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The Reaction of *N*,*N*′-Di-*tert*-butylthiourea (dtbtu) with Antimony(III) Halides – Formation of the Triply Bridged [(dtbtu)SbX_2(μ-X)$_2$(μ-dtbtu)-SbX_2(dtbtu)] (X = Cl, Br) Dimers

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The reactions of *N*,*N*′-di-*tert*-butylthiourea (dtbtu) with SbX_3 (X = Cl, Br) in a 2:1 dtbtu/SbX_3 ratio unexpectedly lead to products with a 3:2 dtbtu/SbX_3 ratio. These complexes have been shown by X-ray crystallographic studies to exist as triply bridged dimers, [(dtbtu)SbX_2(μ-X)$_2$(μ-dtbtu)SbX_2(dtbtu)], (X = Cl, **1**; X = Br, **2**), which feature one bridging dtbtu ligand and two bridging halides. The geometry at antimony is highly distorted octahedral. This distortion is partly due to the bridging ligands, but there is also evidence for the presence of stereochemically active lone pairs. In **1** the lone pair appears to be located towards an edge of the octahedron between a terminal and a bridging halide. The situation is similar in **2**, but the distortion is considerably greater at one of the antimony atoms than at the other. In contrast, the reaction of dtbtu with SbI_3 yields a 1:1 complex, [SbI_3(dtbtu)] (**3**), which is likely to be polymeric with bridging iodide ligands. The low solubility of the iodide complex has precluded characterisation by X-ray crystallography.

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Introduction

The coordination chemistry of the p-block remains considerably less well studied than that of the transition metals, and in the case of group 15 has been most frequently explored for bismuth, with fewer studies appearing on complexes of arsenic and antimony.[1–2] Complexes of antimony(III) with sulfur donors have recently received renewed attention, as antimony(III) thione and thiolate complexes have been shown to exhibit antitumour properties.[3–4] Studies into coordination complexes of group 15 Lewis acids are often hindered by the lability of such complexes in solution, and additionally, the stereochemical activity/non-activity of the lone pair plays an important role in the wide range of solid-state structures which may be accessed for complexes of this type. Significant secondary bonding is also frequently observed in these systems, as a consequence of the M–X σ* antibonding orbital which has the potential to act as an acceptor orbital towards another donor atom.[5] These factors all contribute to the unpredictable structural variations observed for complexes of group-15 trihalides.

A number of complexes of antimony(III) halides with sulfur donor ligands have been reported. Multidentate and macrocyclic thioether complexes usually form polymeric structures with a distorted octahedral or square-pyramidal geometry around the antimony atom.[6–8] In most cases, the complexes consist of different types of polymeric arrays based on primary SbX_3 units, linked by weaker secondary bonding to the thioether ligands. As a consequence, one common feature in these series of complexes is the retention of a pyramidal SbX_3 unit. The reactions of $SbCl_3$ with a series of *N*,*N*′-dialkylthiourea compounds in ethanol (alkyl groups: Et, *i*Pr, Cy) have been reported to yield complexes of the formula [$SbCl_3L_2$], despite the use of three equivalents of the thiourea ligand.[9] ^{121}Sb Mössbauer studies of these complexes suggested a square-pyramidal geometry with weakly bound thiourea ligands.

Structural reports on antimony(III) halide complexes with C=S donors (either thiones or thioureas) are scarce. A small number of examples of complexes with $SbCl_3$ have been reported, although none with $SbBr_3$ or SbI_3. Structural studies have shown that antimony(III) chloride complexes typically exhibit either a 1:1 [$SbCl_3L$] stoichiometry, (based on a "see-saw" geometry), or a 2:1 [$SbCl_3L_2$] stoichiometry (square-based pyramidal geometry), although in most cases secondary interactions are observed resulting in an overall distorted octahedral geometry at the antimony atom, and subtle variations in the structures observed.

Examples of 1:1 [$SbCl_3L$] systems include those with tetramethylthiourea (tmtu),[10] and with the cyclic thioamides dmit and mbit, [dmit = 1,3-dimethyl-2-(3*H*)imidazolethione, mbit = 1,1′-methylenebis(3-methyl-2*H*-imidazole-2-thione)].[11–12] The tmtu complex [$SbCl_3$(tmtu)] is based on a see-saw geometry (as predicted by VSEPR theory), but the coordination sphere is extended because two of the chloride atoms bridge adjacent antimony centres. This results in the formation of a polymeric chain with

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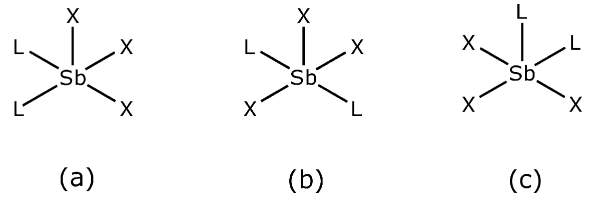
square-pyramidal geometry at antimony, and the tmtu ligand occupying the apical position.[10] A similar situation is observed for [$SbCl_3$(dmit)], although an additional, very weak bridge to a further dmit is observed, giving an overall distorted octahedral geometry.[11] In the related mbit complex the ligand chelates to the antimony, and is thus based on a square-pyramidal geometry, but again shows secondary bonding to a further mbit sulfur atom, again resulting in an octahedral geometry at antimony.[12] The 2:1 square-pyramidal complexes [$SbCl_3L_2$] may exhibit three different isomeric forms, (a) apical halide, with sulfur donors *cis* to each other, (b) apical halide with *trans*-sulfur donors, or (c) apical sulfur donor, (Figure 1) and examples of all three isomers have been observed. The complexes [$SbCl_3$(mbtt)$_2$],[13] [$SbCl_3$(mbzim)$_2$],[4] and [$SbCl_3$(mtzd)$_2$],[4] [mbtt = *N*-methylbenzothiazole-2-thione, mbzim = 2-(mercapto)-benzimidazole, mtzd = 2-(mercapto)thiazolidine] are all type (a) complexes, [$SbCl_3$(Etmbzim)$_2$][4] [Etmbzim = 5-ethoxy-2-(mercapto)benzimidazole] is type (b), whilst [$SbCl_3$(mit)$_2$][13] and [$SbCl_3$(tmt)$_2$][4,14] (mit = 3-methylimidazole-2-thione, tmt = trimethylenethiourea) are type (c). Most of these complexes feature additional weak secondary Sb···X (X = Cl or S) interactions to give a distorted octahedral geometry at antimony.



(a) (b) (c)

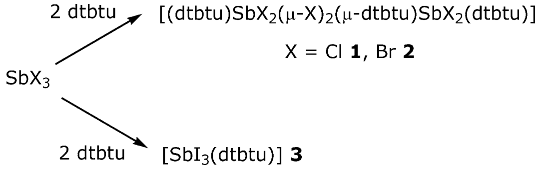
Figure 1. Different possible isomers of square-pyramidal complexes of formula [SbX_3L_2], where L = sulfur donor ligand.

Thus, whilst a number of antimony(III) complexes with cyclic thione donors have been structurally characterised, examples with substituted thioureas are limited only to [$SbCl_3$(tmtu)].[10] We therefore now report a study of the complexes obtained from the reactions of the bulky *N*,*N*′-di-*tert*-butylthiourea (dtbtu) with the antimony(III) halides SbX_3 (X = Cl, Br, I).

Results and Discussion

Synthesis and Spectroscopic Studies

The series of antimony(III) halides SbX_3 (X = Cl, Br, I) were treated with *N*,*N*′-di-*tert*-butylthiourea (dtbtu) in a 2:1 dtbtu/SbX_3 ratio in anhydrous dichloromethane. The reactions rapidly precipitated yellow- to tan-coloured solids (X = Cl, **1**; Br, **2**; I, **3**). The complexes formed when X = Cl and Br both analysed to a 3:2 dtbtu/SbX_3 ratio, whilst when X = I the product obtained exhibited a 1:1 ratio. Despite the 2:1 ratio of the starting materials these reactions only appear to lead to products of the above stoichiometries, and the 3:2 complexes with $SbCl_3$ and $SbBr_3$ were formed even when a 1:1 ratio was used. The antimony(III) complexes **1**–**3** were found to be stable to air and moisture once formed. X-ray crystallographic studies (see below) have shown that the 3:2 complexes **1** and **2** are triply bridged dimers, [(dtbtu)SbX_2(μ-X)$_2$(μ-dtbtu)SbX_2(dtbtu)] (X = Cl **1**, Br **2**), with two bridging halides and one bridging dtbtu ligand (Scheme 1).



Scheme 1. Products obtained from the reactions of SbX_3 (X = Cl, Br, I) in anhydrous dichloromethane.

Spectroscopic studies of the antimony(III) complexes **1** to **3** were undertaken. The poor solubility of these complexes in a range of common organic solvents hampered the acquisition of meaningful NMR spectroscopic data. Attempts to obtain NMR spectroscopic data of **1** and **2** (which are slightly soluble in $CDCl_3$), resulted only in the observation of peaks for the CH_3 protons (δ_H = 1.48) and carbon atoms (δ_C = 29.6) of the *t*Bu group. These values are very similar to literature values for dtbtu in $CDCl_3$, $\delta_H = 1.46/\delta_C = 29.3$,[15] and suggest that these complexes may dissociate the dtbtu ligands in solution. The complexes were insufficiently soluble to resolve either the *t*Bu or C=S quaternary carbon atoms in the $^{13}C\{^1H\}$ NMR spectrum. The 1:1 product obtained from dtbtu and antimony(III) iodide, [SbI_3(dtbtu)] (**3**), is insoluble in common organic solvents, and as a result, all attempts to obtain NMR spectroscopic data for this complex have been unsuccessful.

Vibrational spectroscopic data were obtained for all three complexes, and also the dtbtu ligand for comparative purposes. Both IR and Raman spectra were obtained as solid samples, with selected peaks for dtbtu and the complexes **1**–**3** shown in Table 1. All three complexes show multiple ν(NH) stretching vibrations [3434–3210 cm^{-1} (**1**), 3433–3232 cm^{-1} (**2**), 3409–3283 cm^{-1} (**3**)], which are consistent with the presence of NH groups orientated both *syn* and *anti* to the C=S group.[16] The crystal structures of **1** and **2**

Table 1. Selected IR and Raman spectroscopic data for complexes **1**–**3**.[a]

Complex	ν(NH)[b]	Thioamide I[b]	Thioamide IV[b]	ν(SbS)/ν(SbX)[c]
1	3434, 3409, 3210	1562	637	259, 162, 142
2	3433, 3415, 3232	1564	637	298, 195, 156
3	3409, 3283	1560	645	279, 167
dtbtu	3303, 3266, 3139, 3059	1541	688	

[a] All values in cm^{-1}. [b] Data taken from the IR spectrum. [c] Data taken from the Raman spectrum.

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(see below) show that the dtbtu groups in both complexes do adopt the *syn–anti* conformation, although the presence of bridging and terminal dtbtu groups in **1** and **2** may also lead to multiple ν(NH) bands. The structure of "free" dtbtu has recently been reported,[15] and shown to adopt an *anti–anti* orientation of the NH groups, with hydrogen bonding between the NH and C=S groups of neighbouring dtbtu molecules leading to the formation of a hydrogen-bonded linear chain. This hydrogen bonding may explain the presence of four ν(NH) bands between 3303 and 3059 cm^{-1} in the free ligand. A shift to higher frequency of the ν(NH) bands in the IR spectra of the compounds **1**–**3** is consistent with the complexation of thiourea ligands which are not nitrogen-bonded,[17] and also with the removal of hydrogen-bonded interactions.[18]

The vibrational spectra of *N*,*N′*-dialkylthiourea compounds commonly show four sets of bands due to mixed vibrations of the R(H)NCS thioamide group.[16,19] The IR spectra of **1**–**3** all show nine medium to strong intensity bands between 1562–1193 cm^{-1} (**1**), 1564–1192 cm^{-1} (**2**), 1560–1192 cm^{-1} (**3**). The thioamide I and IV bands should be the most sensitive to coordination, as these contain the largest contributions from ν(CN) and ν(CS) stretches, respectively.[16,18–20] The thioamide I band of dtbtu in chloroform solution has been reported at 1550 cm^{-1},[16] and we therefore assign the intense band at 1541 cm^{-1} in the solid-state IR spectrum of dtbtu to this band. The IR spectra of **1**–**3** all show prominent bands between 1560 and 1564 cm^{-1} which are assigned to the thioamide I band, and show the expected shift to higher wavenumbers upon coordination. The bands observed between 1509 and 1526 cm^{-1} in the spectra of **1**–**3** are probably due to δ(NH) bending modes.[16] A direct assignment of the thioamide II and III modes has not been attempted due to the presence of a large number of bands in the spectral range 1460 to 1190 cm^{-1}. The intense band in the spectrum of dtbtu at 668 cm^{-1} (assigned to the thioamide IV band) is shifted to 637–645 cm^{-1} in the spectra of **1**–**3**, as expected for a band where the major contribution is from ν(CS) stretching.

The Raman spectra of **1**–**3** show bands at low wavenumbers, assigned either to ν(SbS) or ν(SbX) stretches (Table 1). The spectrum of **1** is of poor quality due to fluorescence, but three bands are observed at 259, 162 and 142 cm^{-1}. The peak at 259 cm^{-1} is very broad and has a shoulder at 276 cm^{-1}. It is likely that this broad feature consists of both the ν(SbS) and ν(SbCl) stretches, as the former have been reported between 280–300 cm^{-1}, and the latter between 320–350 cm^{-1}.[4,21–22] The peaks at 162 and 142 cm^{-1} may arise due to ν(Sb–Cl–Sb) from the bridging chlorides. The Raman spectrum of **2** also shows three peaks at 298 [assigned to ν(SbS)], 195 [assigned to ν(SbBr)], and 156 cm^{-1}, with the latter again possibly due to ν(Sb–Br–Sb) of the bridging bromides. The Raman spectrum of **3** shows an intense ν(SbI) stretch at 167 cm^{-1} which is consistent with vibrational data for thiourea complexes of antimony(III) iodide.[21,23] The peak is broad and it was not possible to distinguish separate stretches for terminal and bridging iodides, but it seems likely that **3** is a 1:1 complex consisting of a polymeric chain similar to [SbCl$_3$(tmtu)],[10] linked by bridging iodides. Two weak bands are also observed in the spectrum of **3** at 279 and 235 cm^{-1}, and the former is assigned to a ν(SbS) stretch.

Structural Studies

The bulk material obtained from the reactions of dtbtu with SbCl$_3$ and SbBr$_3$ is, in both cases, highly crystalline, and the 3:2 ratio was confirmed by X-ray diffraction. Both complexes exist as triply bridged dimers, [(dtbtu)SbX$_2$(μ-X)$_2$(μ-dtbtu)SbX$_2$(dtbtu)] (X = Cl, **1**; Br, **2**), featuring one bridging dtbtu ligand, and two bridging halides (Figure 2 and Figure 3 respectively, with selected bond lengths and

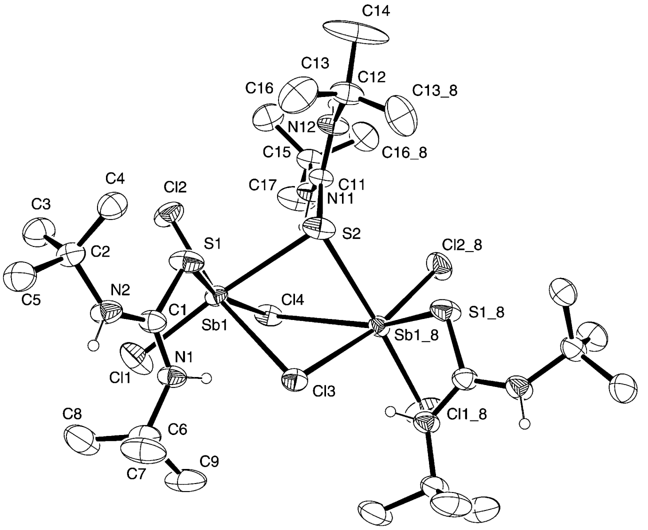

Figure 2. ORTEP representation of the molecular structure of [(dtbtu)SbCl$_2$(μ-Cl)$_2$(μ-dtbtu)SbCl$_2$(dtbtu)] (**1**). Thermal ellipsoids are shown at the 30% probability level, with selected hydrogen atoms omitted for clarity. Cl(4) is disordered over two sites, only one site is shown. Symmetry operation used to generate equivalent atoms: _8: *x*, 3/2 – *y*, *z*.

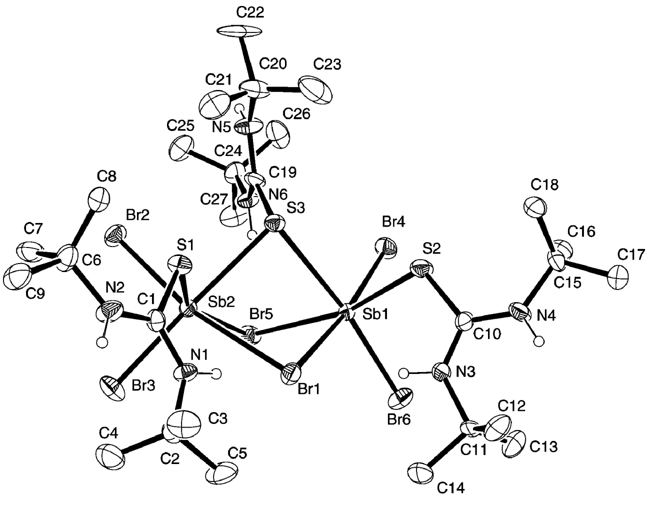

Figure 3. ORTEP representation of the molecular structure of [(dtbtu)SbBr$_2$(μ-Br)$_2$(μ-dtbtu)SbBr$_2$(dtbtu)] (**2**). Thermal ellipsoids are shown at the 30% probability level, with selected hydrogen atoms omitted for clarity.

angles in Table 2 and Table 3). The structure of **2** represents the first crystallographically characterised example of a C=S donor complex with $SbBr_3$.

Table 2. Selected bond lengths [Å] and angles [°] for [(dtbtu)-$SbCl_2$(μ-Cl)$_2$(μ-dtbtu)$SbCl_2$(dtbtu)] (**1**).

Bonds		Angles	
Sb(1)–Cl(1)	2.4372(18)	S(1)–Sb(1)–Cl(4)	165.69(5)
Sb(1)–Cl(2)	2.4380(14)	Cl(1)–Sb(1)–S(2)	171.66(5)
Sb(1)–Cl(3)	2.9586(11)	Cl(2)–Sb(1)–Cl(3)	167.26(4)
Sb(1)–Cl(4)	2.7877(14)	S(1_8)–Sb(1_8)–Cl(4)	155.92(5)
Sb(1_8)–Cl(4)	3.300(2)	Cl(1)–Sb(1)–Cl(2)	94.97(5)
Sb(1)–S(1)	2.6145(12)	Cl(1)–Sb(1)–Cl(3)	97.22(5)
Sb(1)–S(2)	2.9732(13)	S(2)–Sb(1)–Cl(3)	75.74(4)
		S(2)–Sb(1)–Cl(2)	91.81(4)
C(1)–S(1)	1.744(5)	S(1)–Sb(1)–Cl(1)	94.59(5)
C(11)–S(2)	1.726(6)	S(1)–Sb(1)–Cl(2)	88.01(4)
C(1)–N(1)	1.320(6)	S(1)–Sb(1)–Cl(3)	87.34(4)
C(1)–N(2)	1.328(6)	S(1)–Sb(1)–S(2)	80.78(4)
C(11)–N(11)	1.330(7)	Cl(1)–Sb(1)–Cl(4)	99.51(6)
C(11)–N(12)	1.328(8)	Cl(2)–Sb(1)–Cl(4)	93.13(5)
		Cl(3)–Sb(1)–Cl(4)	88.51(5)
		S(2)–Sb(1)–Cl(4)	84.92(5)
		Sb(1)–Cl(3)–Sb(1_8)	85.17(4)
		Sb(1)–Cl(4)–Sb(1_8)	81.78(5)
		Sb(1)–S(2)–Sb(1_8)	84.66(4)

Table 3. Selected bond lengths [Å] and angles [°] for [(dtbtu)-$SbBr_2$(μ-Br)$_2$(μ-dtbtu)$SbBr_2$(dtbtu)] (**2**).

Bond		Angle	
Sb(1)–Br(4)	2.6210(18)	S(1)–Sb(2)–Br(5)	155.06(9)
Sb(1)–Br(6)	2.6010(18)	Br(1)–Sb(2)–Br(2)	168.04(5)
Sb(1)–S(2)	2.657(4)	Br(3)–Sb(2)–S(3)	169.95(9)
Sb(2)–Br(2)	2.6259(17)	S(2)–Sb(1)–Br(5)	164.46(9)
Sb(2)–Br(3)	2.6385(19)	Br(1)–Sb(1)–Br(4)	170.11(6)
Sb(2)–S(1)	2.561(4)	Br(6)–Sb(1)–S(3)	167.80(8)
Sb(1)–Br(1)	3.0548(17)	Br(2)–Sb(2)–Br(3)	94.65(5)
Sb(1)–Br(5)	2.9746(18)	Br(2)–Sb(2)–S(3)	90.51(8)
Sb(1)–S(3)	3.009(3)	Br(1)–Sb(2)–S(3)	78.02(8)
Sb(2)–Br(1)	3.0592(17)	Br(1)–Sb(2)–Br(3)	96.21(5)
Sb(2)–Br(5)	3.3444(18)	S(1)–Sb(2)–Br(1)	85.07(9)
Sb(2)–S(3)	2.900(3)	S(1)–Sb(2)–Br(2)	89.24(9)
		S(1)–Sb(2)–Br(3)	93.61(9)
C(1)–S(1)	1.734(13)	S(1)–Sb(2)–S(3)	77.81(11)
C(10)–S(2)	1.742(13)	Br(1)–Sb(2)–Br(5)	81.40(4)
C(19)–S(3)	1.725(14)	Br(2)–Sb(2)–Br(5)	99.89(5)
C(1)–N(1)	1.332(17)	Br(3)–Sb(2)–Br(5)	108.56(5)
C(1)–N(2)	1.317(17)	S(3)–Sb(2)–Br(5)	78.94(8)
C(10)–N(3)	1.325(17)	Br(1)–Sb(1)–Br(6)	91.39(5)
C(10)–N(4)	1.319(17)	Br(4)–Sb(1)–Br(6)	97.94(6)
C(19)–N(5)	1.334(17)	Br(4)–Sb(1)–S(3)	94.12(8)
C(19)–N(6)	1.336(18)	Br(1)–Sb(1)–S(3)	76.46(7)
		S(2)–Sb(1)–Br(1)	88.65(9)
		S(2)–Sb(1)–Br(6)	97.79(9)
		S(2)–Sb(1)–Br(4)	86.86(9)
		S(2)–Sb(1)–S(3)	80.98(11)
		Br(1)–Sb(1)–Br(5)	87.80(5)
		Br(6)–Sb(1)–Br(5)	97.42(5)
		Br(4)–Sb(1)–Br(5)	94.20(5)
		S(3)–Sb(1)–Br(5)	83.48(8)
		Sb(1)–Br(1)–Sb(2)	82.82(4)
		Sb(1)–Br(5)–Sb(2)	79.34(4)
		Sb(1)–S(3)–Sb(2)	86.35(9)

The structures of **1** and **2** consist of face-shared bioctahedra, with both antimony atoms in each of the structures exhibiting a highly distorted octahedral environment. The terminal dtbtu is located *cis* to the bridging dtbtu at both antimony centres. The structure of **1** (orthorhombic, *Pnma*), features a mirror plane through the centre of the bridging dtbtu and one of the bridging chlorines, Cl(3), whilst the second bridging chlorine, Cl(4), is disordered with one site located either side of the mirror plane. In contrast, the structure of **2** (triclinic, $P\bar{1}$) has no mirror plane. The structures of both **1** and **2** are unusual in that most antimony(III) complexes of sulfur donor ligands feature an intact pyramidal SbX_3 unit, which comprises the primary coordination sphere.[2] In contrast, in **1** and **2** there are two pyramidal SbX_2L units linked by three bridging ligands. The preference for the formation of an SbX_2L unit may be due to the greater donor power of dtbtu compared with many other thione and thiourea ligands. It is also likely that the geometry observed is the least sterically hindered with respect to the bulky dtbtu groups, although the observation of triply bridged dimers has not previously been reported for any antimony(III) complexes of C=S donors. In both structures the bridging sulfur atom and one of the bridging halides lie in the same plane as the antimony atom and the two terminal halides. The other bridging halide is approximately *trans* to the terminal dtbtu ligand, but the S–Sb–X angles between these two groups are highly distorted from 180°, [S(1)–Sb(1)–Cl(4): 165.69(5)°/S(1_8)–Sb(1_8)–Cl(4): 155.92(5)° for **1**; S(2)–Sb(1)–Br(5): 164.46(9)°/S(1)–Sb(2)–Br(5): 155.06(9)° for **2**].

In the structure of **1** the terminal Sb–Cl bonds are 2.4372(18) and 2.4380(14) Å, and are longer than observed in the structure of $SbCl_3$ [Sb–Cl: 2.340(2) to 2.368(1) Å],[24] but consistent with Sb–Cl bonds in [$SbCl_3$(dmit)], Sb–Cl: 2.431(1) Å,[11] and in [$SbCl_3$(tmtu)], Sb–Cl: 2.428(2) Å.[10] One of the bridging chlorine atoms lies on the mirror plane and thus bridges symmetrically, Sb(1)–Cl(3): 2.9586(11) Å, whilst the disordered Cl(4) atom results in unsymmetrical Sb–Cl bonds of 2.7877(14) and 3.300(2) Å. This asymmetry is consistent with the triply halide-bridged $[Sb_2Cl_9]^{3-}$ anion in $[Me_3[9]aneN_3H_2]_2[Sb_2Cl_9]Cl\cdot MeCN\cdot H_2O$,[25] which contains one essentially symmetrical bridge, and two highly unsymmetrical bridges. The terminal Sb–S bond in **1** is 2.6145(12) Å and is slightly longer than that in [$SbCl_3$(dmit)], Sb–S: 2.511(1) Å,[11] or [$SbCl_3$(tmtu)], Sb–S: 2.505(2) Å.[10] The Sb–S bond is much shorter than observed for antimony(III) thioether complexes, (typically 2.95 to 3.29 Å),[7–8] which reflects the greater donor power of thiourea ligands compared to thioether ligands. The bridging dtbtu exhibits a longer Sb–S bond of 2.9732(13) Å, with an Sb–S–Sb angle of 84.66(4)°. The Sb–S bond is similar to that observed for the bridged thione groups in [$SbCl_3$(mbit)], Sb–S: 2.939(2) Å.[12]

The lack of a mirror plane in the structure of **2** results in a slight asymmetry in the Sb–S bonds to the bridging dtbtu ligand, [Sb(1)–S(3): 3.009(3), Sb(2)–S(3): 2.900(3) Å], and in the Sb–Br bonds to one of the bridging bromides, [Sb(1)–Br(1): 3.0548(17) Å, Sb(2)–Br(1): 3.0592(17) Å], whilst the other bridging bromide, Br(5), displays highly unsymmetrical Sb–Br bond lengths, [Sb(1)–Br(5): 2.9746(18) Å, Sb(2)–Br(5): 3.3444(18) Å]. This asymmetry contrasts greatly with structures containing the triply bridged $[Sb_2Br_9]^{3-}$ anion, which generally contain symmetrically bridged bromines, with Sb–Br bonds ranging between 2.97 and 3.05 Å.[26–28] However, the related $[Sb_2Br_7(PEt_3)_2]^-$ anion in $[Et_3PH][Sb_2Br_7(PEt_3)_2]$ is similar to **2** in that it contains one bridging bromide which is close to symmetrical, and two that are not, with Sb–Br bonds lying over a large range, 2.855(2) to 3.564(3) Å.[29] In this anion the asymmetry was interpreted as a result of the strong *trans* influence of the Et_3P ligands, lengthening the Sb–Br bonds to the bridging bromine atoms *trans* to Et_3P. The structure of **2** differs from $[Et_3PH][Sb_2Br_7(PEt_3)_2]$, in that in the latter the Et_3P ligands are *trans* to different bridging bromine atoms, and are thus on opposite faces of the dimer. In contrast, in **2**, the dtbtu ligands are *trans* to the same bridged bromine, Br(5), leading to a greater degree of distortion from octahedral geometry than observed for $[Et_3PH][Sb_2Br_7(PEt_3)_2]$, although the presence of a stereochemically active lone pair (see below) is likely to have a more significant contribution to the observed distortion. The Sb–S bonds to the terminal dtbtu ligands in **2** also show considerable variation. At Sb(1) a long Sb–S bond of 2.657(4) Å is observed to the dtbtu group *trans* to the shorter Sb(1)–Br(5) bond, whilst at Sb(2) the opposite is observed, with a much shorter Sb–S bond of 2.561(4) Å *trans* to the longer Sb(2)–Br(5) bond. It should be noted that the average of the two, [2.609(4) Å], is close to the observed Sb–S bond length to the terminal dtbtu ligands in **1**, 2.6134(14) Å. Taking steric arguments into consideration, the least hindered configuration for **2** is likely to be that where the terminal dtbtu ligands are *trans* to different bridging bromines, as seen in the $[Sb_2Br_7(PEt_3)_2]^-$ anion. However, the presence of an additional bridged dtbtu rules this isomer out as severe steric congestion would result, which is minimised in the isomer observed. The terminal Sb–Br bonds do not appear to be especially influenced by which ligand they are *trans* to, varying between 2.6010(18) and 2.6385(19) Å, and are somewhat longer than those observed for the two polymorphs of $SbBr_3$ [Sb–Br: 2.46(2) to 2.54(2) Å],[30] and in thioether complexes of antimony(III) bromide,[7–8] but are similar to the range observed in $[Et_3PH][Sb_2Br_7(PEt_3)_2]$.[29]

The distortion around the antimony centres in both structures is particularly high in angles involving the bridging ligands, e.g. S(2)–Sb(1)–Cl(3): 75.74(4)° **1**; S(3)–Sb(1)–Br(1): 76.46(7)°/S(3)–Sb(2)–Br(1): 78.02(8)° **2**. This suggests that the steric requirements of the bridging ligands may play some part in the high degree of distortion of the geometry, although a close inspection of all the angles around the antimony atoms in both structures also suggests the likely presence of a stereochemically active lone pair. In **1** the Cl(1)–Sb(1)–Cl(3) and Cl(1)–Sb(1)–Cl(4) angles are much wider than expected, 97.22(5)° and 99.51(6)° respectively, whilst conversely the S(2)–Sb(1)–Cl(3) and S(1)–Sb(1)–S(2) angles are narrower, 75.74(4)° and 80.78(4)°. This suggests that the lone pair in **1** may be located towards the edge of the octahedron between atoms Cl(1) and Cl(4), or towards the face of the octahedron between atoms Cl(1), Cl(3) and Cl(4).

In the structure of **2** the distortion appears to be considerably greater at atom Sb(2) than at Sb(1), as there is an extremely wide angle, Br(3)–Sb(2)–Br(5): 108.56(5)°, and the other terminal bromine atom also displays a widened Br–Sb–Br angle to the bridging bromide Br(5), Br(2)–Sb(2)–Br(5): 99.89(5)°. The angles Br(1)–Sb(2)–S(3) and S(1)–Sb(2)–S(3) are particularly acute, 78.02(8) and 77.81(11), respectively, and it therefore seems likely that the lone pair is located towards the edge of the octahedron between atoms Br(3) and Br(5), i.e in a similar orientation to that observed for **1**. In contrast, at atom Sb(1) the lone pair appears to be less active, with widened Br(4)–Sb(1)–Br(6), S(2)–Sb(1)–Br(6) and Br(6)–Sb(1)–Br(5) angles of 97.94(6)°, 97.79(9)° and 97.42(5)° respectively, and narrow angles on the opposite side of the octahedron, S(2)–Sb(1)–S(3): 80.98(11)°, S(3)–Sb(1)–Br(5): 83.48(8)°, S(3)–Sb(1)–Br(1): 76.46(7)°. This suggests that the lone pair is most likely to be located towards the edge of the octahedron between atoms Br(4) and Br(6)

Within the dtbtu groups themselves a considerable lengthening of the C=S bond is seen upon complexation to antimony. In the structure of dtbtu the C=S bond is 1.6961(14) Å,[15] whereas the C=S bonds to the terminal dtbtu groups in **1** and **2** vary between 1.734(13) and 1.744(5) Å. The C=S bonds to the bridging dtbtu groups are not elongated to the same extent, 1.726(6) Å in **1**, 1.725(14) Å in **2**. In the structures of both **1** and **2** all the dtbtu groups show a *syn-anti* conformation, as suggested by the IR data. This contrasts with the structure of dtbtu where the *anti–anti* conformation results in extensive hydrogen bonding.[15] When the dtbtu ligand is complexed the *anti–anti* conformation will be too sterically demanding, with both *t*Bu groups pointing towards the antimony atom, and thus the orientation switches to *syn–anti*.

Conclusions

The products formed from the reactions of C=S donor molecules with antimony(III) halides clearly display great structural diversity. The formation of triply bridged dimers observed for the $SbCl_3$ and $SbBr_3$ complexes with dtbtu has not been previously observed in antimony(III) complexes with C=S donors. The halide dependency of these reactions is illustrated by the formation of a 1:1 complex with SbI_3, which is likely to be polymeric. In view of the emerging interest into the therapeutic properties of antimony thiourea/thione complexes, the dimers reported herein show that new structural motifs can be accessed for these types of complexes by varying the choice of donor molecules. This may lead to developments in the study of structural-activity relationships in these types of complexes, and further studies of the reactions of antimony(III) halides with thiourea and selenourea ligands are currently underway.

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Experimental Section

General Details: The syntheses of all the antimony(III) complexes described herein were undertaken under anhydrous and anaerobic conditions using standard Schlenk techniques. Once formed, samples of **1** to **3** are stable, even in moist air, for several days, and are stable for many months if stored in pre-dried argon filled ampoules. Anhydrous dichloromethane, antimony(III) chloride, and antimony(III) iodide were purchased commercially (Aldrich), whilst *N*,*N*′-di-*tert*-butylthiourea and antimony(III) bromide were purchased from Alfa Aesar. All were used as received. Elemental analyses were performed by the University of Manchester Chemistry Department Microanalytical service. IR spectra were recorded as powdered samples with an ATR Perkin–Elmer Spectrum BX FT-IR spectrometer. Raman spectra were recorded as solid samples with a Nicolet-Nexus combined FT-IR/FT-Raman spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded with a Bruker DPX400 spectrometer operating at 399.9 and 100.6 MHz, respectively. Peak positions are quoted relative to external TMS using the high frequency positive convention throughout.

The IR spectrum of the free ligand dtbtu was also obtained for comparison with the IR spectra of **1** to **3**, which were collected in the same fashion.

***N*,*N*′-Di-*tert*-butylthiourea (dtbtu):** IR: $\tilde{\nu}$ = 3303 (vs), 3266 (vs), 3139 (m), 3059 (m), 2961 (s), 1578 (m), 1541 (vs), 1463 (s), 1392 (s), 1358 (s), 1320 (vs), 1231 (m), 1202 (s), 1040 (w), 1014 (m), 922 (w), 806 (w), 688 (s), 668 (m), 595 (w) cm^{-1}.

Synthesis of Complexes 1–3

[(dtbtu)SbCl$_2$(μ-Cl)$_2$(μ-dtbtu)SbCl$_2$(dtbtu)] (1): The ligand dtbtu (0.963 g, 5.11 mmol) was added to a CH_2Cl_2 solution (20 mL) containing $SbCl_3$ (0.583 g, 2.55 mmol). Formation of a yellow-green crystalline solid occurred rapidly, and the reaction mixture was stirred for 24 h. The solid was isolated by using standard Schlenk techniques and dried in vacuo. Yield 0.934 g (71.6%). Yellow-green crystals (m.p. 127 °C). $C_{27}H_{60}Cl_6N_6S_3Sb_2$ (1021.19): calcd. C 31.8, H 5.9, N 8.2, Sb 23.9, Cl 20.8; found C 31.8, H 6.0, N 8.1, Sb 23.6, Cl 21.0. IR: $\tilde{\nu}$ = 3434 (m), 3409 (m), 3210 (m), 2923 (s), 2854 (s), 1562 (vs), 1526 (s), 1465 (s), 1415 (s), 1400 (s), 1372 (vs), 1296 (vs), 1233 (s), 1193 (vs), 977 (m), 925 (m), 814 (m), 706 (m), 637 (m), 505 (m). Raman: $\tilde{\nu}$ = 2999, 2952, 2895, 1300, 759, 276, 259, 162, 142 cm^{-1}.

[(dtbtu)SbBr$_2$(μ-Br)$_2$(μ-dtbtu)SbBr$_2$(dtbtu)] (2): This compound was synthesised with the method outlined for **1**, by reacting $SbBr_3$ (0.830 g, 2.30 mmol) with dtbtu (0.865 g, 4.59 mmol) in CH_2Cl_2 (20 mL). Yield 1.130 g (76.4%). Bright yellow crystals (m.p. 130 °C). $C_{27}H_{60}Br_6N_6S_3Sb_2$ (1287.95): calcd. C 25.2, H 4.7, N 6.5, Br 37.2; found C 25.0, H 4.6, N 6.3, Br 36.9. IR: $\tilde{\nu}$ = 3433 (m), 3415 (m), 3232 (m), 2923 (s), 2854 (s), 1564 (vs), 1523 (s), 1465 (s), 1417 (m), 1399 (m), 1372 (s), 1298 (vs), 1232 (s), 1192 (s), 978 (m), 924 (w), 813 (m), 722 (w), 699 (w), 637 (m), 507 (m). Raman: $\tilde{\nu}$ = 3007, 2976, 2910, 1463, 1298, 1227, 760, 601, 298, 195, 156 cm^{-1}.

[SbI$_3$(dtbtu)] (3): Compound **3** was synthesised with the method outlined for **1**, by reacting SbI_3 (0.850 g, 1.69 mmol) with dtbtu (0.637 g, 3.38 mmol) in CH_2Cl_2 (20 mL). Yield 0.680 g (58.2%). Tan solid (m.p. 196 °C). $C_9H_{20}I_3N_2SSb$ (690.60): calcd. C 15.6, H 2.9, N 4.1, I 55.1; found C 15.3, H 3.0, N 4.3, I 54.9. IR: $\tilde{\nu}$ = 3409 (m), 3283 (m), 2925 (s), 2855 (s), 1560 (vs), 1509 (s), 1464 (s), 1413 (w), 1400 (m), 1373 (s), 1289 (vs), 1231 (s), 1192 (s), 974 (m), 924 (w), 814 (w), 721 (w), 696 (w), 645 (m), 505 (m) cm^{-1}. Raman: $\tilde{\nu}$ = 2977, 2911, 1458, 1289, 1230, 923, 755, 595, 279, 235, 167 cm^{-1}.

Crystallographic Details: Details of the structural analysis for compounds **1** and **2** are summarised in Table 4. Diffraction data were recorded with a Nonius κ-CCD four-circle diffractometer at 200(2) K. Graphite-monochromated Mo-K_{α} radiation (λ = 0.71073 Å) was used in all cases. The structural data was solved by direct methods (SHELXS97) and refined by full-matrix least-squares against F^2 using all data (SHELXL97).[31] Absorption corrections were carried out with the multiscan method, and applied with the SORTAV program.[32] Non-hydrogen atoms were refined with non-isotropic thermal parameters. All hydrogen atoms were modelled in ideal positions. All thermal ellipsoid plots were generated using ORTEP-3 for the computer operating system Microsoft Windows®.[33]

CCDC-656025 (for **1**) and -656026 (for **2**) contain the supplementary crystallographic data for this paper. These data can be ob-

Table 4. Crystallographic parameters for compounds **1** and **2**.

	[(dtbtu)SbCl$_2$(μ-Cl)$_2$(μ-dtbtu)SbCl$_2$(dtbtu)] (**1**)	[(dtbtu)SbBr$_2$(μ-Br)$_2$(μ-dtbtu)SbBr$_2$(dtbtu)] (**2**)
Empirical formula	$C_{27}H_{60}Cl_6N_6S_3Sb_2$	$C_{27}H_{60}Br_6N_6S_3Sb_2$
Fw	1021.19	1287.95
Colour, habit	yellow, prism	yellow, prism
Crystal system	orthorhombic	triclinic
Space group	*Pnma*	$P\bar{1}$
Crystal size	$0.14 \times 0.12 \times 0.07$ mm^{-3}	$0.15 \times 0.15 \times 0.10$ mm^{-3}
Unit cell dimensions	a = 21.1821(4) Å, b = 23.3535(6) Å c = 9.0631(2) Å, $\alpha = \beta = \gamma$ = 90°	a = 9.2060(2) Å, b = 10.6980(3) Å, c = 23.8550(7) Å α = 91.0440(10)°, β = 90.4610(10)° γ = 90.4330(10)°
Volume	4483.30(17) Å^{-3}	2348.84(11) Å^{-3}
T	200(2) K	200(2) K
Z	4	2
$D_{\text{calcd.}}$	1.513 mg/m^3	1.821 mg/m^3
λ	0.71073 Å	0.71073 Å
μ(Mo-K_{α})	1.728 mm^{-1}	6.412 mm^{-1}
F(000)	2064	1248
θ range	3.00 to 27.50°	2.93 to 26.50°
Number of reflections	9754 (5249 unique)	8853 (8853 unique)
R_{int}	0.038	0.084
$R1/wR2$	0.0585/0.1526	0.0746/0.1672
$R1/wR2$ (all data)	0.0930/0.1789	0.1026/0.1815
Largest diff. peak and hole	1.724 and –1.167 eÅ^{-3}	1.178 and –1.314 eÅ^{-3}
GOF	1.038	1.067

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tained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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