$ unit. Trends in the $^{125}Te\{^1H\}$ NMR shifts for this series of Te(IV) halides chalcogenoether complexes are discussed.

Introduction

Recent years have seen greatly increased interest in the coordination chemistry of the heavier p-block elements.[1] Much of the drive has stemmed from the importance particularly of the metallic elements (Ga, In, Ge *etc.*) in electronics,[2,3] and from the need to develop organ-specific carriers for medicinal radioisotopes (*e.g.* ^{68}Ga, ^{111}In, ^{113m}In, ^{117m}Sn).[4,5] Similar chemistry of the more non-metallic elements has received less attention, particularly with neutral donor ligands.[6,7] Tellurium(IV) halides, TeX_4 (X = F, Cl, Br, I) are Lewis acids, but whilst there are a modest number of complexes of $TeCl_4$ or $TeBr_4$, TeI_4 seems to have little affinity for neutral donors,[8] whilst TeF_4 has been very little studied.[9,10] We recently reported[11] the first examples of thioether adducts of $TeCl_4$ and $TeBr_4$, including $[X_3(SMe_2)Te(\mu\text{-}X)_2TeX_3(SMe_2)]$ and $[TeX_4\{RS(CH_2)_2SR\}]$ (X = Cl or Br, R = Me, Et or ^iPr), which have distorted octahedral coordination at Te, composed of short (primary) Te–X bonds and longer

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† Dedicated to Professor David Cole-Hamilton on the occasion of his retirement and for his outstanding contribution to transition metal catalysis.

‡ Electronic supplementary information (ESI) available. CCDC 881025–881039. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30968h

(secondary) Te–S bonds. The formal lone pair on the Te(IV) centre was not apparently stereochemically active, although there is no simple explanation for the (small) distortions from regular six-coordinate geometries (similar effects are seen in Te(IV) complexes of charged sulfur ligands, including dithiocarbamates, and dithiolates).[12] TeX_4 adducts of the diphosphine disulfide $Ph_2P(S)CH_2P(S)Ph_2$ are also known,[13,14] but with other phosphine sulfides and with phosphine selenides reduction to Te(II) occurs.[13] We also note that TeX_4 cause halogenation of tertiary phosphines,[15,16] and that no adducts are known.

Here we report the preparation, spectroscopic and structural properties of the first series of complexes of TeX_4 (X = Cl or Br) with selenoether coordination and the reactions of TeX_4 with $TeMe_2$. Thioether complexes, which reveal new structure types, are described, together with the first examples with TeF_4. Selected OPR_3 complexes with TeF_4 are included for comparison.

Results and discussion

TeF_4 complexes

Crystalline TeF_4 contains square pyramidal TeF_5 units linked *via* two (*cis*) basal fluorines into zig-zag chains,[17,18] whilst in the gas phase it has a monomeric *pseudo*-trigonal bipyramidal ("saw-horse") geometry.[9] The anion $[TeF_5]^-$ is also square pyramidal,[19,20] but despite claims in the older literature, $[TeF_6]^{2-}$ has never been certainly identified.[20,21] The common structural features in the solid compounds are that the Te is situated somewhat below the TeF_4 plane and $Te–F_{ax} < Te–F_{eq}$,[9] consistent with the vacant vertex being occupied by the lone pair. The only structurally authenticated Group 16 donor ligand complexes of TeF_4 are with ether ligands, including $[TeF_4(thf)_2]$,[10] $[TeF_4\{MeO(CH)_2OMe\}_2]$, $[TeF_4(dioxane)]$ and $[TeF_4(OEt_2)]$.[9] The last has a structure close to that of solid TeF_4 with a weakly associated ether molecule (Te–O = 2.44(1), 2.42(1) Å), but the others contain discrete TeF_4 molecules similar to the gas phase, with very long contacts to the oxygens (~2.45–2.98 Å). For comparison, the covalent radii sum for Te–O is ~2.15 Å and the Van der Waals radii sum is ~3.5 Å.[22] We suspected that since ether ligands form only weak adducts with other p-block fluorides including SnF_4,[23] GeF_4,[24] and SiF_4,[25] and do not complex with AsF_3 or SbF_3,[26] these complexes might not be representative of other neutral oxygen donors. In contrast, phosphine oxides form stable adducts with all five of these fluorides,[26–29] and hence we synthesised examples with TeF_4 as model oxygen donor complexes.

The reaction of finely powdered TeF_4 with a solution of OPR_3 (R = Me or Ph) in a 1 : 1 molar ratio, in anhydrous dichloromethane, resulted in the formation of colourless solutions from which colourless crystals of $[TeF_4(OPR_3)]$ were isolated in good yield. The same complexes were formed using a two-fold excess of phosphine oxide, and *in situ* NMR studies showed no evidence for other complexes. Crystals of both complexes were obtained by refrigerating CH_2Cl_2/hexane solutions, and their structures (Fig. 1 and 2) reveal discrete square pyramidal molecules with apical fluorine. The pattern of Te–F bond lengths is much as expected from the structure of solid TeF_4 discussed above, with $Te–F_{ax} < Te–F_{transO} < Te–F_{transF}$ and with $F_{ax}–Te–F_{basal} < 90°$.

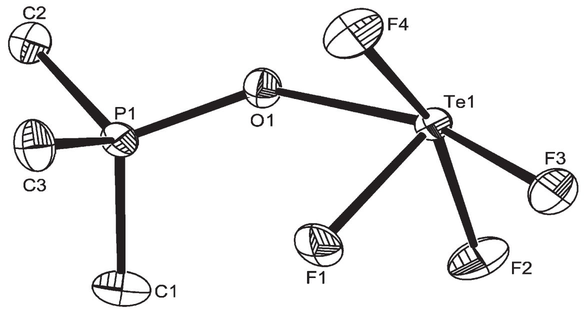

Fig. 1 Crystal structure of $[TeF_4(OPMe_3)]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Te1–F1 = 1.897(2), Te1–F2 = 1.971(2), Te1–F3 = 1.923(2), Te1–F4 = 1.962(2), Te1–O1 = 2.122(2), P1–O1 = 1.556(2), F1–Te1–F2 = 79.23(8), F1–Te1–F3 = 82.04(7), F1–Te1–F4 = 81.43(9), F2–Te1–F3 = 88.23(8), F2–Te1–F4 = 160.56(8), F3–Te1–F4 = 87.06(8), F1–Te1–O1 = 80.83(7), F2–Te1–O1 = 89.52(8), F3–Te1–O1 = 162.84(7), F4–Te1–O1 = 89.44(8).

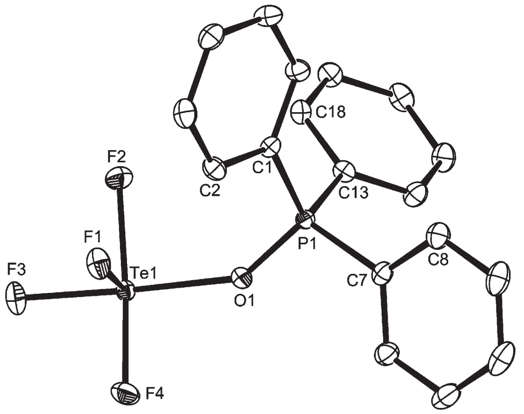

Fig. 2 Crystal structure of $[TeF_4(OPPh_3)]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The phenyl groups are numbered cyclically starting at the *ipso* C atom, and an adjacent C atom is labelled to indicate the sequence order. Selected bond lengths (Å) and angles (°): Te1–F1 = 1.8575(12), Te1–F2 = 1.9488(14), Te1–F3 = 1.9005(13), Te1–F4 = 1.9464(16), Te1–O1 = 2.1849(14), P1–O1 = 1.5275(14), F1–Te1–F2 = 80.71(6), F1–Te1–F3 = 82.95(6), F1–Te1–F4 = 80.64(6), F2–Te1–F3 = 89.92(6), F2–Te1–F4 = 161.31(5), F3–Te1–F4 = 88.98(6), F1–Te1–O1 = 80.04(6), F2–Te1–O1 = 89.85(6), F3–Te1–O1 = 62.80(5), F4–Te1–O1 = 85.76(6).

However, significantly, the Te–O bonds are much shorter than in the ether adducts (2.122(2) Å (R = Me) and 2.185(1) Å (R = Ph)). The d(P–O) are lengthened by ~0.05 Å compared to the parent phosphine oxides,[27] similarly suggesting a strong Te–O bond. In contrast, TeX_4 (X = Cl or Br) give *cis* octahedral $[TeX_4(OPR_3)_2]$ adducts, with slightly longer d(Te–O) bonds,[13,14] although this may mostly reflect the higher coordination number at Te and screening by the stereochemically inactive lone pair in the 5s orbital. In $[TeF_4(OPMe_3)]$ long intermolecular Te···F contacts (2.965(2) Å) weakly associate the molecular units into zig-zag chains.

The IR and Raman spectra of $[TeF_4(OPR_3)]$ show single strong ν(PO) vibrations (R = Me 1032 cm^{-1}, R = Ph, 1048 cm^{-1}), markedly lowered from those in the parent OPR_3 (1166 and 1196 cm^{-1} respectively),[28] and several strong bands 480–650 cm^{-1} assigned as terminal Te–F modes (theory C_s = 3A′ + A″), consistent with the crystal structures. In solution in anhydrous CD_2Cl_2 at 295 K, the $^{19}F\{^1H\}$ NMR spectra show very broad single resonances indicative of dynamic systems, but on cooling the solution of $[TeF_4(OPMe_3)]$ to 178 K, three broad singlets with ^{125}Te satellites were resolved δ = −23.8 (s, [1F], $^1J_{FTe}$ = 2325 Hz), −40.3 (s, [2F], $^1J_{FTe}$ = 1313 Hz), −58.6 (s, [1F], $^1J_{FTe}$ = 1721 Hz), which from the integrals and by comparison with the spectrum of $[TeF_5]^-$ [20] are assigned to TeF_{ax}, TeF_{transF} and TeF_{transO} respectively. The 178 K spectrum of $[TeF_4(OPPh_3)]$ (Experimental section) is similar. Notably, for both complexes the resonances are still quite broad and no $^2J_{FF}$ couplings were resolved. The $^{31}P\{^1H\}$ NMR spectra of both complexes at 178 K were singlets with substantial high frequency coordination shifts. Neither complex exhibited a $^{125}Te\{^1H\}$ NMR spectrum at 220 K, but on further cooling a broad resonance appeared and then split, and at 178 K both spectra approximated to twelve line multiplets centred ∼δ + 1150 (expect d,d,t). However, even at this temperature the lines were still quite broad and somewhat distorted, showing that the low temperature limiting spectrum had not been reached at the freezing point of CD_2Cl_2. Addition of a small excess of the appropriate OPR_3 to solutions of $[TeF_4(OPR_3)]$ showed only a singlet in the $^{31}P\{^1H\}$ NMR spectrum of each even at 178 K, consistent with fast exchange of the OPR_3. Excess OPR_3 caused some sharpening of the $^{19}F\{^1H\}$ resonances, suggesting suppression of ligand dissociation, although no new complexes formed. The solution data show that the complexes are dynamic down to very low temperatures, both dissociative exchange of the OPR_3 and fluxionality of the TeF_4 unit being present.

The reaction of TeF_4 with $OAsPh_3$ in anhydrous CH_2Cl_2 solution gave a good yield of colourless crystals identified by their unit cell[30] and $^{19}F\{^1H\}$ NMR spectrum (δ = −89.5)[26] as Ph_3AsF_2, showing fluorination of the arsine oxide instead of coordination. Tertiary arsine oxide complexes are known for SnF_4 [29] and GeF_4,[28] but AsF_3 causes only fluorination,[26] whilst with SbF_3, the square pyramidal $[SbF_3(OAsR_3)_2]$ are the major products, although some R_3AsF_2 also form.[26]

The reaction of TeF_4 with neat SMe_2 led to dissolution of the TeF_4 to give a colourless solution, and following removal of the excess SMe_2, a sticky yellow solid formed, which could be stored for some days in the freezer, but darkened over *ca.* 24 h at room temperature. TeF_4 and $SeMe_2$ react similarly in CH_2Cl_2 to form a yellow, unstable product. ^1H NMR spectroscopy shows a single resonance for each complex substantially to high frequency of the ‘free’ ligand resonance, which is little changed over the temperature range 295 to 193 K. Room temperature $^{19}F\{^1H\}$ NMR spectra on each showed a relatively sharp singlet which broadened on cooling the solution to 193 K, but remained a single resonance. Together with the absence of any $^{77}Se\{^1H\}$ or $^{125}Te\{^1H\}$ NMR resonances over this temperature range, these data are consistent with the complexes being dynamic in solution. These observations are consistent with expectations for a soft chalcogenoether complex of the hard Lewis acidic TeF_4. As discussed above, even the hard OPR_3 donor complexes are dynamic down to very low temperatures. The IR spectra for each complex shows strong features in the region expected for Te–F stretching vibrations, and comparable with those for the structurally authenticated $[TeF_4(OPR_3)]$, suggesting a similar 1 : 1 $TeF_4 : EMe_2$ formulation. The instability of the complexes at ambient temperatures precluded outsourced microanalytical measurements. Upon cooling (−18 °C) a yellow-orange CH_2Cl_2 solution of the selenoether product for several days, a few small, colourless crystals formed. X-Ray structural analysis on one of these showed it to be $[Me_2SeSeMe][TeF_5]$ (ESI‡), formed as a minor decomposition product. The $[Me_2SeSeMe]^+$ cation has been reported previously as its $[BF_4]^-$ salt,[31] however, in the $[TeF_5]^-$ salt reported here there are four intermolecular F⋯Se contacts.

TeX_4 (X = Cl or Br) selenoether complexes

The addition of $SeMe_2$ to a suspension of TeX_4 in anhydrous CH_2Cl_2 or thf at 0 °C, produced intensely coloured solutions, which deposited almost black crystals of the 2 : 1 adducts $[TeX_4(SeMe_2)_2]$. This contrasts with the SMe_2 reactions,[11] which gave only the 1 : 1 complexes, $[X_3(SMe_2)Te(\mu\text{-}X)_2TeX_3(SMe_2)]$, even with excess SMe_2. The $[TeX_4(SeMe_2)_2]$ are isomorphous and the structures reveal (Fig. 3a and ESI‡) they are centrosymmetric *trans* isomers. The d(Te–Se) are very similar, indicating little difference in Lewis acidity between the two tellurium centres. There are two long intermolecular contacts, Se1⋯Cl1′ = 3.592(1) and Se1⋯Cl2″ = 3.485(1) Å, which complete an approximate square pyramid around Se1 (C1 axial), and links the molecules into a 3-D network (Fig. 3b). Similar intermolecular contacts are present in the bromide.

The IR spectrum of the chloro-complex shows the E_u Te–Cl stretch at 246 cm^{-1} and the Raman spectrum has strong bands at 256 and 280 cm^{-1} (A_{1g} + B_{2g}), consistent with the D_{4h} geometry, but the corresponding bands in the bromo complex are expected to lie near the lower limits (∼200 cm^{-1}) of the spectrometers and were not reliably identified. Neither complex exhibits a $^{77}Se\{^1H\}$ or $^{125}Te\{^1H\}$ NMR resonance in solution at room temperature due to fast ligand exchange, but at 183 K singlets are observed, consistent with the presence of a single isomer, presumably the *trans* form found in the crystals (Table 1). The complexes decompose quite rapidly in solution at ambient temperatures with fragmentation of the selenoether (see ESI‡).

Similar reaction of $MeSe(CH_2)_3SeMe$ with TeX_4 produced dark orange (Cl) or red (Br) complexes $[TeX_4\{MeSe(CH_2)_3SeMe\}]$, while $o\text{-}C_6H_4(SeMe)_2$ gives $[TeCl_4\{o\text{-}C_6H_4(SeMe)_2\}]$ as dark-red crystals. The $[TeCl_4\{MeSe(CH_2)_3SeMe\}]$ decomposed quite rapidly at room temperature and was very poorly soluble in non-coordinating solvents, precluding NMR studies. However, the more soluble bromo-analogue exhibited a $^{77}Se\{^1H\}$ and a $^{125}Te\{^1H\}$ NMR resonance in CH_2Cl_2 solution at 183 K, with reasonable chemical shifts (Table 1). Spectroscopic data on $[TeCl_4\{o\text{-}C_6H_4(SeMe)_2\}]$ complex also support *cis*-chelation, although in solution the complex is dynamic at room temperature. This assignment is supported by a crystal structure determination (Fig. 4) which shows the molecule has mirror symmetry with *cis*-chelate coordination, Te–Se = 2.969(1) Å.

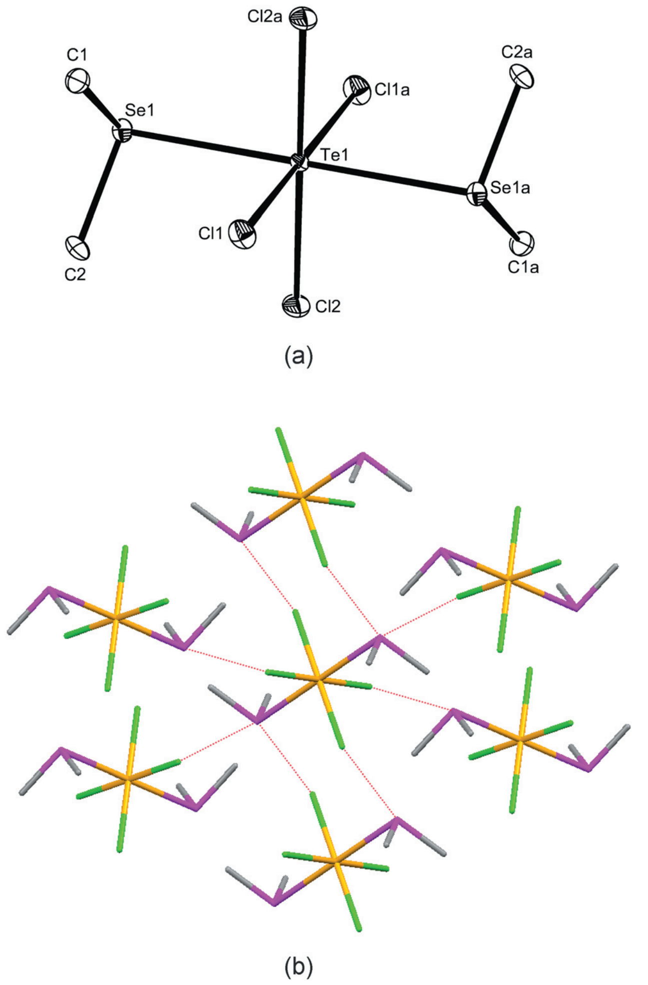

Fig. 3 (a) Crystal structure of the centrosymmetric [$TeCl_4(SeMe_2)_2$] molecule showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: $a = -x, -y, -z$. Selected bond lengths (Å) and angles (°): Te1–Cl1 = 2.5133(8), Te1–Cl2 = 2.5086(8), Te1–Se1 = 2.8727(6), Cl1–Te1–Cl2 = 89.48(3), Cl1–Te1–Se1 = 89.85(2), Cl2–Te1–Se1 = 89.04(3), C1–Se1–C2 = 97.38(10), C1–Se1–Te1 = 98.10(7), C2–Se1–Te1 = 97.73(7). (b) View of [$TeCl_4(SeMe_2)_2$] showing the intermolecular Se⋯Cl contacts (red dotted lines).

The Se–Te–Se of 68.61(4)° is extremely acute. Long intermolecular Se⋯Cl contacts of 3.626(2) Å are also evident from the crystal structure.

The *o*-xylyl selenoether, *o*-$C_6H_4(CH_2SeMe)_2$ fragmented on reaction with TeX_4 to form high yields of the cyclic selenonium hexahalotellurates(IV), [*o*-$C_6H_4CH_2Se(CH_3)CH_2]_2[TeX_6]$. The selenonium cation has been observed as a fragmentation product of this ligand on reaction with $GaCl_3$ [32] and also forms on reaction with MeI.[33] Further details are given in ESI.‡

Reaction of TeX_4 (X = F, Cl or Br) with telluroethers

The addition of $TeMe_2$ to a suspension of the TeX_4 (X = F, Cl or Br) in anhydrous CH_2Cl_2 resulted in immediate black precipitates, which were identified by powder XRD as elemental tellurium. The supernatant solutions were examined by multinuclear NMR spectroscopy (^1H, $^{125}Te\{^1H\}$ and for X = F, $^{19}F\{^1H\}$) which unequivocally identified $TeMe_2X_2$ as the only significant new product in each system. The comparisons with literature NMR data[34,35] are detailed in the Experimental section. The reactions of related p-block element halides and alkyls show a range of behaviour. Arsenic(III) halides form crystallographically authenticated complexes with tertiary arsines, including [As_2X_6-{*o*-$C_6H_4(AsMe_2)_2\}_2$] (X = Cl, Br or I)[36] and [{$AsCl_3(AsEt_3)\}_2$].[37] In contrast, with the sole exception of the very unstable [$Sb_2I_6(thf)_2(SbMe_3)_2$][38] the reactions of EX_3 with ER_3 (E = Sb or Bi, R = Me, Ph, *etc.*) result in substituent scrambling to form $EX_{3-n}R_n$.[39] The reactions of TeX_4 and $TeMe_2$ described here differ in that they involve redox chemistry as well as substituent scrambling – the dimethyltellurium(II) is converted to dimethyldihalotellurium(IV) and Te(0). The solution from the reaction of $TeBr_4$ with $TeMe_2$ deposited colourless crystals on standing for a few days, which proved to be the oxo-bridged $Me_2BrTe(\mu\text{-}O)$-$TeMe_2Br$ (Fig. 5), which presumably formed by hydrolysis of $TeMe_2Br_2$. The molecule has two-fold symmetry and a non-linear bridge Te1–O1–Te1a = 121.3(3)°. Several structures of related molecules, including $^nBu_2BrTeOTe^nBu_2Br$[40] and Me_2I-$TeOTeMe_2I$,[41] are known and the core dimensions of the current compound are unexceptional. Longer secondary Br⋯Te interactions (3.4–3.6 Å) link the molecules.

TeX_4 (X = Cl or Br) thioether complexes

In our initial study of TeX_4/thioether systems we observed two types of complex, six-coordinate dinuclear [$X_3(SMe_2)Te(\mu\text{-}X)_2$-$TeX_3(SMe_2)$] and mononuclear [$TeX_4\{RS(CH_2)_2SR\}$] with five-membered chelate rings. P-block complexes are often strongly influenced by ligand architecture and hence we explored a wider range of thioethers seeking other structural motifs. The reaction of the cyclic thioether, tetrahydrothiophene (tht) with TeX_4 (X = Cl or Br) in a 2 : 1 mol. ratio, gave almost black crystals of [$TeX_4(tht)_2$]. The crystal structures show very similar *trans* octahedral geometries (Fig. 6 and ESI‡), although the crystals are not isomorphous, with Te–S very slightly longer in the bromide (2.7502(8) Å (X = Cl), 2.7598(7) Å (X = Br)), and both are markedly shorter than the Te–S observed in [$X_3(SMe_2)Te$-$(\mu\text{-}X)_2TeX_3(SMe_2)$] (2.813(2), 2.822(2) Å).[11] The differences are readily explained by the nature of the *trans* ligands in each case. In the tht complexes, symmetrical 3c–4e bonds are present, whereas in the SMe_2 there are asymmetric 3c–4e bonds with a strong Te–X interaction and a correspondingly weaker Te–S. The $^{125}Te\{^1H\}$ NMR spectrum of [$TeCl_4(tht)_2$] was a sharp singlet at 295 K (δ = 1500) and showed a considerable low frequency shift on cooling, reaching δ = 1475 at 183 K. However, the $^{125}Te\{^1H\}$ NMR spectrum of [$TeBr_4(tht)_2$] showed no resonances at room temperature, but at 183 K two resonances with integrals ~5 : 1 were present at δ = 1655 and 1508. The initial possibility that these were *cis* and *trans* isomers was ruled out when red crystals deposited over a few days in the solution used for NMR studies. The structure (Fig. 7) showed these to be the centrosymmetric dimer [$Br_3(tht)Te(\mu\text{-}Br)_2TeBr_3(tht)$] with similar bond lengths and angles to the [$Br_3(SMe_2)Te(\mu\text{-}Br)_2$-$TeBr_3(SMe_2)$] reported previously.[11] The 1 : 1 dimer complex accounts for the $^{125}Te\{^1H\}$ NMR resonance at 1655 ppm.

Table 1 Selected NMR spectroscopic data[a]

Complex	δ^{125}Te{^{1}H} (ppm)	δ^{77}Se{^{1}H} (ppm)	Temperature	Reference
[TeF$_4$(OPPh$_3$)]	1148[b]	—	183 K	This work
[TeF$_4$(OPMe$_3$)]	1151[b]	—	183 K	This work
[TeCl$_4$(SeMe$_2$)$_2$]	1280	233	183 K	This work
[TeCl$_4${*o*-C$_6$H$_4$(SeMe)$_2$}]	1437	291	193 K	This work
[TeCl$_4${MeSe(CH$_2$)$_3$SeMe}]	n.o.	n.o.	(poor solubility)	This work
[{Cl$_3$(Me$_2$S)Te}$_2$(μ-Cl)$_2$]	1484	—	200 K	11
[TeCl$_4$(tht)$_2$]	1475	—	183 K	This work
[TeCl$_4${MeS(CH$_2$)$_2$SMe}]	1504	—	200 K	11
[TeCl$_4${^{i}PrS(CH$_2$)$_2$S^{i}Pr}]	1531	—	200 K	11
[TeCl$_4${MeS(CH$_2$)$_3$SMe}]	1517	—	203 K	This work
[TeCl$_4${*o*-C$_6$H$_4$(SMe)$_2$}]$_n$	n.o.	—		This work
[TeCl$_4${*o*-C$_6$H$_4$(CH$_2$SMe)$_2$}]	1433	—	193 K	This work
[TeBr$_4$(SeMe$_2$)$_2$]	1317	226	183 K	This work
[TeBr$_4${MeSe(CH$_2$)$_3$SeMe}]	1455	169	183 K	This work
[{Br$_3$(Me$_2$S)Te}$_2$(μ-Br)$_2$]	1650	—	200 K	11
[TeBr$_4$(tht)$_2$]	1507	—	183 K	This work
[{Br$_3$(tht)Te}$_2$(μ-Br)$_2$]	1655	—	183 K	This work
[TeBr$_4${MeS(CH$_2$)$_2$SMe}]	1760	—	200 K	11
[TeBr$_4${^{i}PrS(CH$_2$)$_2$S^{i}Pr}]	1702	—	200 K	11
[TeBr$_4${MeS(CH$_2$)$_3$SMe}]	1705	—	223 K	This work

[a] Spectra recorded in CH$_2$Cl$_2$ solution. [b] See text.

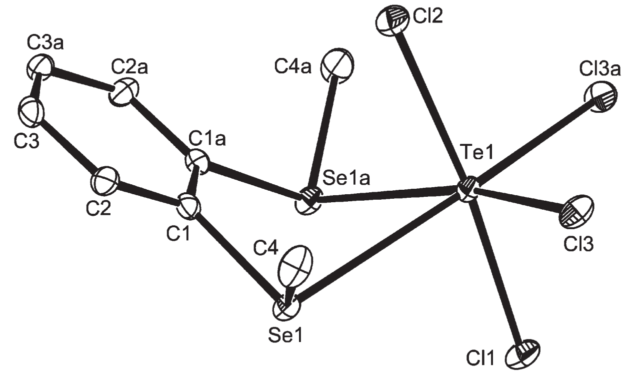

Fig. 4 Crystal structure of [TeCl$_4${*o*-C$_6$H$_4$(SeMe)$_2$}] showing the atom numbering scheme. The molecule has mirror symmetry. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: $a = x, 1/2 - y, z$. Selected bond lengths (Å) and angles (°): Te1–Cl1 = 2.445(2), Te1–Cl3 = 2.463(1), Te1–Cl2 = 2.579(2), Te1–Se1 = 2.969(1), Cl1–Te1–Cl3 = 91.93(5), Cl3–Te1–Cl3a = 94.62(7), Cl1–Te1–Cl2 = 174.21(6), Cl3–Te1–Cl2 = 91.99(5), Cl3–Te1–Se1a = 166.52(3), Cl1–Te1–Se1 = 83.74(5), Cl3–Te1–Se1 = 98.28(5), Cl2–Te1–Se1 = 91.49(4), Se1–Te1–Se1a = 68.61(4).

We also explored the effects of changing the linking backbone within the dithioether ligands. The RS(CH$_2$)$_2$SR ligands gave *cis* chelate complexes [TeX$_4${RS(CH$_2$)$_2$SR}],[11] and replacing the –(CH$_2$)$_2$– links by –(CH$_2$)$_3$– led only to [TeX$_4${RS(CH$_2$)$_3$SR}] which are also *cis* chelates (ESI‡). However, replacing the –(CH$_2$)$_2$– links by *o*-C$_6$H$_4$–, as in *o*-C$_6$H$_4$(SMe)$_2$, led to [TeCl$_4${*o*-C$_6$H$_4$(SMe)$_2$}]$_n$ in which the dithioether does not chelate, but instead bridges to an adjacent Te centre, forming a chain polymer (Fig. 8), with the two S atoms coordinated to Te mutually *cis*. The Te–S bond distances in this complex are 3.0375(8) and 3.0580(9) Å, significantly longer than in the chelate complexes. The S–Te–S angle is also very much more

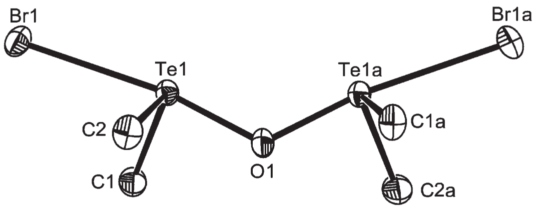

Fig. 5 Crystal structure of (BrMe$_2$Te)$_2$O·*n*CH$_2$Cl$_2$ (*n* = 0.6) showing the atom numbering scheme. The molecule has 2-fold symmetry. Ellipsoids are drawn at the 50% probability level and H atoms and the solvate are omitted for clarity. Symmetry operation: $a = 3/4 - z, 3/4 - y, 3/4 - x$. Selected bond lengths (Å) and angles (°): Te1–O1 = 1.985(3), Te1–C2 = 2.099(5), Te1–C1 = 2.115(5), Te1–Br1 = 2.8858(7), O1–Te1–C2 = 88.6(2), O1–Te1–C1 = 89.4(2), C2–Te1–C1 = 96.6(2), O1–Te1–Br1 = 171.1(1), C2–Te1–Br1 = 86.4(2), C1–Te1–Br1 = 83.9(1), Te1–O1–Te1a = 121.3(3).

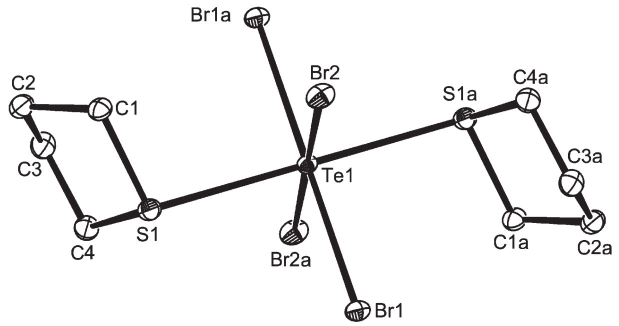

Fig. 6 Crystal structure of the centrosymmetric *trans*-[TeBr$_4$(tht)$_2$] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: $a = -x, 1 - y, -z$. Selected bond lengths (Å) and angles (°): Te1–Br1 = 2.6830(7)), Te1–Br2 = 2.26814(5), Te1–S1 = 2.7598(7), Br1–Te1–Br2 = 90.775(11), Br1–Te1–S1 86.01(2), Br2–Te1–S1 = 84.59(2).

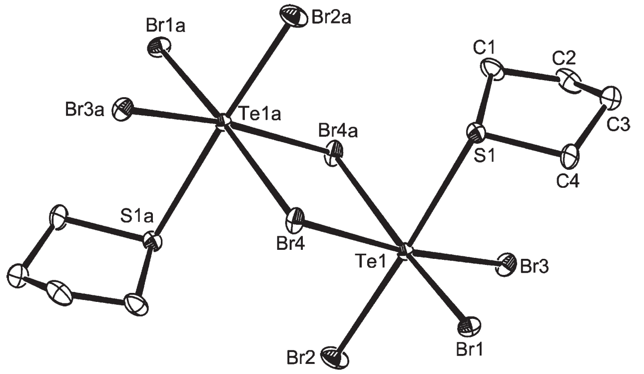

Fig. 7 Crystal structure of the centrosymmetric [Br_3(tht)Te-(μ-$Br)_2TeBr_3$(tht)] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: $a = 2 - x, 1 - y, -z$. Selected bond lengths (Å) and angles (°): Te1–Br1 = 2.5367(7), Te1–Br2 = 2.5757(7), Te1–Br3 = 2.5364(9), Te1–Br4 = 2.921(1), Te1–Br4a = 2.9350(8), Te1–S1 = 2.876(1), Br1–Te1–Br2 = 94.08(2), Br1–Te1–Br3 = 92.32(1), Br1–Te1–Br4 = 89.32(1), Br1–Te1–Br4a = 174.81(1), Br1–Te1–S1 = 84.92(3), Br2–Te1–Br3 = 93.92(1), Br2–Te1–Br4 = 91.94(1), Br2–Te1–Br4a = 90.64(2), Br2–Te1–S1 = 175.33(2), Br3–Te1–Br4 = 173.79(1), Br3–Te1–Br4a = 89.49(1), Br3–Te1–S1 = 90.69(2), S1–Te1–Br4 = 83.49(2), S1–Te1–Br4a = 90.21(3), Br4–Te1–Br4a = 88.37(1), Te1–Br4–Te1a = 91.63(1).

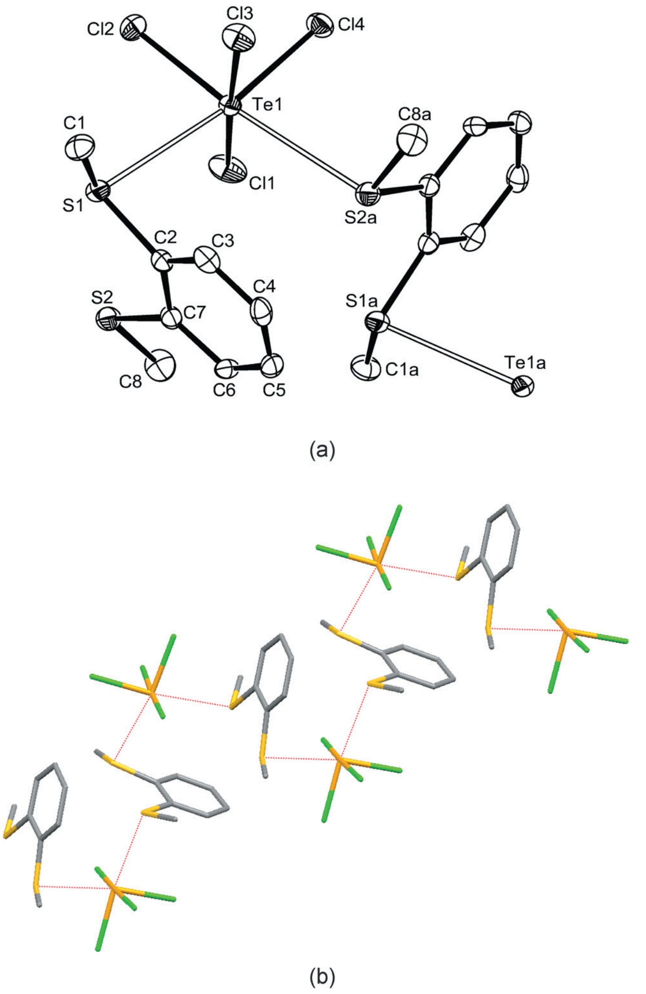

Fig. 8 (a) Crystal structure of [$TeCl_4\{o\text{-}C_6H_4(SMe)_2\}]_n$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The structure forms a chain of which part is shown. The long bonds from Te1 to S atoms are shown with open bonds. Symmetry operation: $a = 2 - x, 1 - y, 1/2 + z$. Selected bond lengths (Å) and angles (°): Te1–Cl1 = 2.4389(7), Te1–Cl2 = 2.3521(9), Te1–Cl3 = 2.5212(8), Te1–Cl4 = 2.3435(9), Te1–S1 = 3.0580(9), Te1–S2a = 3.0375(8), Cl1–Te1–Cl2 = 91.10(3), Cl1–Te1–Cl3 = 177.32(4), Cl1–Te1–Cl4 = 89.64(3), Cl2–Te1–Cl3 = 90.16(3), Cl2–Te1–Cl4 = 90.57(3), Cl3–Te1–Cl4 = 87.99(3), Cl1–Te1–S1 = 93.56(3), Cl2–Te1–S1 = 81.98(3), Cl3–Te1–S1 = 88.96(2), Cl4–Te1–S1 = 171.93(3), Cl1–Te1–S2a = 87.20(3), Cl2–Te1–S2a = 172.79(3), Cl3–Te1–S2a = 91.25(3), Cl4–Te1–S2a = 82.42(3), S1–Te1–S2a = 105.11(2). (b) View of part of the polymeric structure of [$TeCl_4\{o\text{-}C_6H_4\text{-}(SMe)_2\}]_n$.

obtuse at 105.11(2)°. It seems likely that the small bite angle of the $o\text{-}C_6H_4(SMe)_2$ ligand is insufficient to favour chelation to the large Te(IV) atom, and hence leads to the observed bridging coordination mode, which is very unusual for the orthophenylene dichalcogenoether ligand family, the only precedent being the polymeric $[Ag_n\{\mu\text{-}o\text{-}C_6H_4(SeMe)_2\}_n\{o\text{-}C_6H_4(SeMe)_2\}_n]^{n+}$.[42] Attempts to isolate a $TeBr_4$ complex with this ligand were unsuccessful. Replacing the rigid small bite $o\text{-}C_6H_4\text{–}$ linkage with the more flexible, wider bite angle $o\text{-}C_6H_4(CH_2)_2\text{–}$ linkage resulted in a return to chelation in the complexes $[TeX_4\{o\text{-}C_6H_4\text{-}(CH_2SMe)_2\}]$ as shown crystallographically for $[TeCl_4\{o\text{-}C_6H_4\text{-}(CH_2SMe)_2\}]$. This complex is a molecular monomer with crystallographic mirror symmetry and with the thioether bidentate, forming a seven-membered chelate ring (Fig. 9). The bond angles at Te are severely distorted from a regular octahedron, with <S–Te–S = 108.78(2)°, and in this case the Te–S = 2.8675(6) Å, in line with the Te–S distances in the other chelate monomers.

Attempts to prepare TeX_4 complexes with the macrocyclic thioether [14]aneS_4, gave yellow insoluble powders which were not single species. However, from one preparation some small yellow crystals grew amongst colourless crystals (of the macrocycle itself) by cooling the CH_2Cl_2 filtrate. The former proved to be $[TeCl_4([14]aneS_4)]_n$, the structure showing a zig-zag polymer with *exo*-coordinated [14]aneS_4 units linked *via* alternate S atoms to a *cis*-$TeCl_4$ unit (Fig. 10). The macrocyclic rings are centrosymmetric. The Te–S distances in this complex are in a similar range to those in the thioether examples described above. While *exocyclic* coordination in tetrathia-crown complexes is very rare in transition metal chemistry[43] a notable structurally authenticated exception being $[(NbCl_5)_2([14]aneS_4)]$,[44] it has been observed more frequently in p-block coordination complexes, possibly a result of the relatively low affinity of the soft, modest σ-donor thioether functions for the harder p-block Lewis acids, and their tendency not to displace halide co-ligands.[6,45]

Multinuclear NMR trends

Table 1 lists selected $^{125}Te\{^1H\}$ and $^{77}Se\{^1H\}$ NMR parameters for the TeX_4 chalcogenoether complexes. The complexes are extensively dissociated at ambient temperatures and even at the lowest temperatures it is likely that some dynamic processes are still significant. For example, resonances for individual invertomers are not observed in the *cis*-chelates. However, some trends are very clear from the low temperature data reported. Firstly, the ^{77}Se{^{1}H} NMR shifts in the selenoether complexes are substantially to high frequency of the parent selenoether.

For a common chalcogenoether, from the ^{125}Te{^{1}H} NMR spectra we observe that the bromo complexes all have resonances to high frequency of those of the chlorides, although the geometric isomer has a significant effect, *i.e.* where X is *trans* to X the differences in $\delta(^{125}\mathrm{Te})$ for X = Cl *vs.* X = Br is much less than for the *cis* chelates, where X is *trans* to chalcogen. Finally, we note that the ^{125}Te NMR resonances for the selenoether complexes are typically at a frequency than their thioether analogues. Therefore, the ^{125}Te NMR shifts provide a useful guide to the coordination geometry and donor set present in these complexes.

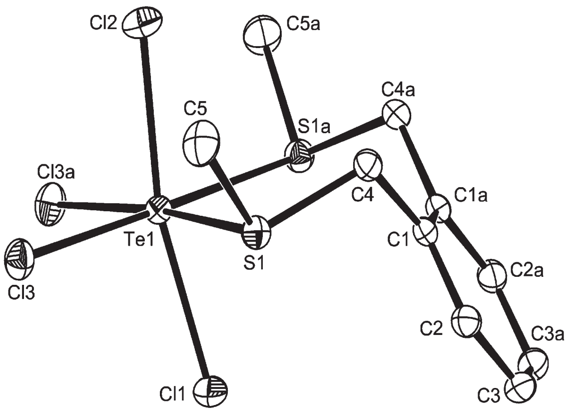

Fig. 9 Crystal structure of $[\mathrm{TeCl_4}\{o\text{-}\mathrm{C_6H_4(CH_2SMe)_2}\}]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: $a = x, 1/2 - y, z$. Selected bond lengths (Å) and angles (°): Te1–Cl1 = 2.5052(8), Te1–Cl2 = 2.5049(8), Te1–Cl3 = 2.4213(6), Te1–S1 = 2.8675(6), Cl1–Te1–Cl2 = 168.57(3), Cl1–Te1–Cl3 = 93.83(2), Cl2–Te1–Cl3 = 94.41(2), Cl3–Te1–Cl3a = 87.62(3), Cl3–Te1–S1a = 169.29(2), Cl1–Te1–S1a = 85.44(2), Cl2–Te1–S1 = 87.92(2), Cl3–Te1–S1 = 81.78(2), S1–Te1–S1a = 108.78(2).

Conclusions

We have prepared and fully characterised the first examples of selenoether complexes of $\mathrm{TeX_4}$ Lewis acids, as well as demonstrating that Se–C bond cleavage occurs in some cases. In contrast, there are no telluroether complexes formed with $\mathrm{TeX_4}$; dimethyltelluride is halogenated to $\mathrm{X_2TeMe_2}$ (X = F, Cl or Br).

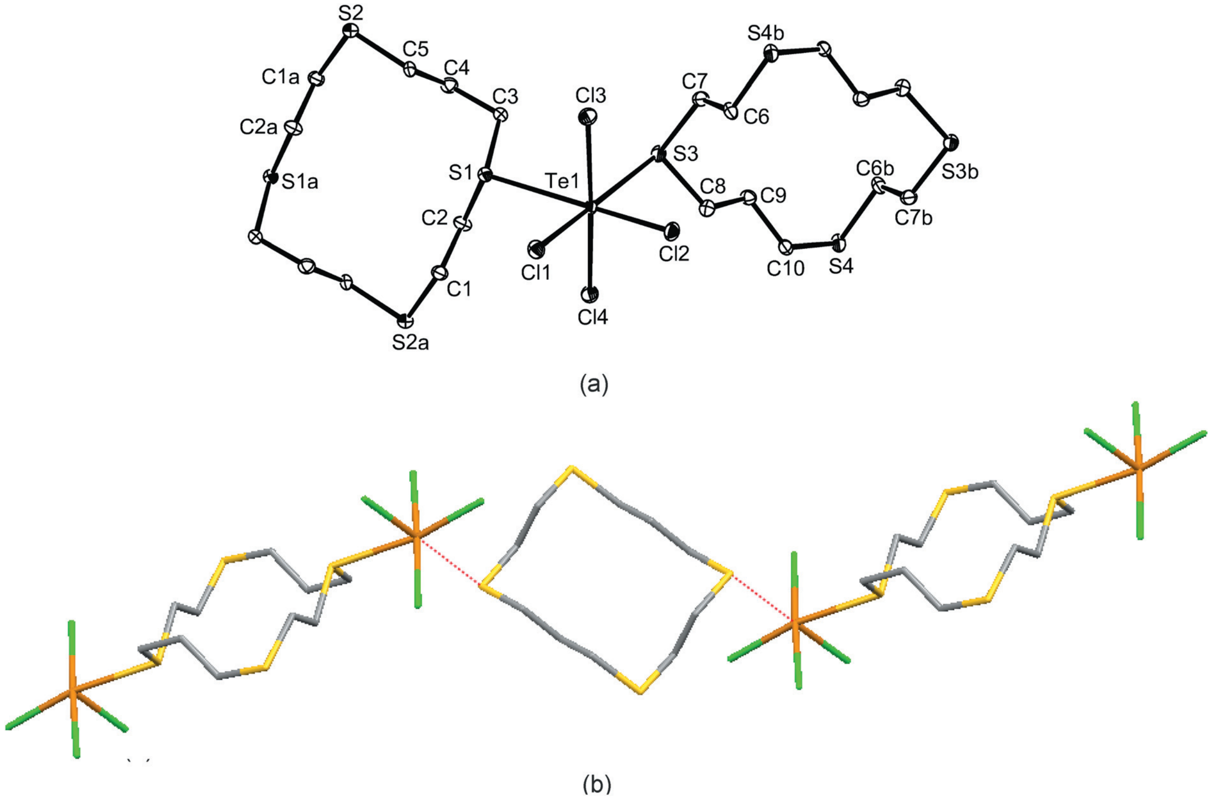

Fig. 10 (a) Crystal structure of a portion of the $[\mathrm{TeCl_4}([14]\mathrm{aneS_4})]_n$ polymer showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operations: $a = -x + 1, -y - 1, -z$; $b = -x + 1, -y, -z$. Selected bond lengths (Å) and angles (°): Te1–Cl1 = 2.3799(9), Te1–Cl2 = 2.3859(9), Te1–Cl4 = 2.492(1), Te1–Cl3 = 2.499(1), Te1–S1 = 2.885(1), Te1–S3 = 3.014(1), Cl1–Te1–Cl2 = 90.58(4), Cl1–Te1–Cl4 = 89.19(3), Cl2–Te1–Cl4 = 92.93(3), Cl1–Te1–Cl3 = 92.76(3), Cl2–Te1–Cl3 = 91.28(3), Cl4–Te1–Cl3 = 175.34(3), Cl1–Te1–S1 = 81.77(3), Cl2–Te1–S1 = 170.40(3), Cl4–Te1–S1 = 92.75(3), Cl3–Te1–S1 = 83.35(3), Cl1–Te1–S3 = 179.03(3), Cl2–Te1–S3 = 90.33(3), Cl4–Te1–S3 = 90.43(3), Cl3–Te1–S3 = 87.55(3), S1–Te1–S3 = 97.36(3). (b) View of the polymeric structure of $[\mathrm{TeCl_4}([14]\mathrm{aneS_4})]_n$.

A range of new structure types has been identified for thioether complexes of Te(IV) halides, which are subtly dependent on the ligand architecture, and include a rare example of bridging by an *o*-phenylene dithioether in $[TeCl_4\{o\text{-}C_6H_4(SMe)_2\}]_n$.

TeF_4 forms stable five-coordinate complexes with hard O-donor phosphine oxides, but much less stable adducts form with thio- or selenoethers. It appears that the TeF_4 is a considerably harder Lewis acid than the heavier halides, and while there is little evidence for a stereochemically active Te-based lone pair in the chloro or bromo complexes, there is a vacant vertex obvious in the $[TeF_4(L)]$ species, which is assumed to be occupied by the lone pair. Systematic shifts in the ^{125}Te NMR spectra of the complexes with halide, chalcogen and geometric isomer are observed, and are consistent with the Te–X bonding dominating the electronic environment at Te(IV).

Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm^{-1}. Raman spectra were obtained using a Perkin-Elmer FT2000R with a Nd:YAG laser. ^{1}H NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 unless otherwise stated, using a Bruker AV300 spectrometer. $^{19}F\{^1H\}$, $^{31}P\{^1H\}$, $^{77}Se\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectra were recorded using a Bruker DPX400 spectrometer and are referenced to $CFCl_3$, 85% H_3PO_4, external, neat $SeMe_2$ and $TeMe_2$ respectively. Electrospray (ES) MS data were obtained from solutions in MeCN using a VG Biotech Platform. Microanalyses were undertaken by Medac Ltd. Solvents were dried by distillation prior to use, CH_2Cl_2 from CaH_2, hexane from sodium benzophenone ketyl. TeF_4 was prepared by heating TeO_2 with SF_4 in a Monel autoclave (120 °C) according to the method of Seppelt and co-workers.[46] Tht, SMe_2, [14]aneS_4, $TeCl_4$ and $TeBr_4$ (Aldrich) were used as received. Ligands $OPPh_3$ and $OAsPh_3$ (Aldrich) were dried *in vacuo* and $OPMe_3$ was freshly sublimed prior to use. $SeMe_2$, $TeMe_2$, $MeSe(CH_2)_3SeMe$, $o\text{-}C_6H_4(SMe)_2$, $o\text{-}C_6H_4(SeMe)_2$, $o\text{-}C_6H_4(CH_2SMe)_2$ and $o\text{-}C_6H_4(CH_2SeMe)_2$ were prepared *via* the literature methods.[47,48] All preparations were performed under an atmosphere of dry N_2 using Schlenk techniques, with samples stored and spectroscopic samples prepared in a dry N_2-purged glove box.

Preparations

$[TeF_4(OPPh_3)]$

A Schlenk tube was loaded with TeF_4 (0.101 g, 4.96×10^{-4} mol) and $OPPh_3$ (0.140 g, 5.03×10^{-4} mol). CH_2Cl_2 (20 mL) was added at room temperature, giving a colourless solution with some undissolved TeF_4. After stirring for approximately 30 min, the mixture had become almost clear. It was then filtered, concentrated *in vacuo* to *ca.* 5 mL, layered with hexane (15 mL) and refrigerated. Colourless crystals suitable for X-ray diffraction formed rapidly. These were collected by filtration, washed with a small amount of hexane and dried *in vacuo*. Yield: 0.132 g, 55%. Required for $C_{18}H_{15}F_4OPTe$: C, 44.9; H, 3.1. Found: C, 45.3; H, 3.3%. ^{1}H NMR ($CDCl_3$, 295 K): 7.4–7.7(m). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): −38.4 (s, [4F]); (178 K): −25.9 (s, [1F], $^1J_{FTe}$ = 2850 Hz), −36.5 (s, [2F], $^1J_{FTe}$ = 1290 Hz), −59.8 (s, [1F], $^1J_{FTe}$ = 1830 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 178 K): 44.8 (s). $^{125}Te\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 178 K): see text. IR (Nujol/cm^{-1}): 501s, 576s, 647s Te–F, 1048s P═O. Raman (cm^{-1}): 571, 620, 647 Te–F.

$[TeF_4(OPMe_3)]$

Analogous procedure, using TeF_4 (0.100 g, 4.91×10^{-4} mol) and $OPMe_3$ (0.048 g, 5.21×10^{-4} mol). Colourless crystals. Yield: 0.088 g, 61%. Required for $C_3H_9F_4OPTe$: C, 12.2; H, 3.1. Found: C, 12.2; H, 3.1. ^{1}H NMR ($CDCl_3$, 298 K): 1.78 (d, [9H], $^2J_{HP}$ = 13 Hz). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): −39.8 (s, [4F]); (183 K): −23.8 (s, [1F], $^1J_{FTe}$ = 2325 Hz), −40.3 (s, [2F], $^1J_{FTe}$ = 1313 Hz), −58.6 (s, [1F], $^1J_{FTe}$ = 1721 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): 64.5 (s); (243 K): 66.1 (s); (183 K): 68.3 (s). $^{125}Te\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 183 K): ~1151 see text. IR (Nujol/cm^{-1}): 480s, 514s, 543s, 624s Te–F, 1032s, P═O. Raman (cm^{-1}): 482, 518, 535, 620 Te–F, 1032 P═O.

$[TeF_4(SMe_2)]$

SMe_2 (*ca.* 2 mL) was condensed directly onto solid TeF_4 (0.05 g, 2.46×10^{-4} mol). Upon warming to room temperature, a colourless solution was obtained. This was stirred for 15 min, and then the excess SMe_2 was removed *in vacuo*. The sticky yellow solid that remained darkened considerably over 24 h at room temperature in the glove box. A freshly prepared sample was dissolved in CD_2Cl_2 for NMR studies. ^{1}H NMR (CD_2Cl_2, 295 K): 2.38 (s); 188 K: 2.38(s). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): −45.9 (br, s); 188 K: −46.6 (br, s, $w_{1/2}$ = 1500 Hz). No $^{125}Te\{^1H\}$ NMR resonance observed at any temperature down to 185 K. IR (Nujol/cm^{-1}): 450 sh, 468 br s, 622 m Te–F.

$[TeF_4(SeMe_2)]$

TeF_4 (0.05 g, 2.46×10^{-4} mol) was suspended in CH_2Cl_2 (10 mL) and stirred at room temperature with $SeMe_2$ (0.02 mL, 0.028 g, 2.58×10^{-4} mol), forming a cloudy yellow solution. After 15 min the volatiles were removed *in vacuo* to leave a sticky yellow solid which darkened over a few hours at room temperature. A freshly prepared sample was used for spectroscopic studies. ^{1}H NMR (CD_2Cl_2, 295 K): 2.43 (s); 188 K: 2.45 (s). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): −43.4 (br, s); 188 K: −41.7 (br, s, $w_{1/2}$ = 1600 Hz). No $^{77}Se\{^1H\}$ or $^{125}Te\{^1H\}$ NMR resonance observed at any temperature down to 185 K. IR (Nujol/cm^{-1}): 447 s, 470 br s, 623 m Te–F.

trans-$[TeCl_4(SeMe_2)_2]$

$TeCl_4$ (0.268 g, 9.95×10^{-4} mol) was suspended in THF (20 mL) and cooled to 0 °C with the aid of an external ice-bath. With stirring, $SeMe_2$ (0.09 mL, 0.127 g, 1.16×10^{-3} mol) was added, causing a rapid colour change to very dark orange-black. After stirring for 30 min, the mixture was concentrated *in vacuo* to *ca.* 5 mL, filtered to remove any solids and the filtrate was placed in the freezer. Small almost black crystals suitable for

X-ray diffraction appeared over a few days. Yield: 0.262 g, 54%. Required for $C_4H_{12}Cl_4Se_2Te$: C, 9.9; H, 2.5. Found: C, 9.9; H, 2.3%. ^1H NMR ($CDCl_3$, 298 K): 2.59 (s). $^{125}Te\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 183 K): 1280 (s). $^{77}Se\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 183 K): 233 (s). IR (Nujol/cm^{-1}): 246 br Te–Cl. Raman (cm^{-1}): 280 s, 254 m Te–Cl.

trans-[$TeBr_4(SeMe_2)_2$]

Analogous procedure, using $TeBr_4$ (0.440 g, 9.84×10^{-4} mol) and $SeMe_2$ (0.08 mL, 0.113 g, 1.04×10^{-3} mol). Small, almost black crystals of X-ray quality formed over a few days in the freezer. Yield: 0.181 g, 54%. Required for $C_4H_{12}Br_4Se_2Te$: C, 7.2; H, 1.8. Found: C, 7.1; H, 1.9%. ^1H NMR ($CDCl_3$, 298 K): 2.66 (s). $^{125}Te\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 183 K): 1317 (s). $^{77}Se\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 183 K): 226 (s).

[$TeCl_4\{MeSe(CH_2)_3SeMe\}$]

$TeCl_4$ (0.271 g, 1.01×10^{-3} mol) was suspended in CH_2Cl_2 (20 mL), and the mixture was cooled to 0 °C with the aid of an external ice-bath. With stirring, $MeSe(CH_2)_3SeMe$ (0.269 g, 1.17×10^{-3} mol) was added, which caused a rapid colour change to orange-brown, concomitant with the formation of an orange precipitate. After stirring for approximately 1 h, the amount of solid had increased, and this was collected by filtration and dried *in vacuo*. Yield: 0.373 g, 75%. This compound has very low solubility in all common non- or weakly-coordinating solvents, and darkens rapidly at room temperature. Required for $C_5H_{12}Cl_4Se_2Te$: C, 12.0; H, 2.4. Found: C, 12.0; H, 2.4%.

[$TeBr_4\{MeSe(CH_2)_3SeMe\}$]

$TeBr_4$ (0.225 g, 5.03×10^{-4} mol) was dissolved in THF (20 mL), and the solution was cooled to 0 °C with the aid of an external ice-bath. With stirring, $MeSe(CH_2)_3SeMe$ (0.151 g, 6.56×10^{-4} mol) was added, giving an opaque red-black solution. After stirring for 15 min, the mixture was concentrated *in vacuo* to *ca.* 10 mL, which caused the precipitation of a deep-red solid. This was collected by filtration and dried *in vacuo*. Yield: 0.160 g, 47%. Required for $C_5H_{12}Br_4Se_2Te$: C, 8.9; H, 1.8. Found: C, 8.9; H, 1.8%. ^1H NMR (CD_2Cl_2, 298 K): 2.10 (br m, [2H], $CH_2CH_2CH_2$), 2.21 (br s, [6H], $SeCH_3$), 2.83 (m, [4H], $CH_2CH_2CH_2$). $^{125}Te\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 183 K): 1455 (s). $^{77}Se\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 183 K): 169 (s).

[$TeCl_4\{o\text{-}C_6H_4(SeMe)_2\}$]

$TeCl_4$ (0.271 g, 1.01×10^{-3} mol) was suspended in CH_2Cl_2 (20 mL), and the mixture was cooled to 0 °C. With stirring, o-$C_6H_4(SeMe)_2$ (0.263 g, 9.97×10^{-4} mol) was added giving a very deep red solution. After stirring for approximately 30 min, the solution had become almost clear, and was then concentrated *in vacuo* to *ca.* 10 mL. The resulting dark red precipitate, was collected by filtration, washed with a small amount of CH_2Cl_2 and dried *in vacuo*. Storage of the filtrate at *ca.* −18 °C yielded single crystals suitable for X-ray diffraction. Yield: 0.388 g, 73%. Required for $C_8H_{10}Cl_4Se_2Te$: C, 18.0; H, 1.9. Found: C, 17.3; H, 2.3%. ^1H NMR (CD_2Cl_2, 298 K): 2.74 (s, [6H], Me), 7.39 (m, [2H], aromatic H), 7.49 (m, [2H], aromatic H). $^{77}Se\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2, 298 K): 272; (193 K): 291. IR (Nujol/cm^{-1}): 235, 287 Te–Cl. Raman (cm^{-1}): 226, 244, 272, 296 Te–Cl.

Reaction of TeX_4 (X = F, Cl or Br) with $TeMe_2$

$^1H/^{19}F$ NMR experiments

A 5 mm diameter NMR tube was loaded with *ca.* 0.01 g of the appropriate tellurium halide. Against a flow of N_2, CD_2Cl_2 was added followed by *ca.* 0.01 mL of $TeMe_2$.

$^{125}Te\{^1H\}$ NMR experiments

A 10 mm diameter NMR tube was loaded *ca.* 0.03 g of the appropriate tellurium halide. Against a flow of N_2, a mixture of CD_2Cl_2 and CH_2Cl_2 was added, followed by *ca.* 0.02 mL of $TeMe_2$.

In all cases an immediate black precipitate formed, identified as elemental Te by powder XRD. The supernatants were examined by multinuclear NMR spectroscopy at 295 K, each showing only one significant new resonance in addition to residual $TeMe_2$ [^1H NMR (CD_2Cl_2): 1.91 (s, $^1J_{TeH}$ = 22 Hz); $^{125}Te\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 295 K): −16.9 (s); note the substantial solvent shift for the ^{125}Te resonance compared to neat $TeMe_2$, $\delta = 0$[49]). The small variations between the ^{125}Te chemical shifts reported in the present work and the literature data are due to similar sensitivities to solvent and concentration, but set against the very wide chemical shift range of tellurium are unequivocal confirmation of the products.]

X = F: ^1H NMR (CD_2Cl_2 295 K): 2.57 (t, $^1J_{TeH}$ = 7 Hz). $^{19}F\{^1H\}$ (CD_2Cl_2 295K): −123.5(s, $^1J_{125TeF}$ = 860 Hz). $^{125}Te\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 295 K): +1207 (t, $^1J_{125TeF}$ = 860 Hz). [Lit:[35] ^1H NMR ($CDCl_3$ 298 K): 2.57 (t, $^1J_{TeH}$ = 7 Hz). $^{19}F\{^1H\}$ ($CDCl_3$ 298 K): −124.9 (s, $^1J_{125TeF}$ = 871 Hz). Proton coupled ^{125}Te NMR ($CDCl_3$, 298 K): +1232 (t of sept)].

X = Cl: ^1H NMR (CD_2Cl_2 295 K): 3.12 (s, $^1J_{TeH}$ = 25 Hz). $^{125}Te\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 295 K): +739 (s). [Lit.[34] (neat liquid): ^1H NMR (295 K): 3.13 (s, $^1J_{TeH}$ = 26 Hz). ^{125}Te NMR (neat liquid by $INDOR_2$, 295 K): +749 (s)].

X = Br: ^1H NMR (CD_2Cl_2 295 K): 3.20 (s, $^1J_{TeH}$ = 25 Hz). $^{125}Te\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 295 K): +653 (s). [Lit.[34] (neat liquid): ^1H NMR (295 K): 3.19 (s, $^1J_{TeH}$ = 26 Hz). ^{125}Te NMR (neat liquid by $INDOR_2$, 295 K): +669 (s)].

The reaction mixture from the $TeBr_4$ reaction deposited colourless crystals over a few days which were identified as the hydrolysis product $Me_2BrTe(\mu\text{-}O)TeMe_2Br$ by an X-ray crystal structure.

trans-[$TeCl_4(tht)_2$]

$TeCl_4$ (0.269 g, 9.98×10^{-4} mol) was suspended in CH_2Cl_2 (20 mL) at room temperature, and tht (0.175 mL, 0.175 g, 1.98×10^{-3} mol) was added, causing a rapid colour change to orange-brown. After heating briefly, the mixture was stirred at room temperature for approximately 1 h, and then filtered.

The filtrate was concentrated *in vacuo* to *ca.* 7 mL, over-layered with hexane (20 mL) and stored at *ca.* −18 °C. A large mass of nearly black X-ray quality crystals appeared over a period of a few days. These were collected by filtration, washed with hexane and dried *in vacuo*. Yield: 0.180 g, 40%. Required for $C_8H_{16}Cl_4S_2Te$: C, 21.5; H, 3.6. Found: C, 20.9; H, 3.3%. ^1H NMR (CD_2Cl_2, 298 K): 2.10 (m, [8H], CH_2), 3.25 (m, [8H], CH_2). $^{125}Te\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2): 1500 (295 K); 1475 (183 K). IR (Nujol/cm^{-1}): 248 br Te–Cl. Raman (cm^{-1}): 255, 283 Te–Cl.

trans-[TeBr$_4$(tht)$_2$]

Analogous procedure, using $TeBr_4$ (0.224 g, 5.01×10^{-4} mol) and tht (0.09 mL, 0.09 g, 1.02×10^{-3} mol). Black crystals. Yield: 0.182 g, 58%. Required for $C_8H_{16}Br_4S_2Te$: C, 15.4; H, 2.6. Found: C, 15.5; H, 2.5%. ^1H NMR (CD_2Cl_2, 298 K): 2.10 (m, [8H], CH_2), 3.28 (m, [8H], CH_2). $^{125}Te\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 193 K): 1507.

[TeCl$_4${MeS(CH$_2$)$_3$SMe}]

$TeCl_4$ (0.265 g, 9.84×10^{-4} mol) was suspended in CH_2Cl_2 (20 mL) and stirred at room temperature. $MeS(CH_2)_3SMe$ (0.14 mL, 0.14 g, 1.04×10^{-3} mol) was added, causing a rapid change from colourless to bright orange. After stirring for 1 h, the mixture was filtered to remove excess $TeCl_4$. The orange filtrate was concentrated *in vacuo* to *ca.* 5 mL, which caused the precipitation of an orange solid. Addition of hexane (20 mL) caused further precipitation, and the product was collected by filtration, washed with hexane and dried *in vacuo*. Yield: 0.235 g, 59%. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a CH_2Cl_2 solution. Required for $C_5H_{12}Cl_4S_2Te$: C, 14.8; H, 3.0. Found: C, 14.1; H, 2.6%. ^1H NMR ($CDCl_3$, 298 K): 2.28 (quintet, [2H], CH_2), 2.51 (s, 6H, Me), 3.06 (t, [4H], SCH_2); (400 MHz, CD_2Cl_2, 183 K): 2.32 (br, [2H], CH_2), 2.56 (br s, [6H], Me), 3.13 (br, [4H], SCH_2). $^{125}Te\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 203 K): 1517 (s). IR (Nujol/cm^{-1}): 248, 261, 278, 290 Te–Cl.

[TeBr$_4${MeS(CH$_2$)$_3$SMe}]

Analogous procedure, using $TeBr_4$ (0.446 g, 9.97×10^{-4} mol) and $MeS(CH_2)_3SMe$ (0.14 mL, 0.14 g, 1.04×10^{-3} mol). Bright red solid. Yield: 0.171 g, 30%. ^1H NMR ($CDCl_3$, 298 K): 2.28 (quintet, [2H], CH_2), 2.58 (s, [6H], Me), 3.05 (t, [4H], SCH_2); (400 MHz, CD_2Cl_2, 183 K): 2.34 (br, [2H], CH_2), 2.69 (br s, [6H], Me), 3.12 (br s, [4H], SCH_2). $^{125}Te\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 223 K): 1705 (s).

[TeCl$_4${*o*-C$_6$H$_4$(SMe)$_2$}]$_n$

$TeCl_4$ (0.265 g, 9.84×10^{-4} mol) was suspended in CH_2Cl_2 (20 mL), and the mixture was cooled to 0 °C with the aid of an external ice-bath. With stirring, *o*-$C_6H_4(SMe)_2$ (0.15 mL, 0.17 g, 9.98×10^{-4} mol) was added, which caused a rapid change from colourless to intense orange-yellow. The mixture was allowed to stir at 0 °C for a further 2 h, warmed to room temperature for a period of approximately 30 min and then filtered to remove any unreacted $TeCl_4$. The clear orange filtrate was concentrated *in vacuo* to *ca.* 5 mL, layered with hexane (15 mL) and refrigerated. Large bright-red crystals formed over a few days, which were collected by filtration, washed with hexane and dried *in vacuo*. Yield: 0.254 g, 59%. Required for $C_8H_{10}Cl_4S_2Te$: C, 21.8; H, 2.3. Found: C, 21.3; H, 2.6%. ^1H NMR (300 MHz, $CDCl_3$, 298 K): 2.69 (s, [6H], Me), 7.32 (m, [4H], aromatic H); (400 MHz, CD_2Cl_2, 183 K): 2.72 (s, [6H], Me), 7.33 (br, [2H], aromatic H), 7.37 (br, [2H], aromatic H). IR (Nujol/cm^{-1}): 250, 282, 323, 337 Te–Cl.

[TeCl$_4${*o*-C$_6$H$_4$(CH$_2$SMe)$_2$}]

A Schlenk tube was loaded with $TeCl_4$ (0.266 g, 9.87×10^{-4} mol) and *o*-$C_6H_4(CH_2SMe)_2$ (0.201 g, 1.01×10^{-3} mol). CH_2Cl_2 (20 mL) was added at room temperature, causing the rapid formation of an orange suspension. This was stirred for a further 2 h, then filtered. Owing to the low solubility of this compound, it was washed several times with CH_2Cl_2 to separate it from any unreacted $TeCl_4$. The orange extracts were combined and concentrated *in vacuo*, causing the precipitation of an orange solid. After addition of hexane (20 mL), the product was collected by filtration, washed with hexane and dried *in vacuo*. Yield: 0.217 g, 47%. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a CH_2Cl_2 solution. Required for $C_{10}H_{14}Cl_4S_2Te$: C, 25.7; H, 3.0. Found: C, 26.2; H, 3.4%. ^1H NMR (CD_3CN, 298 K): 2.40 (s, [6H], Me), 4.04 (s, [4H], CH_2), 7.32 (m, [2H], aromatic H), 7.39 (m, [2H], aromatic H); (400 MHz, CD_2Cl_2, 183 K): 2.65 (br s, [6H], Me), 4.07 (br s, [4H], CH_2), 7.40 (br, [2H], aromatic H), 7.46 (br, [2H], aromatic H). $^{125}Te\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 193 K): 1433 (s). IR (Nujol/cm^{-1}): 256, 265, 284, 303 Te–Cl.

[TeBr$_4${*o*-C$_6$H$_4$(CH$_2$SMe)$_2$}]

A Schlenk tube was loaded with $TeBr_4$ (0.445 g, 9.95×10^{-4} mol) and *o*-$C_6H_4(CH_2SMe)_2$ (0.203 g, 1.02×10^{-3} mol). THF (20 mL) was added, and with stirring the mixture was heated to reflux. The resulting clear red solution was filtered while hot. Upon cooling, the filtrate began to deposit a deep-red solid. Concentration *in vacuo* to *ca.* 5 mL caused further precipitation, leaving the supernatant almost colourless. The product was collected by filtration, washed with hexane (10 mL) and dried *in vacuo*. Yield: 0.400 g, 62%. Required for $C_{10}H_{14}Br_4S_2Te$: C, 18.6; H, 2.2. Found: C, 19.0; H, 2.1%. ^1H NMR (CD_3CN, 298 K): 2.07 (s, [6H], Me), 3.88 (s, [4H], CH_2), 7.24 (m, [2H], aromatic H), 7.28 (m, [2H], aromatic H).

[TeCl$_4$([14]aneS$_4$)]$_n$

$TeCl_4$ (0.077 g, 2.86×10^{-4} mol) and [14]aneS_4 (0.078 g, 2.90×10^{-4} mol) were loaded into a Schlenk tube, and THF (20 mL) was added forming a clear, colourless solution. After stirring at room temperature for one hour, the THF was removed *in vacuo* leaving a yellow solid residue. Addition of CH_2Cl_2 (20 mL) gave a yellow suspension, and the solid yellow product was removed by filtration and washed with CH_2Cl_2.

Concentration of the filtrate and storage at *ca.* −18 °C furnished a few small yellow crystals suitable for X-ray diffraction. IR (Nujol/cm^{-1}): 240 br, 265, 278, 314 Te–Cl. Raman (cm^{-1}): 262, 280, 343 Te–Cl.

X-ray crystallography

Summary details of the crystallographic data collection and refinement are given in Table 2. Crystals were obtained as described above. Data collection used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating anode generator with VHF Varimax optics (100 μm focus) with the crystal held at 100 K (N_2 cryostream) or a Bruker-Nonius FR591 rotating anode diffractometer fitted with confocal mirrors and with the crystal held at 120 K (N_2 cryostream)([$TeCl_4\{MeS(CH_2)_3SMe\}$], [$TeCl_4\{o\text{-}C_6H_4(SMe)_2\}]_n$). Structure solution and refinement were straightforward,[50,51] except as detailed below, with H atoms being placed in calculated positions using the default C–H distance. For [$TeCl_4\{MeS(CH_2)_3SMe\}$] the systematic absences suggested space group $I4_1/a$ (Laue group $4/m$), but there was a query over the *hhl* reflections which suggested space group $I4_1/amd$ (Laue group $4/mmm$). In practice, attempts to refine the structure in $I4_1/amd$

Table 2 Crystal data and structure refinement details[a]

Compound	[$TeF_4(OPMe_3)$]	[$TeF_4(OPPh_3)$]	[$TeCl_4(SeMe_2)_2$]	[$TeBr_4(SeMe_2)_2$]	[$TeCl_4\{o\text{-}C_6H_4(SeMe)_2\}$]	$(BrMe_2Te)_2O\cdot 0.6CH_2Cl_2$	[$TeCl_4\{o\text{-}C_6H_4(SMe)_2\}]_n$
Formula	$C_3H_9F_4OPTe$	$C_{18}H_{15}F_4OPTe$	$C_4H_{12}Cl_4Se_2Te$	$C_4H_{12}Br_4Se_2Te$	$C_8H_{10}Cl_4Se_2Te$	$C_4H_{12}Br_2OTe_2\cdot 0.6CH_2Cl_2$	$C_8H_{10}S_2Cl_4Te$
M	295.67	481.87	487.46	665.30	533.48	542.11	439.68
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Cubic	Orthorhombic
Space group (no.)	$P2_12_12_1$ (19)	$P2_1/n$ (14)	$P2_1/n$ (14)	$P2_1/n$ (14)	$P2_1/m$ (11)	$Ia\bar{3}d$ (230)	$Pna2_1$ (33)
a (Å)	6.500(4)	9.933(3)	6.487(2)	6.720(2)	6.804(3)	25.509(3)	10.038(2)
b (Å)	10.790(5)	18.151(5)	12.872(4)	13.138(4)	10.725(5)	25.509(3)	14.622(2)
c (Å)	12.442(8)	10.604(7)	8.215(3)	8.486(3)	9.969(5)	25.509(3)	9.5760(10)
α (°)	90	90	90	90	90	90	90
β (°)	90	113.90(4)	108.245(8)	107.967(5)	99.156(7)	90	90
γ (°)	90	90	90	90	90	90	90
U (Å^3)	872.6(9)	1747.9(14)	651.4(4)	712.7(4)	718.3(6)	16 599(4)	1405.5(4)
Z	4	4	2	2	2	48	4
μ(Mo-K$_\alpha$) (mm^{-1})	3.598	1.836	8.641	18.361	7.850	10.187	3.140
F(000)	552	936	448	592	492	11 674	840
Total number reflns	2336	7751	3103	2502	3583	34 117	16 155
R_{int}	0.019	0.018	0.019	0.020	0.028	0.026	0.032
Unique reflns	1815	3965	1475	1387	1717	1585	3181
No. of params, restraints	94, 0	226, 0	54, 0	54, 0	74, 0	54, 0	138, 1
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.014, 0.033	0.018, 0.043	0.016, 0.034	0.020, 0.035	0.034, 0.080	0.029, 0.077	0.020, 0.038
R_1, wR_2 (all data)	0.014, 0.034	0.020, 0.044	0.019, 0.034	0.023, 0.036	0.045, 0.084	0.031, 0.078	0.022, 0.039

[a] Common items: temperature = 100 K; wavelength (Mo-K$_\alpha$) = 0.71073 Å; θ(max) = 27.5°. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

Compound	[$TeCl_4\{MeS(CH_2)_3SMe\}$]	[$TeCl_4\{o\text{-}C_6H_4(CH_2SMe)_2\}$]	[$TeCl_4(tht)_2$]	[$TeBr_4(tht)_2$]	[$Br_3(tht)Te(\mu\text{-}Br)_2TeBr_3(tht)$]	[$TeCl_4([14]aneS_4)]_n$
Formula	$C_5H_{12}Cl_4S_2Te$	$C_{10}H_{14}Cl_4S_2Te$	$C_8H_{16}Cl_4S_2Te$	$C_8H_{16}Br_4S_2Te$	$C_8H_{16}Br_8S_2Te_2$	$C_{10}H_{20}Cl_4S_4Te$
M	405.67	467.73	445.73	623.57	1070.81	537.90
Crystal system	Tetragonal	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group (no.)	$I4_1/a$ (88)	*Pnma* (62)	$P2_1/n$ (14)	$P2_1/n$ (14)	$P\bar{1}$ (2)	$P2_1/n$ (14)
a (Å)	9.881(3)	19.451(3)	7.882(3)	8.624(2)	8.502(3)	9.080(2)
b (Å)	9.881(3)	11.603(2)	9.450(3)	7.5542(12)	8.623(3)	20.950(5)
c (Å)	26.388(8)	7.1757(10)	10.280(5)	12.754(2)	8.734(3)	9.990(4)
α (°)	90	90	90	90	71.099(5)	90
β (°)	90	90	97.08(2)	109.630(5)	87.043(6)	96.068(7)
γ (°)	90	90	90	90	72.783(5)	90
U (Å^3)	2576.4(14)	1619.5(4)	759.8(5)	782.6(3)	577.9(3)	1889.8(9)
Z	8	4	2	2	1	4
μ(Mo-K$_\alpha$) (mm^{-1})	3.416	2.732	2.905	12.350	16.523	2.567
F(000)	1552	904	432	576	480	1056
Total number reflns	12 362	12 485	4432	5336	5419	13 343
R_{int}	0.054	0.029	0.019	0.024	0.023	0.044
Unique reflns	1596	1937	1721	1774	2630	4293
No. of params, restraints	58, 0	83, 0	70, 0	70, 0	91, 0	172, 0
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.041, 0.067	0.020, 0.042	0.013, 0.031	0.018, 0.041	0.019, 0.037	0.032, 0.060
R_1, wR_2 (all data)	0.042, 0.067	0.021, 0.043	0.014, 0.032	0.020, 0.042	0.022, 0.038	0.047, 0.065

failed, while refinement in space group $I4_1/a$ using a TWIN/BASF command led to successful refinement. The structure of $(BrMe_2Te)_2O$ was found to contain a partially occupied (0.6) disordered CH_2Cl_2 solvent molecule which was evident as three Q peaks close together which were modelled as fractional Cl atoms. There were two recognisable CH_2Cl_2 residues (from Cl⋯Cl distances). Cl1⋯Cl1′ (atom C3 was located) and Cl2⋯Cl3 as overlapping solvate molecules (no C atom was located for this).

Acknowledgements

We thank EPSRC for support (EP/I010890/1) and Dr M. Webster for assistance with the X-ray crystallographic analyses.

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