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Synthesis, characterisation and coordinating properties of the small ring S_2Te-donor macrocycles [9]aneS_2Te, [11]aneS_2Te and [12]aneS_2Te

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The reaction of Na_2Te with various α,ω-dichlorodithioether reagents in thf–NH_3(l) at *ca.* −78 °C produces moderate yields of the [1+1] cyclisation products, [9]aneS_2Te (1,4-dithia-7-telluracyclononane), [11]aneS_2Te (1,4-dithia-8-telluracycloundecane) and [12]aneS_2Te (1,5-dithia-9-telluracyclododecane), together with polymer. These new small ring macrocycles may be purified by flash column chromatography on silica (11-and 12-membered rings) or by recrystallisation from MeOH–thf (9-membered ring), affording yellow waxy solids. The products have been characterised by NMR (^{1}H, ^{13}C{^{1}H} and ^{125}Te{^{1}H}) and IR spectroscopy, mass spectrometry and the crystal structures of [11]aneS_2Te and [12]aneS_2Te have been obtained. The more stable organo-Te(IV) derivatives [*n*]aneS_2TeI_2 (*n* = 11 or 12) and [*n*]aneS_2TeMeI (*n* = 9, 11 or 12) are obtained in high yield as powdered solids by reaction with I_2 or MeI and these have been characterised similarly. A crystal structure of [12]aneS_2TeI_2 has also been determined and is compared with the parent macrocycle. The synthesis of [9]aneS_2Te is more sensitive to the precise reaction conditions than the others, and is accompanied by the formation of the ring-contraction products 1-thia-4-telluracyclohexane and 1,4-dithiane. These too have been characterised by NMR and IR spectroscopy and by mass spectrometry. The former has been unambiguously identified by X-ray crystallography and its Te(IV) methiodide derivative has been prepared for comparison. The ligating properties of the new dithiatellura-macrocycles have been investigated with a variety of transition metal species giving *fac*-[Mn(CO)$_3$(L)]CF_3SO_3, *cis*-[MCl_2(L)] (M = Pd or Pt), [Rh(Cp*)(L)]-(PF_6)$_2$, [Cu(L)]BF_4 and [Ag(L)]CF_3SO_3. Where possible, the mode of coordination has been established by spectroscopic methods, ring-size effects established and the data compared with other complexes incorporating related cyclic and acyclic ligands.

Introduction

Despite organotellurium compounds having a history dating back to 1840, it still remains a relatively little studied area of modern chemistry. Much of the difficulty associated with this chemistry arises from the weakness of Te–H and Te–C bonds and is exemplified by the fact that the first chelating bidentate telluroether compounds were reported only in the late 1980s,[1–4] and prior to our description of routes to RTe(CH_2)$_3$Te(CH_2)$_3$-TeR (R = Me or Ph) in 2000,[5] the only known tritelluroethers were the tripodal MeC(CH_2TeR)$_3$.[2,6] Routes associated with the preparation of thio- and seleno-ether ligands cannot generally be employed for telluroethers. The analogous tellurium chemistry associated with thiols is almost unknown. Similarly, the well-known reduction of RSeCN to RSe^- functions using Na/NH_3(l) as a route to form a variety of multidentate and macrocyclic selenoether ligands is not easily transferred into tellurium chemistry. The analogous tellurocyanates are generally unstable and although systems such as ArCH_2TeCN (Ar = 4-ClC_6H_4 and 4-$MeOC_6H_4$) are known, attempts to synthesise ditellurocyanates have failed.[7] Therefore, the preparation of species such as NaTe(CH_2)$_3$TeNa is far more challenging than first inspection would suggest. Further difficulties often arise from attempts to carry out reaction chemistry with tellurium-containing fragments since reaction at tellurium (Te–C cleavage) is frequently observed in preference to the required transformation.

However, the preparation of new telluroether ligands is of considerable interest because of the rich coordination chemistry these ligands possess and their enhanced σ-donor properties to low valent metal centres.[8] The preparation of medium and large ring organo-tellurium compounds is of particular interest since this will enable tellurium to be studied in a macrocyclic environment. There is just one report concerning a tritelluroether macrocycle, [12]aneTe_3 (1,5,9-tritelluracyclododecane) formed (apparently serendipitously) from 1,5-ditelluracyclooctane, although no data have been published on its associated metal ion chemistry.[9] There is also an example of a tellurium containing macrocyclic Schiff base with Te_2N_4 donor set in a 22-membered ring.[10]

In this paper we describe the preparation and characterisation of the three small ring S_2Te-donor macrocycles, [9]ane-S_2Te (1,4-dithia-7-telluracyclononane), [11]aneS_2Te (1,4-dithia-8-telluracycloundecane) and [12]aneS_2Te (1,5-dithia-9-telluracyclododecane), together with an examination of their ligating properties towards a series of transition metal fragments. The crystal structures of the parent compounds [11]aneS_2Te and [12]aneS_2Te, the diiodo Te(IV) derivative [12]aneS_2TeI_2 and the ring contraction product, 1-thia-4-telluracyclohexane, are also described. We have already reported on our preliminary results in this area.[11] Few related compounds have been reported prior to this work, although 1-thia-4-telluracyclohexane has been obtained *via* the low yielding reaction of bis(2-chloroethyl)sulfide with Na_2Te in water using high dilution techniques.[12] We have described the preparation and coordinating properties of the related open-chain compound MeS(CH_2)$_3$Te(CH_2)$_3$SMe.[13]

Results and discussion

The routes employed for the thia–tellura-macrocycle syntheses are illustrated in Scheme 1.

[11]aneS_2Te: The dichloro-compound Cl(CH_2)$_3$S(CH_2)$_2$-S(CH_2)$_3$Cl was prepared according to the literature procedure.[14] Addition of HS(CH_2)$_2$SH dropwise to a solution of sodium in ethanol followed by dropwise addition of Cl(CH_2)$_3$OH gave the compound HO(CH_2)$_3$S(CH_2)$_2$S(CH_2)$_3$OH, after work up, as a white waxy solid. Addition of $SOCl_2$ to a solution of this species in $CHCl_3$ subsequently gave Cl(CH_2)$_3$S(CH_2)$_2$S(CH_2)$_3$Cl

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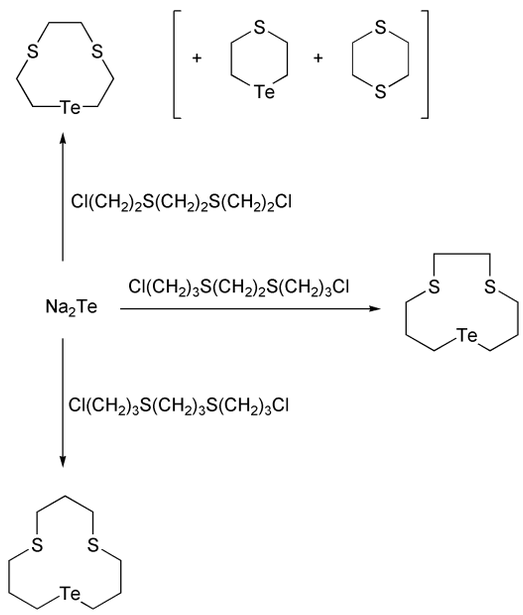
Table 1 NMR spectroscopic data for the Te-containing rings ($CDCl_3$)

Compound	^{1}H δ (ppm)		^{13}C{^{1}H} δ (ppm)		^{125}Te{^{1}H} δ (ppm)
1,thia-4-telluracyclohexane	3.08 [a]	CH_2Te	−5.8	CH_2Te	264
		CH_2S	30.1	CH_2S	
[9]aneS_2Te	2.84, s	SCH_2CH_2S	38.9	CH_2S	345
	2.93, t	SCH_2CH_2Te	32.9	CH_2S	
	3.06, t	CH_2Te	2.9	CH_2Te	
[11]aneS_2Te	2.05, quin.	$CH_2CH_2CH_2$	34.7	$CH_2CH_2CH_2$	234
	2.67, t	CH_2Te	2.2	CH_2Te	
	2.73, t	$SCH_2CH_2CH_2Te$	32.6	CH_2S	
	2.74, s	SCH_2CH_2S	32.9	CH_2S	
[12]aneS_2Te	1.86, quin.	$SCH_2CH_2CH_2S$	27.7	$SCH_2CH_2CH_2S$	217
	2.06, quin.	$SCH_2CH_2CH_2Te$	33.5	$SCH_2CH_2CH_2Te$	
	2.66, t	CH_2Te	1.0	CH_2Te	
	2.73, t	CH_2S	29.0	CH_2S	
	2.78, t	CH_2S	30.1	CH_2S	

[a] AA′BB′ multiplet.



Scheme 1

as a brown oil [**CAUTION:** this dichloro derivative and the other analogues are powerful vesiccants and may cause severe blistering upon skin contact]. The macrocyclic ligand was prepared *via* the addition of this dichloro-species in THF to a solution of Na_2Te prepared in NH_3(l) at −78 °C. The ammonia was allowed to boil off overnight and the resulting mixture hydrolysed and extracted with CH_2Cl_2 to give a red oil. Purification by silica flash chromatography using ethyl acetate : hexane of 1 : 3 gave the ligand as a light yellow solid in 28% yield.

The ^{125}Te{^{1}H} NMR spectrum showed one peak at δ 234, a similar shift to that obtained for the acyclic $MeS(CH_2)_3Te(CH_2)_3SMe$.[13] The EIMS showed a cluster of peaks at m/z = 306, with the correct isotope pattern, corresponding to the molecular ion $[C_8H_{16}S_2{}^{130}Te]^+$ (m/z = 306), along with fragmentation peaks associated with $[Te(CH_2)_3S]^+$ due to the loss of $(CH_2)_3S(CH_2)_2$ through cleavage of Te–C and S–C bonds. The EI mass spectrum of the crude product was also obtained in order to look for evidence of larger ring systems, *e.g.* the [2+2] cyclisation product [22]aneS_4Te_2. However, the isotope pattern and m/z for the highest mass peak we observed corresponded to [11]aneS_2Te. The NMR spectroscopic data are presented in Table 1. The expected coupling pattern is observed in the ^{1}H NMR spectrum, and although the two signals from the SCH_2 groups overlap, the overall singlet and triplet pattern may be clearly discerned. The ^{13}C{^{1}H} NMR spectrum shows four resonances corresponding to the four carbon environments, with the shift for δ(TeCH_2) markedly to low frequency compared to the other three resonances, consistent with other telluroether ligands and the related acyclic compound $MeS(CH_2)_3Te(CH_2)_3SMe$.[4,13]

[12]aneS_2Te: This compound was prepared similarly *via* the addition of a solution of $Cl(CH_2)_3S(CH_2)_3S(CH_2)_3Cl$ in THF to Na_2Te in NH_3(l) at −78 °C. Upon work up and purification *via* flash column chromatography using ethyl acetate : hexane of 1 : 3, a light yellow oily solid was obtained in 18% yield. The ^{125}Te{^{1}H} NMR spectrum showed one peak at δ 217, consistent with a $Te\{(CH_2)_3\}_2$ unit. The EI mass spectrum showed a cluster of peaks at m/z = 320, corresponding to the molecular ion (m/z for $[C_9H_{18}S_2{}^{130}Te]^+$ = 320) along with peaks associated with the loss of $[S(CH_2)_3]$ and $[(CH_2)_3S(CH_2)_3]$. The ^{1}H, ^{13}C{^{1}H} NMR data (Table 1), together with elemental analysis, confirmed the purity of the ligand. We also observed a side-product in the crude product from some of the preparations, with δ(^{125}Te) 126. This is tentatively attributed to a ditelluride on the basis of mass spectrometry (major species corresponds to $[C_9H_{18}S_2Te_2]^+$), and could be removed by chromatography as above.

The crystal structures of [11]aneS_2Te (Fig. 1, Table 2) and [12]aneS_2Te (Fig. 2, Table 3) have been determined and establish unambiguously the formation of the [1+1] cyclisation products from these reactions. The structures show discrete molecular species, with no significant intermolecular contacts. The crystal structure of the related trithia crown, [12]aneS_3 was reported some years ago[15] and shown to adopt an approximately square arrangement with one S atom at a corner and the other two S atoms on edges. Analysis of the torsion angles in this molecule revealed that four out of six CSCC torsions and four out of

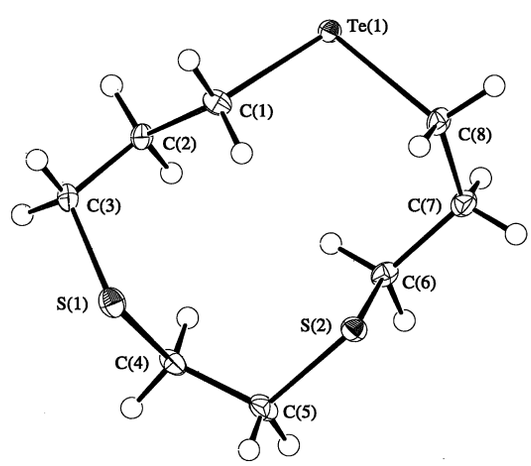


Fig. 1 View of the structure of [11]aneS_2Te with numbering scheme adopted. Ellipsoids are drawn at 40% probability.

Table 2 Selected bond lengths (Å) and angles (°) for [11]aneS_2Te

Te(1)–C(1)	2.151(6)
Te(1)–C(8)	2.158(5)
S(1)–C(3)	1.821(6)
S(1)–C(4)	1.812(7)
S(2)–C(5)	1.807(6)
S(2)–C(6)	1.813(7)
C(1)–C(2)	1.512(8)
C(2)–C(3)	1.530(9)
C(4)–C(5)	1.536(9)
C(6)–C(7)	1.531(8)
C(7)–C(8)	1.521(9)
C(1)–Te(1)–C(8)	95.5(2)
C(3)–S(1)–C(4)	103.4(3)
C(5)–S(2)–C(6)	100.1(3)
Te(1)–C(1)–C(2)	113.9(5)
C(1)–C(2)–C(3)	113.4(6)
S(1)–C(3)–C(2)	115.8(4)
S(1)–C(4)–C(5)	111.8(5)
S(2)–C(5)–C(4)	116.2(4)
S(2)–C(6)–C(7)	110.7(4)
C(6)–C(7)–C(8)	114.8(5)
Te(1)–C(8)–C(7)	116.3(4)

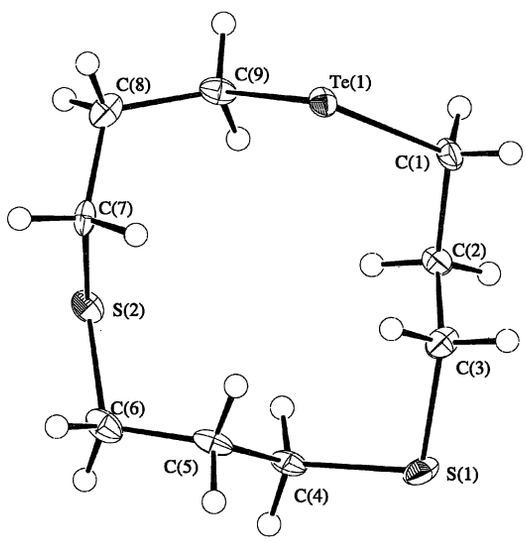


Fig. 2 View of the structure of [12]aneS_2Te with numbering scheme adopted. Ellipsoids are drawn at 40% probability.

six SCCC torsions adopt *gauche* (*ca.* 60°) arrangements, the remainder being approximately *anti* (*ca.* 180°). The dithia–tellura analogue, [12]aneS_2Te, adopts a very similar distribution of torsion angles in the solid state, with one *gauche* and one *anti* CTeCC torsion and three of the four CSCC torsions being *gauche*, and with an S atom occupying a corner of the approximate square. The C(1)–Te(1)–C(9) angle of 94.2(2)° is considerably smaller than the C–S–C angles (100.4(3) and 101.3(2)°), consistent with less s orbital character in the Te–C bonding (owing to the larger energy gap between the s and p orbitals on Te compared to S). This trend in bond angles is also observed in the structure of [11]aneS_2Te, although the torsion angles show much greater deviations from strictly *gauche* or *anti*, presumably due to restrictions imposed by the smaller ring size. This species also adopts an approximately square arrangement, in this case with the Te atom on a corner and the S atoms on edges.

[9]aneS_2Te: This small ring analogue of the much studied [9]aneS_3 was obtained similarly from the sulfur mustard derivative $Cl(CH_2)_2S(CH_2)_2S(CH_2)_2Cl$ by reaction with Na_2Te at *ca.* −45 °C, as a pale yellow microcrystalline solid in *ca.* 20% yield. This reaction is more temperamental than for the 11- and 12-membered rings and the yield was found to vary quite substantially with reaction temperature. Thus, at −78 °C

Table 3 Selected bond lengths (Å) and angles (°) for [12]aneS_2Te

Te(1)–C(1)	2.163(5)
Te(1)–C(9)	2.148(6)
S(1)–C(3)	1.814(6)
S(1)–C(4)	1.820(6)
S(2)–C(6)	1.810(7)
S(2)–C(7)	1.818(5)
C(1)–C(2)	1.521(8)
C(2)–C(3)	1.511(10)
C(4)–C(5)	1.510(8)
C(5)–C(6)	1.525(9)
C(7)–C(8)	1.518(8)
C(8)–C(9)	1.533(8)
C(1)–Te(1)–C(9)	94.2(2)
C(3)–S(1)–C(4)	101.3(2)
C(6)–S(2)–C(7)	100.4(3)
Te(1)–C(1)–C(2)	114.8(4)
C(1)–C(2)–C(3)	113.3(6)
S(1)–C(3)–C(2)	114.3(4)
S(1)–C(4)–C(5)	113.1(4)
C(4)–C(5)–C(6)	113.1(5)
S(2)–C(6)–C(5)	113.7(4)
S(2)–C(7)–C(8)	110.6(4)
C(7)–C(8)–C(9)	113.9(5)
Te(1)–C(9)–C(8)	113.8(4)

polymer formation dominates (this may be a function of the low solubility of the sulfur mustard precursor in the NH_3(l)–THF solvent mixture at this temperature, resulting in the reaction occurring in a much less controlled fashion as the NH_3(l) boils off and the temperature rises). The $^{125}Te\{^1H\}$ NMR spectrum of [9]aneS_2Te is characterised by a singlet at 345 ppm, with $^{13}C\{^1H\}$ NMR spectroscopy revealing three resonances of equal intensity at 35.9, 32.9 and 2.9 ppm, the lowest frequency resonance being attributed to the CH_2Te unit. The EI mass spectrum reveals a cluster of peaks associated with the molecular ion at m/z = 278 (calculated for $[C_6H_{12}S_2{}^{130}Te]$ m/z = 278) as well as a series of fragmentation products at lower m/z arising from successive loss of C_2H_4 and S.

A colourless by-product from this particular cyclisation procedure, formed in *ca.* 15–20% yield, has been identified unambiguously as the ring-contraction product 1-thia-4-telluracyclohexane, with $\delta(^{125}Te)$ 254 and $\delta(^{13}C\{^1H\})$ 30.1 and −5.8, consistent with the CH_2S and CH_2Te units respectively. The GC-EI mass spectrum of this species shows a single species with m/z = 218, corresponding to $[C_4H_8S^{130}Te]^+$. Fragment peaks associated with successive loss of C_2H_4 inter-donor units are also evident. Crystals of this species were obtained by re-crystallisation from CH_2Cl_2 solution. The structure shows (Fig. 3) the 6-membered ring disordered over a crystallographic inversion centre at the centre of the ring, with the ring adopting a chair conformation. As a result of the disorder, the S–C and Te–C bond distances are unreliable, precluding detailed comparisons. This crystal has the same cell parameters and

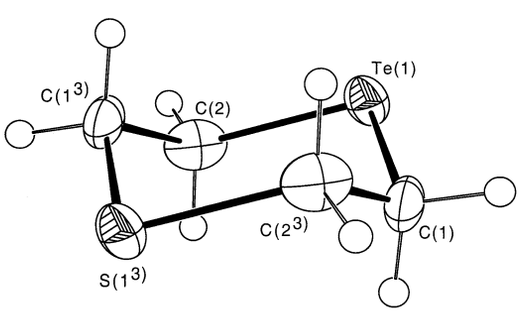


Fig. 3 View of the structure of 1-thia-4-telluracyclohexane with numbering scheme adopted. Ellipsoids are drawn at 40% probability. The ring is disordered over a crystallographic inversion centre and atoms $S(1^3)$, $C(1^3)$ and $C(2^3)$ are related by the operation $-x, -y, -z$.

space group as those reported by McCullough,[12] although as a result of the disorder he did not pursue complete refinement, but went on to structurally characterise the 1-thia-4-telluracyclohexane 4,4-diiodide derivative.[12] However, our structure does establish beyond doubt the identity of this by-product. We have not seen any evidence for ring contraction from the [11]aneS_2Te or [12]aneS_2Te preparations. The reason for its occurrence in the [9]aneS_2Te preparation is not clear, however it may well be due to the presence of the C_2H_4 linkages between the S and Te atoms. These units are unknown in di- and tri-telluroethers owing to the ease of elimination of ethene, with concomitant formation of ditelluride species.[1,4] A very minor species at 2.85 ppm (*ca.* 5%) in the ^{1}H NMR spectrum of the crystals of 1-tellura-4-thiacyclohexane is attributed to 1,4-dithiane, a second ring-contraction product from the [9]aneS_2Te preparation. The EIMS of 1-thia-4-telluracyclohexane shows M^+ at 218, together with fragments corresponding to successive loss of C_2H_4 inter-donor units. 1,4-Dithiane is also evident in this mass spectrum at m/z = 120. The formation of 1,4-dithiane is not unexpected, however it is somewhat surprising that 1-tellura-4-thiacyclohexane is obtained, as its formation shows that although the S–C bonds are expected to be considerably stronger than Te–C, significant S–C bond cleavage occurs.

Reaction of each of the three S_2Te-donor compounds and 1-thia-4-telluracyclohexane with excess MeI in CH_2Cl_2 affords the corresponding air stable methiodide derivatives in high yield, *via* quaternisation specifically at the Te centre. The ^{125}Te{^{1}H} and ^{13}C{^{1}H} NMR spectra of these Te(IV) species were obtained in dmso solution owing to their very low solubilities in chlorocarbons. The site of quaternisation is confirmed by a significant high frequency shift in the ^{125}Te{^{1}H} NMR resonance in each case,[16] and for the CH_2Te resonance by ^{13}C{^{1}H} NMR spectra (accompanied by the appearance of a new resonance corresponding to TeMe). The 11- and 12-membered ring methiodides and the 1-thia-4-telluracyclohexane methiodide each display a cluster of peaks in the electrospray mass spectra which match exactly the predicted isotopic distribution associated with $[LMe]^+$. This provides further evidence that the macrocycles are indeed the [1+1] cyclisation products and not the [2+2] rings (both the m/z values and the isotope distributions for $\{[n]\text{ane}S_2\text{TeMe}\}^+$ rings with only one Te atom are significantly different to those predicted for the [2+2] rings even if they were dicationic *i.e.* $\{[2n]\text{ane}S_4Te_2Me_2\}^{2+}$). The corresponding peak for the 9-membered ring is much less intense, although the methiodide derivative of this compound is very poorly soluble in MeCN.

The 11- and 12-membered ring macrocycles were also converted to the corresponding Te(IV) diiodide species [11]aneS_2TeI_2 and [12]aneS_2TeI_2 by treatment of a thf–CH_2Cl_2 solution of the parent macrocycle with I_2. The products were isolated as deep red solids in good yield. Iodination was chosen rather than chlorination since using Cl_2 would result not only in chlorination of the Te atom, but would also attack the thioether functions resulting in chlorination of the α-carbon, affording SCHCl functions. The ES mass spectra of the diiodo derivatives reveal the major cluster of peaks to be associated with $([n]\text{ane}S_2\text{TeI})^+$. Crystals of [12]ane$S_2TeI_2$ suitable for X-ray analysis were obtained by slow evaporation from a solution of the diiodo species in CH_2Cl_2–$CHCl_3$. The structure shows (Fig. 4, Table 4) a neutral, molecular Te(IV) species involving distorted *pseudo* trigonal bipyramidal Te with the iodines *trans* (axial) and a lone pair of electrons is assumed to be occupying the open vertex. The angles around the Te centre in this compound are in accord with those in, for example, Me_2TeI_2,[17] suggesting that the ring structure does not influence the geometry at Te. In [12]aneS_2TeI_2 the ring adopts a similar conformation to that of the parent macrocycle, except that the Te atom occupies a corner position rather than a S atom. This is reflected in the torsion angle distribution which shows both CTeCC torsions *gauche* and two CSCC torsions *gauche* and the other two *anti*.

Table 4 Selected bond lengths (Å) and angles (°) for [12]aneS_2TeI_2

I(1)–Te(1)	2.8990(9)
I(2)–Te(1)	2.9179(9)
Te(1)–C(1)	2.189(9)
Te(1)–C(9)	2.155(9)
S(1)–C(3)	1.819(11)
S(1)–C(4)	1.829(11)
S(2)–C(6)	1.815(10)
S(2)–C(7)	1.820(10)
C(1)–C(2)	1.50(1)
C(2)–C(3)	1.528(12)
C(4)–C(5)	1.52(1)
C(5)–C(6)	1.516(12)
C(7)–C(8)	1.54(1)
C(8)–C(9)	1.50(1)
I(1)–Te(1)–I(2)	176.77(3)
I(1)–Te(1)–C(1)	96.0(3)
I(1)–Te(1)–C(9)	86.3(3)
I(2)–Te(1)–C(1)	86.8(3)
I(2)–Te(1)–C(9)	95.2(3)
C(1)–Te(1)–C(9)	93.3(4)
C(3)–S(1)–C(4)	99.7(5)
C(6)–S(2)–C(7)	98.9(5)
Te(1)–C(1)–C(2)	117.2(6)
C(1)–C(2)–C(3)	110.7(8)
S(1)–C(3)–C(2)	112.4(6)
S(1)–C(4)–C(5)	110.5(7)
C(4)–C(5)–C(6)	112.9(8)
S(2)–C(6)–C(5)	111.9(7)
S(2)–C(7)–C(8)	113.1(6)
C(7)–C(8)–C(9)	110.0(9)
Te(1)–C(9)–C(8)	119.6(7)

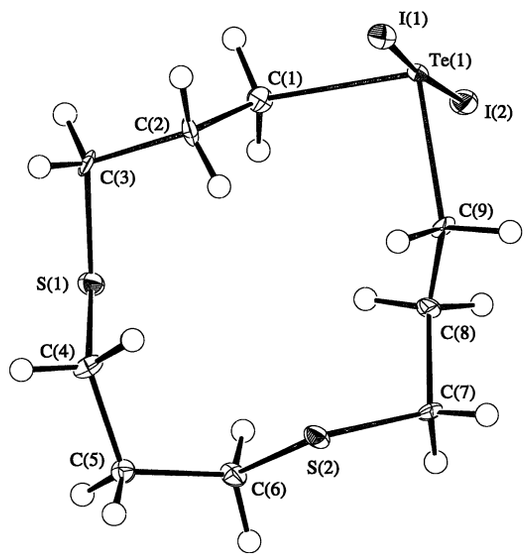


Fig. 4 View of the structure of [12]aneS_2TeI_2 with numbering scheme adopted. Ellipsoids are drawn at 40% probability.

Metal complexes

We have conducted reactions of the S_2Te-macrocycles with a variety of transition metal centres, including Mn(I), Mo(0), Rh(III), Pd(II), Pt(II), Ag(I) and Cu(I), in order to explore their ligating behaviour, including their modes of coordination and the effects of altering the macrocycle ring-size.

Reaction of $[Mn(CO)_3(Me_2CO)_3]CF_3SO_3$[18] with one mole equivalent of [n]aneS_2Te in acetone solution yields the Mn(I) species *fac*-$[Mn(CO)_3([n]\text{ane}S_2\text{Te})]CF_3SO_3$ in moderate yield for the 9- and 11-membered rings, but low yield for [12]aneS_2Te. The isolated solids are characterised by microanalytical measurements, ESMS (the major cluster of peaks corresponds to $[Mn(CO)_3([n]\text{ane}S_2\text{Te})]^+$ for n = 11 and 12) and by two strong CO stretching vibrations in the IR spectra associated with the *fac*-tricarbonyl moiety [the cations have C_s symmetry and hence

three bands are predicted from group theory, although the a′ and a″ modes are poorly resolved]. The $[Mn(CO)_3([12]aneS_2Te)]CF_3SO_3$ is unstable in solution, hence we were unable to obtain NMR data on it. Even $[Mn(CO)_3([11]aneS_2Te)]CF_3SO_3$ decomposes during $^{13}C\{^1H\}$ NMR data acquisition, however, ^{55}Mn and $^{125}Te\{^1H\}$ NMR data were obtained for this and the 9-membered ring analogue. The ^{55}Mn spectra show a fairly sharp resonance at −821 and −817 ppm for the 9- and the 11-membered ring complexes respectively. The corresponding resonance for the related *fac*-$[Mn(CO)_3\{MeS(CH_2)_3Te(CH_2)_3SMe\}]CF_3SO_3$ occurs at −645 ppm,[13] while *fac*-$[Mn(CO)_3([n]aneS_3)]CF_3SO_3$ give $\delta(^{55}Mn) = -963$ and −764 for $n = 9$ and 10 respectively, *i.e.* revealing significant dependence of the ^{55}Mn chemical shift upon ring-size and donor atom type.[6] Singlet $^{125}Te\{^1H\}$ NMR resonances are seen at 214 and 110 ppm for $[Mn(CO)_3([9]aneS_2Te)]CF_3SO_3$ and $[Mn(CO)_3([11]aneS_2Te)]CF_3SO_3$, *i.e.* to low frequency of the 'free' ligand, a pattern also mirrored for the open chain analogue.

Attempts were made to prepare the *fac*-trisubstituted Mo(0) complex $[Mo(CO)_3([11]aneS_2Te)]$ both by reaction of $[Mo(CO)_3(MeCN)_3]$ with the macrocycle in refluxing MeCN and by direct reaction of $[Mo(CO)_6]$ with the ligand in refluxing $MeNO_2$. However, neither was successful, the IR spectra revealing the presence of some *cis*-tetracarbonyl species, but no *fac*-tricarbonyl. We subsequently prepared the *cis*-$[Mo(CO)_4([11]aneS_2Te)]$ directly from $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene)[19] and ligand in CH_2Cl_2. The product was characterised by microanalysis, ^1H NMR and IR spectroscopy which shows three CO stretching vibrations at 2021, 1900 and 1846 cm^{-1} (observation of three bands rather than the four predicted for the C_{2v} molecule is not unusual due to failure to resolve the a_1 and b_1 modes at *ca.* 1900 cm^{-1}). However, it is not clear on the basis of these data alone whether coordination to Mo(0) is *via* STe or S_2 since the differences in the CO stretching vibrations are not expected to be large.[20] The $^{125}Te\{^1H\}$ NMR spectrum shows a singlet at 282 ppm, clearly indicating that the only isomer present in solution involves coordination *via* one S and one Te atom. Prolonged standing in CH_2Cl_2 solution leads to some decomposition and the appearance of a further resonance at 194 ppm and hindered acquisition of $^{13}C\{^1H\}$ NMR data for the compound. The analogous reaction with $[12]aneS_2Te$ and $[Mo(CO)_4(nbd)]$ yielded a small amount of an unidentified brown solid which rapidly turned black even when stored under N_2. This chemistry was not pursued further.

The Pd(II) and Pt(II) complexes $[MCl_2([n]aneS_2Te)]$ (n = 11 or 12) were obtained as yellow solids in good yield *via* reaction of $[MCl_2(NCMe)_2]$ with the macrocycles in CH_2Cl_2. The IR spectra of these complexes reveal weak features in the region *ca.* 320 cm^{-1} expected for ν(M–Cl), although there are also features in this region in the IR spectra of the uncoordinated macrocycles, thus unambiguous identification of the isomer on the basis of IR spectroscopy is not possible. The $^{125}Te\{^1H\}$ NMR spectra of the Pd complexes show single resonances at 330 and 387 ppm for the 11- and 12-membered ring complexes respectively, *i.e.* to high frequency of the parent macrocycles. The Pt(II) compounds are rather poorly soluble, hence NMR spectra used d^6-dmf. For $[PtCl_2([11]aneS_2Te)]$ the $^{125}Te\{^1H\}$ NMR spectrum is a singlet at 299 ppm, with ^{195}Pt satellite couplings giving $^1J_{PtTe} = 753$ Hz, while the ^{195}Pt NMR resonance is observed at −3834 ppm. The $[PtCl_2([12]aneS_2Te)]$ gives $\delta(^{125}Te) = 374$ and $\delta(^{195}Pt) = -3890$ with $^1J_{PtTe} = 1034$ Hz. These data are consistent with a *cis*-dichloro species involving S,Te-coordination *via* the macrocycle in each case. For comparison $[Pt\{MeTe(CH_2)_3TeMe\}Cl_2]$ has $\delta(^{195}Pt)$ −4434, −4379, $^1J_{PtTe}$ = 1140, 820 Hz[21] and $[Pt\{MeS(CH_2)_3SMe\}Cl_2]$ has $\delta(^{195}Pt)$ −3538, −3570 (the two resonances in each case are due to *meso* and DL isomers).[22]

The distorted octahedral Rh(III) species $[Rh(Cp^*)([n]aneS_2Te)](PF_6)_2$ (n = 9, 11 or 12) were obtained as yellow solids in good yield from reaction of $[Rh(Cp^*)Cl_2]_2$[23] with 2 molar equivalents of macrocycle and 4 molar equivalents of $TlPF_6$ in CH_2Cl_2 solution. Microanalyses are consistent with the above formulation, while IR spectroscopy shows peaks associated with the PF_6^- anion, coordinated macrocycle and Cp* and hence a distorted octahedral half-sandwich complex in each case. For all three Rh(III) complexes ESMS shows clusters of peaks corresponding to loss of one PF_6^- anion, although for the 11- and 12-membered rings the most intense peaks correspond to the dicationic $[Rh(Cp^*)([n]aneS_2Te)]^{2+}$. $^{125}Te\{^1H\}$ NMR spectroscopy shows a doublet for each complex to high frequency of 'free' ligand ($[Rh(Cp^*)([9]aneS_2Te)]^{2+}$ δ = 397, $^1J_{RhTe}$ = 75 Hz; $[Rh(Cp^*)([11]aneS_2Te)]^{2+}$ δ = 282, 106 Hz; $[Rh(Cp^*)([12]aneS_2Te)]^{2+}$ δ = 275, 102 Hz). The coupling constants are similar to those observed in $[Rh(Cp^*)\{RTe(CH_2)_3Te(CH_2)_3TeR\}]^{2+}$ (R = Me: 80 Hz; R = Ph: 80 Hz)[5] and $[Rh(Cp^*)\{MeS(CH_2)_3Te(CH_2)_3SMe\}]^{2+}$ (J = 94 Hz).[13] ^1H and $^{13}C\{^1H\}$ NMR data and microanalyses are also consistent with the formulation of these as half-sandwich compounds.

The coordination chemistry of the three S_2Te macrocycles has also been investigated with $Ag(CF_3SO_3)$. In a typical preparation, the macrocyclic ligand (1 mol equiv.) was dissolved in 25 cm^3 of CH_2Cl_2 and $Ag(CF_3SO_3)$ (1 mol equiv.) added. The reaction mixture was stirred for approximately one hour, during which time the $Ag(CF_3SO_3)$ dissolved and a light yellow solid was precipitated, which was filtered and washed with diethyl ether. These species were found to be very poorly soluble even in coordinating solvents, probably as a combination of the insolubility of the ligands with the formation of an extended structure, common in Ag(I) chemistry. ^1H NMR spectra show resonances associated with the coordinated ligands. However, the ES^+ mass spectra gave clusters of peaks corresponding to $[Ag([n]aneS_2Te)]^+$ for the 11- and 12-membered ring systems, and $[Ag([n]aneS_2Te)_2]^+$ for all three ring sizes. IR spectroscopy exhibits peaks identified with the $CF_3SO_3^-$ anion[24] and the macrocyclic ligand. Elemental analysis showed a good match for the $[9]aneS_2Te$ and $[11]aneS_2Te$ complexes consistent with a 1 : 1 complex. However, the isolated $[12]aneS_2Te$ complex was extremely unstable, decomposing rapidly even when protected from visible light and stored under N_2. Hence, we were unable to obtain satisfactory microanalytical data for this compound. However, the corresponding BF_4^- salt, $[Ag([12]aneS_2Te)]BF_4$ is more stable, shows similar spectroscopic properties associated with the cation and satisfactory microanalytical data have been obtained for this compound.

We described the structure of $[Ag([11]aneS_2Te)]BF_4$ in a preliminary communication on this work.[11] The complex cation adopts a chain polymer form, involving distorted trigonal planar coordination at the Ag(I) centres *via* two S and one Te atom from three distinct macrocycles which bridge to adjacent Ag centres, Ag–S = 2.521(3), 2.634(3); Ag–Te = 2.674(1) Å. It seems likely that polymeric structures probably also occur for the other Ag(I) species.

Reaction of $[11]aneS_2Te$ or $[12]aneS_2Te$ with one molar equivalent of $[Cu(NCMe)_4]BF_4$ in CH_2Cl_2 solution affords the 1 : 1 species $[Cu([n]aneS_2Te)]BF_4$ as cream coloured solids. IR spectroscopy confirms the presence of the macrocycle and of BF_4^- anions, while ESMS shows clusters of peaks attributed to $[Cu([n]aneS_2Te)_2]^+$ and $[Cu([n]aneS_2Te)]^+$, suggesting that these species too may adopt extended structures, although we have not been able to obtain suitable crystals to prove this.

Comparisons and conclusions

Three new small ring dithia–tellura macrocycles have been prepared in modest yield using a generally applicable synthetic method involving a [1+1] cyclisation reaction. Synthesis of $[9]aneS_2Te$ is more temperamental than for the 11- and 12-membered ring analogues, probably reflecting the susceptibility of the dimethylene linkages adjacent to Te to elimination. This is supported by the characterisation of 1,4-dithiane and

1-thia-4-telluracyclohexane ring contraction by-products from the preparation of [9]aneS_2Te.

No evidence for higher rings such as the [2+2] cyclisation products has been observed. This contrasts with the analogous reaction of Na_2Te with $Cl(CH_2)_2O(CH_2)_2O(CH_2)_2Cl$ which yields [18]aneO_4Te_2 as the major product, with the [1+1] cyclisation product, [9]aneO_2Te, the minor product.[25] This difference may be due to the absence of an effective template in the thia–tellura reaction chemistry, whereas the Na^+ may template formation of the larger 18-membered ring in the oxa–tellura chemistry. The solid state conformation of the ring in [12]aneS_2Te is very similar to that seen in [12]aneS_3 and in the parent hydrocarbon cyclododecane, despite the distribution of Te–C bond lengths and C–Te–C angles associated with introduction of the heavy (and large) Te atom.

We have shown that the macrocycles readily coordinate to a range of transition metal ions in medium to low oxidation states, functioning as bi- or tri-dentate (face-capping) ligands through STe or S_2Te donor sets. Complexes of [12]aneS_2Te are less stable than for the 9- and 11-membered ring analogues. Cooper and co-workers have highlighted similar behaviour for 3d and 4d transition metal complexes containing [12]aneS_3, whereas [9]aneS_3 complexes are typically very robust and resistant to dissociation or solvolysis.[26] While the 9-membered ring is apparently the optimal ring-size for *fac*-coordination to d-block metal ions, the 12-membered ring is considered to be too large, resulting in ring strain and hence much lower complex stability.

Experimental

Infrared spectra were recorded in CH_2Cl_2 solution using a Perkin Elmer 1710 spectrometer over the range 2200–1700 cm^{-1} or as CsI discs or neat oils between CsI plates over the range 4000–200 cm^{-1} using a Perkin Elmer 983G spectrometer. Mass spectra were run by low resolution electron impact (EI) on a VG 70-SE Normal geometry double focusing spectrometer, or by GC-EI on a ThermoQuest Trace MS gas chromatography mass spectrometer or positive ion electrospray (ESMS) in MeCN solution on a VG Biotech platform. ^{1}H NMR spectra were recorded using a Bruker AM300 spectrometer. $^{13}C\{^1H\}$, ^{55}Mn, ^{125}Te and ^{195}Pt NMR spectra were recorded using a Bruker DPX400 spectrometer operating at 100.6, 99.1, 126.3 or 85.7 MHz respectively and are referenced to external Me_4Si, aqueous $KMnO_4$, neat external Me_2Te or aqueous 1 mol dm^{-3} $Na_2[PtCl_6]$, respectively (δ = 0). For the carbonyl compounds [Cr(acac)$_3$] was added to the NMR solutions prior to recording $^{13}C\{^1H\}$ NMR spectra and a pulse delay of 2 s was introduced to accommodate the long relaxation times. Microanalyses were obtained from the University of Strathclyde microanalytical service. The sulfur mustard precursors, $Cl(CH_2)_nS(CH_2)_nS(CH_2)_nCl$, n = 2 or 3, were prepared by the literature methods[14] [**CAUTION:** these compounds are powerful vesiccants and may cause severe blistering upon skin contact].

Preparations

[9]aneS_2Te. Ammonia (600 cm^3) was condensed in a flask at −78 °C and freshly cut Na (1.113 g, 48 mmol) added over the course of several minutes to give a deep blue solution. Freshly ground Te powder (3.089 g, 24 mmol) was added and the mixture allowed to warm until a blue solution with a white precipitate of Na_2Te was observed. The solution was re-cooled to −40 °C and $Cl(CH_2)_2S(CH_2)_2S(CH_2)_2Cl$ (5.307 g, 24 mmol) in THF (100 cm^3) added dropwise over 30 min to give a deep red solution. The ammonia was allowed to boil off and the reaction warmed to room temperature overnight to produce a red–brown mixture with a solid. This was hydrolysed (*ca.* 150 cm^3) and extracted with CH_2Cl_2 (*ca.* 800 cm^3) and the extracts transferred *via* cannula into a flask containing $MgSO_4$ and dried. After filtering, the orange solution was concentrated (*ca.* 400 cm^3) and MeOH (*ca.* 50 cm^3) added before chilling at −18 °C overnight. The resultant precipitate was filtered off and dried *in vacuo* to give a first crop of product which was very poorly soluble and appeared to be mainly polymer. The filtrate was concentrated further (*ca.* 300 cm^3), MeOH (*ca.* 50 cm^3) added and again cooled overnight at −18 °C to produce a second crop of product ([9]aneS_2Te) that was filtered and dried *in vacuo*. Yield 18%. Calc. for $C_6H_{12}S_2Te$: C, 26.1; H, 4.4%. Found: C, 25.8; H, 3.9%. EIMS found: m/z = 278, 250, 222, 190; calc. for $[C_6H_{12}S_2{}^{130}Te]^+$ 278, $[C_4H_8S_2{}^{130}Te]^+$ 250, $[C_2H_4S_2{}^{130}Te]^+$ 222, $[C_2H_4S^{130}Te]^+$ 190. IR ν/cm^{-1} (CsI disk): 2966w, 2927m, 1423s, 1358m, 1261w, 1201m, 1138s, 1099s, 1022w, 869w, 834w, 803w, 713w, 676m, 613w, 575w, 550w, 318w, 309w, 300w, 246m, 223w.

1-thia-4-telluracyclohexane. The pale yellow filtrate from the preparation above was left to slowly evaporate to produce a crop of orange crystals (1-thia-4-telluracyclohexane). Yield 15%. GC-EIMS: found m/z = 218, 190, 162. Calculated for $[C_4H_8S^{130}Te]^+$ 218, $[C_2H_4S^{130}Te]^+$ 190, $[S^{130}Te]^+$ 162. EIMS: found m/z = 218, 190, 162, 120. Calculated for $[C_4H_8S^{130}Te]^+$ 218, $[C_2H_4S^{130}Te]^+$ 190, $[S^{130}Te]^+$ 162, [1,4-dithiane]$^+$ 120. IR ν/cm^{-1} (CsI disk): 2960w, 2921w, 2858w, 1458w, 1406m, 1365m, 1292w, 1263m, 1249m, 1216m, 1159w, 1111m, 992m, 905m, 849w, 821m, 663w, 630m, 509m, 419w, 294w, 224w, 221w.

[11]aneS_2Te. To a solution of sodium (0.93 g, 0.04 mol) in $NH_{3(l)}$ (400 cm^3) at −78 °C was added tellurium powder (2.58 g, 0.02 mol) and the mixture allowed to warm slowly. When a white precipitate of Na_2Te was observed, the mixture was re-cooled to −78 °C and $Cl(CH_2)_3S(CH_2)_2S(CH_2)_3Cl$ (5 g, 0.02 mol) in THF (100 cm^3) added dropwise over 30 minutes. The mixture was warmed to room temperature and the NH_3 allowed to boil off overnight to give a red solution which was hydrolysed (200 cm^3), the organic layer separated and the aqueous layer extracted with dichloromethane (4 × 40 cm^3). The combined organic extracts were dried overnight ($MgSO_4$), filtered and the solvent removed *in vacuo* to leave a red oil. This crude material was purified by flash column chromatography on silica [hexane–ethyl acetate (3 : 1)] to afford the ligand as a pale yellow waxy solid. Yield 1.7 g, 28%. Calc. for $C_8H_{16}S_2Te$: C, 31.6; H, 5.3%. Found: C, 31.9; H, 5.5%. EIMS: found m/z = 306, 204; calc. for $[C_8H_{16}S_2{}^{130}Te]^+$ 306, $[C_3H_6S^{130}Te]^+$ 204. IR ν/cm^{-1} (thin film): 2963m, 2915m, 2847w, 1435s, 1414s, 1337w, 1289m, 1268m, 1246m, 1199s, 1102w, 1037w, 902w, 853w, 811m, 737w, 702m, 688m, 568w, 515w, 321w, 312w, 221w.

[12]aneS_2Te. To a solution of Na_2Te (0.025 mol) in $NH_{3(l)}$ (400 cm^3), prepared by following the procedure detailed above, was added at −78 °C a solution of $Cl(CH_3)_3S(CH_2)_3S(CH_2)_3Cl$ (6.5 g, 0.025 mol) in THF (100 cm^3) over 30 min. After the addition was complete, the mixture was allowed to warm up to room temperature and the NH_3 boiled off overnight. The mixture was worked up as above to give a red oil. Purification by flash column chromatography on silica [hexane–ethyl acetate (3 : 1)] afforded the ligand as a light yellow oily solid. Yield 1.4 g, 18%. Calc. for $C_9H_{18}S_2Te$: C, 34.0; H, 5.7%. Found: C, 33.5; H, 5.3%. EIMS found: m/z = 320, 246, 204; calc. for $[C_9H_{18}S_2{}^{130}Te]^+$ 320, $[C_6H_{12}S^{130}Te]^+$ 246, $[C_3H_6S^{130}Te]^+$ 204. IR ν/cm^{-1} (neat oil): 2958m, 2921m, 2851w, 1437s, 1414s, 1375w, 1338w, 1289m, 1260m, 1201m, 1174w, 1098s, 1021s, 800s, 754w, 693w, 519w, 500w, 395m.

[11]aneS_2TeMeI. To a solution of [11]aneS_2Te (0.120 g, 0.49 mmol) in CH_2Cl_2 (30 cm^3) was added MeI (1 cm^3, excess). The solution was stirred and gently refluxed for one hour, allowed to cool, concentrated (*ca.* 10 cm^3) and pipetted into ice-cold Et_2O. The resultant precipitate was filtered, washed with Et_2O and dried *in vacuo* to produce a white solid. The solid was stored

under nitrogen in the freezer to avoid decomposition to a red–brown sticky solid. Yield 0.159 g, 72%. Calc. for [$C_9H_{19}IS_2Te$]: C, 24.2; H, 4.3%. Found: C, 23.9; H, 3.9%. ESMS: found *m*/*z* = 321; calculated for ([11]aneS_2^{130}TeMe)$^+$ 321. ^{1}H NMR (d^6-dmso): δ 2.90–2.65 (m, SCH_2, 8H), 2.50 (t, $TeCH_2$, 4H), 2.13 (s, TeMe, 3H), 2.11 (m, $SCH_2CH_2CH_2Te$, 4H). ^{13}C{^{1}H} NMR (d^6-dmso): δ 33.9, 33.2 (SCH_2), 25.5, 24.9 ($TeCH_2$, $CH_2CH_2CH_2$), 9.2 (TeMe). ^{125}Te{^{1}H} NMR (d^6-dmso): 542.

[12]aneS_2TeMeI. This was prepared similarly, using [12]aneS_2Te to give a white solid which darkened and became sticky soon after isolation. The freshly isolated product was stored at −18 °C to avoid decomposition. Yield 91%. Calc. for [$C_{10}H_{21}IS_2Te$]·CH_2Cl_2: C, 24.2; H, 4.2%. Found: C, 24.5; H, 4.2%. ESMS: found *m*/*z* = 335; calculated for ([12]aneS_2-^{130}TeMe)$^+$ 335. ^{1}H NMR (d^6-dmso): δ 2.95–2.72 (m, SCH_2, 8H), 2.60 (t, $TeCH_2$, 4H), 2.13 (s, TeMe, 3H), 2.00 (m, SCH_2CH_2Te, 4H), 1.78 (quin., $SCH_2CH_2CH_2S$, 2H). ^{13}C{^{1}H} NMR (d^6-dmso): δ 33.7, 29.6 (SCH_2), 28.3 ($SCH_2CH_2CH_2S$), 24.0 ($TeCH_2CH_2CH_2S$), 20.4 ($TeCH_2$), 4.5 (TeMe). ^{125}Te{^{1}H} NMR (d^6-dmso): 543.

[9]aneS_2TeMeI. Method as above giving an orange solid. Yield 72%. Calc. for [$C_7H_{15}IS_2Te$]: C, 20.1; H, 3.6%. Found: C, 19.8; H, 3.4%. ^{1}H NMR (d^6-dmso): 2.2 (s, Me), 2.7–3.29 (m). ^{13}C{^{1}H} NMR (CH_2Cl_2–$CDCl_3$): 32.8, 32.4 (CH_2S), 28.8 (CH_2Te), 7.5 (Me). ^{125}Te{^{1}H} NMR (CH_2Cl_2–$CDCl_3$): 419.

1-thia-4-telluracyclohexanemethiodide. Method as above giving a cream coloured solid. Yield 68%. Calc. for [$C_5H_{11}ISTe$]: C, 16.8; H, 3.1%. Found: C, 17.5; H, 2.7%. ESMS: found *m*/*z* = 233, 173; calculated for [$C_5H_{11}S^{130}Te$]$^+$ 233, [CH_2CH_2TeMe]$^+$ 173. ^{1}H NMR (d^6-dmso): δ 2.15 (s, Me), 2.8–3.1 (m). ^{13}C{^{1}H} NMR (d^6-dmso): δ 24.0, 20.1 (CH_2), 1.9 (TeMe). ^{125}Te{^{1}H} NMR (d^6-dmso): 434.

[12]aneS_2TeI_2. I_2 (0.056 g, 0.22 mmol) was dissolved in THF (*ca.* 30 cm^3) and [12]aneS_2Te (0.070 g, 0.22 mmol) in CH_2Cl_2 (*ca.* 10 cm^3) was added. The reaction was stirred in a foil-wrapped vessel for two hours, concentrated to half volume and Et_2O added to produce a brick red precipitate that was filtered, washed with Et_2O and dried *in vacuo.* Yield 0.104 g, 83%. Calc. for [$C_9H_{18}I_2S_2Te$]·1/4thf: C, 20.4; H, 3.5%. Found: C, 20.7; H, 4.7%. ESMS: found *m*/*z* = 447; calculated for ([12]ane-S_2^{130}TeI)$^+$ 447. ^{1}H NMR ($CDCl_3$): 3.6 (t, $TeCH_2$), 2.75 (t, SCH_2), 2.62 (t, SCH_2), 2.40 (m, $TeCH_2CH_2CH_2$), 1.80 (quin., $SCH_2CH_2CH_2$). IR/cm^{-1} (CsI disk): 2932w, 2923w, 2858w, 1428m, 1412m, 1359s, 1246w, 1107m, 1067m, 997w, 959w, 835w, 729w, 661w, 541w, 510w, 393w, 311w, 244w, 224w.

[11]aneS_2TeI_2. Procedure as above, using I_2 (0.353 g, 1.39 mmol) and [11]aneS_2Te (0.423 g, 1.39 mmol), giving a deep red solid. Yield 75%. Calc. for [$C_8H_{16}I_2S_2Te$]·CH_2Cl_2: C, 16.8; H, 2.8%. Found: C, 17.2; H, 2.9%. ESMS: found *m*/*z* = 433; calculated for ([11]aneS_2^{130}TeI)$^+$ 433. ^{1}H NMR ($CDCl_3$): 3.50 (t, $TeCH_2$), 2.85–3.02 (m, SCH_2), 2.63 (m, $CH_2CH_2CH_2$). IR/cm^{-1} (CsI disk): 2963w, 2908w, 1428m, 1414m, 1400w, 1358s, 1261m, 1223w, 1205w, 1120m, 1096m, 1020w, 970w, 887w, 804m, 705w, 508w, 394w, 311w, 300w, 247w, 223w.

[Mn(CO)$_3$([11]aneS_2Te)]CF_3SO_3. [Mn(CO)$_5$Cl] (0.038 g, 0.165 mmol) and $AgCF_3SO_3$ (0.043 g, 0.167 mmol) were refluxed in degassed acetone (*ca.* 20 cm^3) for one hour to form the intermediate [Mn(CO)$_3$(Me_2CO)$_3$][CF_3SO_3]. The yellow solution was filtered to remove the AgCl precipitate and transferred into a vessel containing [11]aneS_2Te (0.051 g, 0.166 mmol) in CH_2Cl_2 (10 cm^3). The reaction mixture was stirred for 20 hours at room temperature, after which time solution IR spectroscopy suggested that the reaction was complete. The solvent volume was reduced (*ca.* 10 cm^3) and the concentrate added into ice-cold Et_2O. The precipitate generated was filtered, washed with Et_2O and dried *in vacuo* to give a yellow solid. Yield 0.083 g, 85%. Calc. for [$C_{12}H_{16}F_3MnO_6S_3Te$]: C, 24.4; H, 2.7%. Found: C, 23.7; H, 2.9%. ESMS: found *m*/*z* = 443; calculated for [Mn(CO)$_3$([11]aneS_2^{130}Te)]$^+$ 445. ^{1}H NMR (d^6-Me_2CO): δ 2.0–3.5 (br m). ^{125}Te{^{1}H} NMR (d^6-Me_2CO): 110 (br s). ^{55}Mn NMR (d^6-Me_2CO): δ −817. ν(CO)/cm^{-1} (CsI disk): 2033s, 1950s br; (CH_2Cl_2): 2034s, 1952s br.

[Mn(CO)$_3$([12]aneS_2Te)]CF_3SO_3. The reaction was carried out similarly, but using [12]aneS_2Te. After 20 hours, solution IR spectroscopy indicated a possible mixture of products. The solvent volume was reduced (*ca.* 10 cm^3) and Et_2O (*ca.* 5 cm^3) added to produce a yellow solid that was filtered and dried *in vacuo*. Yield 28%. Calc. for [$C_{13}H_{18}F_3MnO_6S_3Te$]·$CH_2Cl_2$: C, 24.3; H, 2.9%. Found: C, 24.1; H, 2.6%. ESMS: found *m*/*z* = 459; calculated for [Mn(CO)$_3$([12]aneS_2^{130}Te)]$^+$ 459. ^{1}H NMR (d^6-Me_2CO): δ 1.9–3.6 (br m). ν(CO)/cm^{-1} (CsI disk): 2028s, 1945s br.

[Mn(CO)$_3$([9]aneS_2Te)]CF_3SO_3. The reaction was carried out similarly, but using [9]aneS_2Te. Yellow solid. Yield 53%. Calc. for [$C_7H_{12}F_3MnO_6S_3Te$]·1/3Me_2CO: C, 22.7; H, 2.4%. Found: C, 22.9; H, 2.3%. ^{1}H NMR (CD_2Cl_2): δ 2.4–3.5 (br m). ^{125}Te{^{1}H} NMR (CD_2Cl_2): 214 (br s). ^{55}Mn NMR (CD_2Cl_2): δ −821. ν(CO)/cm^{-1} (CsI disk): 2042s, 1963s br.

[Mo(CO)$_4$([11]aneS_2Te)]. To a solution of [Mo(CO)$_4$(nbd)] (0.148 g, 0.49 mmol) in CH_2Cl_2 (40 cm^3) was added a solution of [11]aneS_2Te (0.49 mmol) in CH_2Cl_2 (*ca.* 10 cm^3). The reaction was stirred at room temperature overnight, by which time solution IR spectroscopy indicated that the reaction was complete. The solution was then concentrated (*ca.* 10 cm^3) and a brown solid precipitated by the addition of hexane. This was filtered, washed with hexane and dried *in vacuo*. Yield 0.042 g, 17%. Calc. for [$C_{12}H_{16}MoO_4S_2Te$]: C, 28.2; H, 3.2%. Found: C, 28.3; H, 3.3%. ^{1}H NMR (d^6-Me_2CO): δ 2.6–3.2 (br m). ^{125}Te{^{1}H} NMR (d^6-Me_2CO): 282. ν(CO)/cm^{-1} (CsI disk): 2021s, 1900s br, 1846s.

[PdCl$_2$([12]aneS_2Te)]. [PdCl$_2$(NCMe)$_2$] (0.079 g, 0.30 mmol) was dissolved in CH_2Cl_2 (*ca.* 40 cm^3) and [12]aneS_2Te (0.096 g, 0.30 mmol) added in CH_2Cl_2 (10 cm^3). The solution was stirred at room temperature for two hours, followed by the addition of Et_2O (*ca.* 10 cm^3) to produce a yellow precipitate that was filtered, washed with Et_2O and dried *in vacuo*. Yield 0.090 g, 60%. Calc. for [$C_9H_{18}Cl_2PdS_2Te$]·2CH_2Cl_2: C, 19.9; H, 3.3%. Found: C, 19.4; H, 3.0%. ^{1}H NMR (d^6-dmso): δ 2.0–3.5 (br m). ^{125}Te{^{1}H} NMR (CH_2Cl_2–$CDCl_3$): 387. IR ν/cm^{-1} (CsI disk): 2962w, 2938w, 2921w, 1480w, 1430sh, 1416m, 1356m, 1341m, 1290w, 1256m, 1245m, 1229w, 1207m, 1134w, 1107m, 1085w, 1013w, 853w, 782w, 721m, 616w, 352m, 300w.

[PdCl$_2$([11]aneS_2Te)]. The reaction was carried out as above using [PdCl$_2$(NCMe)$_2$] (0.066 g, 0.25 mmol) and [11]aneS_2Te (0.0773 g, 0.25 mmol). After stirring for two hours at room temperature, the solution was filtered in order to remove a small amount of brown solid, and the remaining clear yellow solution reduced in volume (*ca.* 10 cm^3). Et_2O (*ca.* 10 cm^3) was added to the concentrate and the mixture chilled at −18 °C to form a yellow precipitate that was subsequently filtered, washed with Et_2O and dried *in vacuo*. Yield 0.078 g, 64%. Calc. for [$C_8H_{16}Cl_2PdS_2Te$]: C, 20.0; H, 3.3%. Found: C, 19.6; H, 3.2%. ^{1}H NMR ($CDCl_3$): δ 2.0–3.5 (br m). ^{125}Te{^{1}H} NMR (CH_2Cl_2–$CDCl_3$): 330. IR ν/cm^{-1} (CsI disk): 2973w, 1422m, 1361s, 1262m, 1096s, 1024m, 859w, 804m, 616w, 544w, 348w, 322w, 311w, 300w, 240w, 225w.

[PtCl$_2$([11]aneS_2Te)]. The reaction was carried out similarly, using $PtCl_2$ (0.131 g, 0.49 mmol) and [11]aneS_2Te (0.150 g, 0.49

mmol). The yellow precipitate obtained after stirring at room temperature for two hours was filtered off, washed with Et_2O and dried *in vacuo*. Yield 0.092 g, 33%. Calc. for $[C_8H_{16}Cl_2PtS_2Te]$: C, 16.9; H, 2.8%. Found: C, 16.9; H, 2.6%. ESMS: found *m*/*z* = 534; calculated for $[^{195}Pt^{35}Cl([11]aneS_2{}^{130}Te)]^+$ 536. ^1H NMR (d^6-dmso): δ 2.0–3.4 (br m). $^{125}Te\{^1H\}$ NMR (d^6-dmf): 299 ($^1J_{PtTe}$ = 753 Hz). ^{195}Pt NMR (d^6-dmf): −3834. IR ν/cm^{-1} (CsI disk): 2958w, 2889w, 1410m, 1360m, 1295w, 1248m, 1154w, 1107m, 981m, 932w, 890w, 856m, 770w, 700w, 527w, 318m br.

$[PtCl_2([12]aneS_2Te)]$. $[PtCl_2(NCMe)_2]$ was generated by refluxing $PtCl_2$ (0.126 g, 0.47 mmol) in MeCN (*ca.* 30 cm^3) to form a clear, yellow solution. This was allowed to cool, filtered (celite) and [12]aneS$_2$Te (0.150 g, 0.47 mmol) in CH_2Cl_2 (*ca.* 10 cm^3) added *via* syringe. The mixture was stirred at room temperature for two hours and a small amount of dark material was filtered off. The remaining yellow solution was concentrated (*ca.* 10 cm^3) and added to ice-cold Et_2O. The resultant precipitate was filtered off, washed with Et_2O and dried *in vacuo* to give a bright yellow, powdered solid. Yield 0.132 g, 48%. Calc. for $[C_9H_{18}Cl_2PtS_2Te]\cdot 2CH_2Cl_2$: C, 17.5; H, 2.9%. Found: C, 17.1; H, 2.9%. ESMS: found *m*/*z* = 551; calculated for $[^{195}Pt^{35}Cl([12]aneS_2{}^{130}Te)]^+$ 550. ^1H NMR (d^6-dmso): δ 2.2–3.4 (br m). $^{125}Te\{^1H\}$ NMR (d^6-dmf): 374 ($^1J_{PtTe}$ = 1034 Hz). ^{195}Pt NMR (d^6-dmf): −3890. IR ν/cm^{-1} (CsI disk): 3032w, 2978w, 1430m, 1365m, 1307w, 1264w, 12212, 1109m, 907w, 841w, 806w, 754w, 482w, 354w, 322m br.

$[Rh(Cp^*)([11]aneS_2Te)](PF_6)_2$. $[Rh(Cp^*)Cl_2]_2$ (0.055 g, 0.089 mmol) was dissolved in MeOH (*ca.* 20 cm^3) and [11]aneS$_2$Te (0.054 g, 0.178 mmol) added in CH_2Cl_2 (10 cm^3). $TlPF_6$ (0.137 g, 0.39 mmol) was added to the solution, and the mixture stirred at room temperature overnight to form a clear orange mixture and a white precipitate of TlCl. The mixture was filtered and the solvent removed to give a residue that was then taken up in the minimum volume of acetone (*ca.* 5 cm^3), filtered again (celite) and added to ice-cold Et_2O. The resultant precipitate was filtered, washed with Et_2O and dried *in vacuo* to give a yellow solid. Yield 0.052 g, 35%. Calc. for $[C_{18}H_{31}F_{12}P_2RhS_2Te]\cdot Me_2CO$: C, 28.3; H, 4.2%. Found: C, 27.8; H, 3.7%. ESMS: found *m*/*z* = 689, 272; calculated for $\{[Rh(Cp^*)([11]aneS_2{}^{130}Te)]PF_6\}^+$ 689, calculated for $[Rh(Cp^*)([11]aneS_2Te)]^{2+}$ 272. ^1H NMR (d^6-Me_2CO): δ 2.5–3.6 (br m, [11]aneS$_2$Te), 1.78 (s, Cp*). $^{13}C\{^1H\}$ NMR (d^6-Me_2CO): 106.4 (C_5Me_5), 37.0, 32.9, 32.7 (CH_2S and $CH_2CH_2CH_2$), 24.6 (CH_2Te), 8.5 (C_5Me_5). $^{125}Te\{^1H\}$ NMR (d^6-Me_2CO): 282 ($^1J_{RhTe}$ = 106 Hz). IR ν/cm^{-1} (CsI disk): 3009w, 2976w, 1357m, 1261w, 1094m br, 997w, 835s, 731w, 613w, 560s, 476w, 322w.

$[Rh(Cp^*)([12]aneS_2Te)](PF_6)_2$. The reaction was carried out similarly, but using [12]aneS$_2$Te to produce a yellow–orange solid. Yield 42%. Calc. for $[C_{19}H_{33}F_{12}P_2RhS_2Te]\cdot Me_2CO$: C, 27.0; H, 3.9%. Found: C, 26.8; H, 3.7%. ESMS: found *m*/*z* = 701 (4%), 279 (100%); calculated for $\{[Rh(Cp^*)([11]aneS_2{}^{130}Te)]PF_6\}^+$ 703, calculated for $[Rh(Cp^*)([11]aneS_2Te)]^{2+}$ 279. ^1H NMR (d^6-Me_2CO): δ 2.6–3.5 (br m, [11]aneS$_2$Te), 1.73 (s, Cp*). $^{13}C\{^1H\}$ NMR (d^6-Me_2CO): 106.7 (Cp*), 34.0, 33.2, 32.3 (SCH_2 and $SCH_2CH_2CH_2Te$), 27.1 ($SCH_2CH_2CH_2S$), 25.6 (CH_2Te), 8.7 (C_5Me_5). $^{125}Te\{^1H\}$ NMR (d^6-Me_2CO): 275 ($^1J_{RhTe}$ = 102 Hz). IR ν/cm^{-1} (CsI disk): 2980w, 1481w, 1355m, 1260w, 1093m br, 1022w, 997w, 840s, 733w, 611w, 558s, 436w, 322w.

$[Rh(Cp^*)([9]aneS_2Te)](PF_6)_2$. The reaction was carried out similarly, but using [9]aneS$_2$Te to produce a yellow–orange solid. Yield 63%. Calc. for $[C_{16}H_{27}F_{12}P_2RhS_2Te]\cdot CH_2Cl_2$: C, 23.0; H, 3.3%. Found: C, 22.8; H, 3.1%. ESMS: found *m*/*z* = 515; calculated for $[Rh(Cp^*)([9]aneS_2{}^{130}Te)]^+$ *m*/*z* = 516. ^1H NMR (d^6-Me_2CO): δ 3.0–3.7 (br m, [9]aneS$_2$Te), 1.72 (s, Cp*). $^{13}C\{^1H\}$ NMR (d^6-Me_2CO): 107.5 (Cp*), 37.6, 32.9 (SCH_2), 24.7 (CH_2Te), 7.9 (C_5Me_5). $^{125}Te\{^1H\}$ NMR (d^6-Me_2CO): 397 ($^1J_{RhTe}$ = 75 Hz). IR ν/cm^{-1} (CsI disk): 2972w, 1473m, 1423m, 1382m, 1365m, 1227w, 1082m, 1024m, 838br s, 740w, 614w, 559s, 439w, 321w.

$[Cu([11]aneS_2Te)]BF_4$. $[Cu(MeCN)_4]BF_4$ (0.155 g, 0.49 mmol) and [11]aneS$_2$Te (0.150 g, 0.49 mmol) were stirred in MeOH (30 cm^3). CH_2Cl_2 (*ca.* 10 cm^3) was added to aid dissolution of the ligand. The solution was stirred at room temperature for two hours, concentrated (*ca.* 5 cm^3) and added to ice-cold Et_2O to produce a cream solid that was filtered off and dried *in vacuo*. Yield 0.122 g, 51%. Calc. for $[C_8H_{16}BCuF_4S_2Te]$: C, 21.2; H, 3.6%. Found: C, 21.3; H, 3.3%. ESMS: found *m*/*z* = 673, 410, 369; calculated for $[^{63}Cu([11]aneS_2{}^{130}Te)_2]^+$ *m*/*z* = 673, $[^{63}Cu([11]aneS_2{}^{130}Te)\cdot MeCN]^+$ 410, $[^{63}Cu([11]aneS_2{}^{130}Te)]^+$ 369. ^1H NMR (CD_3NO_2): δ 2.2–3.5 (br m, [11]aneS$_2$Te). IR ν/cm^{-1} (CsI disk): 2973w, 1437m, 1419m, 1356m, 1287w, 1250w, 1209w, 1060 vs br, 913w, 839w, 736w, 521m, 223w.

$[Cu([12]aneS_2Te)]BF_4$. The reaction was carried out similarly, using [12]aneS$_2$Te (0.098 g, 0.31 mmol) and $[Cu(MeCN)_4]BF_4$ (0.097 g, 0.31 mmol). The reagents were stirred in CH_2Cl_2 (*ca.* 40 cm^3) for two hours and worked up similarly to produce a creamy-yellow solid. Yield 0.095 g, 65%. Calc. for $C_9H_{18}BCuF_4S_2Te$: C, 23.1; H, 3.9%. Found: C, 22.5; H, 4.0%. ^1H NMR ($CDCl_3$, 300 K): δ 2.98 (br, SCH_2), 2.80 (m, $TeCH_2$), 2.10 (br, $CH_2CH_2CH_2$). ESMS: found *m*/*z* = 701, 424, 383; calc. for $[^{63}Cu([12]aneS_2{}^{130}Te)_2]^+$ 701, $[^{63}Cu([12]aneS_2{}^{130}Te)(MeCN)]^+$ 424, $[^{63}Cu([12]aneS_2{}^{130}Te)]^+$ 383. IR/cm^{-1} (CsI disk): 2962w, 2926w, 1436m, 1355m, 1285m, 1251w, 1066 br s, 905w, 847m, 824w, 804w, 763w, 519s.

$[Ag([11]aneS_2Te)]CF_3SO_3$. $Ag(CF_3SO_3)$ (0.025 g, 0.097 mmol) was added to a solution of [11]aneS$_2$Te (0.029 g, 0.097 mmol) in dry CH_2Cl_2 (30 cm^3) and the reaction stirred for 1 hour, during which time a light yellow precipitate was observed that was filtered off, washed with Et_2O and dried *in vacuo*. Yield 0.030 g, 63%. Calc. for $C_9H_{16}AgF_3O_3S_3Te$: C, 19.3; H, 2.9%. Found: C, 19.5; H, 3.0%. ^1H NMR ($CDCl_3$, 300 K): δ 2.2 (br, $TeCH_2CH_2CH_2S$), 2.7 (br, $TeCH_2$), 2.8–3.2 (m, SCH_2). ESMS: found *m*/*z* = 717, 454, 413; calc. for $[^{107}Ag([11]aneS_2{}^{130}Te)_2]^+$ 719, $[^{107}Ag([11]aneS_2{}^{130}Te)(NCMe)]^+$ 454, $[^{107}Ag([11]aneS_2{}^{130}Te)]^+$ 413. IR/cm^{-1} 2959w, 2948w, 1364m, 1263s, 1155m, 1098m, 1030m, 834w, 797w, 668w, 636m, 572w, 517w.

$[Ag([9]aneS_2Te)]CF_3SO_3$. Method as above, but using [9]aneS$_2$Te. Light yellow solid. Yield 60%. Calc. for $C_7H_{12}AgF_3O_3S_3Te$: C, 15.2; H, 2.3%. Found: C, 15.4; H, 2.2%. ^1H NMR ($CDCl_3$, 300 K): δ 2.2 (br, $TeCH_2$), 2.9–3.1 (m, SCH_2). ESMS: found *m*/*z* = 661, 382; calc. for $[^{107}Ag([9]aneS_2{}^{130}Te)_2]^+$ 663, $[^{107}Ag([9]aneS_2{}^{130}Te)]^+$ 385. IR/cm^{-1} (CsI disk): 2962w, 2946w, 1360s, 1263m, 1242w, 1150sh, 1096br s, 986m, 850w, 834w, 636m, 538w.

$[Ag([12]aneS_2Te)]CF_3SO_3$. Method as above, but using [12]aneS$_2$Te. Light yellow solid decomposes rapidly to give a black solid. Yield 38%. Analysis: see text. ^1H NMR ($CDCl_3$): δ 1.8 (br, $SCH_2CH_2CH_2S$), 2.1 (br, $TeCH_2CH_2CH_2S$), 2.4–3.0 (m, SCH_2, $TeCH_2$). ESMS: found *m*/*z* = 745, 427; calc. for $[^{107}Ag([12]aneS_2{}^{130}Te)_2]^+$ 747, $[^{107}Ag([12]aneS_2{}^{130}Te)]^+$ 427. IR/cm^{-1} (CsI disk): 2965w, 2945w, 1359s, 1275s, 1154m, 1090m, 1032m, 970w, 637m, 510w, 482w.

$[Ag([12]aneS_2Te)]BF_4$. [12]aneS$_2$Te (0.141 g, 0.44 mmol) and $AgBF_4$ (0.086 g, 0.44 mmol) were stirred in CH_2Cl_2 (*ca.* 40 cm^3) in a foil-wrapped vessel for one hour at room temperature. The solution was then concentrated (*ca.* 10 cm^3) and added to

Table 5 Crystallographic parameters[a]

Complex	[11]aneS_2Te	[12]aneS_2Te	1-thia-4-tellura-cyclohexane	[12]aneS_2TeI_2
Formula	$C_8H_{16}S_2Te$	$C_9H_{18}S_2Te$	C_4H_8Ste	$C_9H_{18}I_2S_2Te$
M	303.93	317.96	215.76	571.77
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$Pna2_1$	$P2_1$	$P2_1/n$	$P2_1/c$
a/Å	15.3529(4)	7.7448(3)	7.020(2)	10.4800(3)
b/Å	12.6938(3)	5.5407(3)	5.6344(15)	8.5703(3)
c/Å	5.50550(10)	13.7720(4)	8.009(3)	16.6779(5)
β/°	90	94.666(2)	93.635(10)	94.309(2)
U/Å^3	1072.95(4)	589.02(4)	316.13(16)	1493.72(7)
Z	4	2	2	4
μ(Mo-Kα)/mm^{-1}	3.104	2.832	4.899	6.375
Unique reflections	1452	1479	706	3494
Obs. reflections [$I_o > 2\sigma(I_o)$]	1251	1437	650	2701
R	0.0340	0.0315	0.0266[b]	0.0563
R_w	0.0410	0.0380	0.0683[b]	0.0700

[a] $R = \Sigma\,(|F_{obs}|_i - |F_{calc}|_i)/\Sigma\,|F_{obs}|_i$; $R_w = \sqrt{[\Sigma\, w_i(|F_{obs}|_i - |F_{calc}|_i)^2/\Sigma\, w_i|F_{obs}|_i^2}$. [b] R_1 ($I > 2\sigma(I)$); wR_2 ($I > 2\sigma(I)$) from SHELXL-97.[29]

ice-cold Et_2O to form a creamy-yellow solid that was filtered and dried *in vacuo*. Yield 0.043 g, 19%. Calc. for $C_9H_{18}AgBF_4S_2Te$: C, 21.1; H, 3.5%. Found: C, 20.8; H, 3.3%. ^{1}H NMR ($CDCl_3$, 300 K): δ 1.8 (br, 1H, $SCH_2CH_2CH_2S$), 2.0 (br, 2H, $TeCH_2CH_2CH_2S$), 2.55–2.95 (br, 6H, SCH_2, $TeCH_2$). ESMS: found m/z = 745, 427; calc. for $[^{107}Ag([12]ane S_2{}^{130}Te)_2]^+$ 747, $[^{107}Ag([12]ane S_2{}^{130}Te)]^+$ 427. IR/cm^{-1} (CsI disk): 2921m, 2843w, 1438m, 1344m, 1291m, 1245m, 1209m, 1062br s, 798w, 729m, 667w, 520s.

X-ray crystallography

Details of the crystallographic parameters are given in Table 5. Crystals of [11]aneS_2Te, [12]aneS_2Te and 1-thia-4-telluracyclohexane were grown from CH_2Cl_2 solutions, while [12]aneS_2TeI_2 crystals were obtained from CH_2Cl_2–$CHCl_3$ solution. Data collection used a Nonius Kappa CCD diffractometer equipped with an Oxford Systems open-flow cryostat operating at 120K, using graphite-monochromated Mo-Kα X-radiation (λ = 0.71073 Å). Structure solution and refinement were routine except for 1-thia-4-telluracyclohexane which crystallises in space group $P2_1/n$ with Z = 2 and the 6-membered ring disordered across a crystallographic inversion centre. The refinement used a 50 : 50 split occupancy for the S and Te atoms.[27–30] Selected bond lengths and angles are given in Tables 2–4.

CCDC reference numbers 206527–206530.

See http://www.rsc.org/suppdata/dt/b3/b302985a/ for crystallographic data in CIF or other electronic format.

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