Preparation and Crystal Structures of Diphenylantimony(III) Thiocyanate and Bis(2,6-dimethylphenyl)antimony(III) Thiocyanate†

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Diphenylantimony(III) and bis(2,6-dimethylphenyl)antimony(III) thiocyanates have been prepared by metathesis reactions between the appropriate diarylantimony(III) halide and potassium thiocyanate in acetonitrile solution. The second compound was also obtained by thermal decomposition of tris(2,6-dimethylphenyl)antimony(V) dithiocyanate. Crystal structure determinations showed that in $SbPh_2(NCS)$ the thiocyanate group bridges between antimony centres to give an infinite polymer, while the 2,6-dimethyl-substituted analogue is an *N*-bonded monomer. The diphenylantimony structure is probably unique in that the asymmetric unit consists of three formula units and, although each thiocyanate group is bridging, two are primarily *N*-bonded while the third is primarily *S*-bonded. Angles at the bridging nitrogens are large (150.4–174.9°) while those at sulfur are close to 90° (85.7–98.6°). These in conjunction with the presence of thiocyanate groups in the axial positions of pseudo-trigonal-bipyramidal arrangements about antimony lead to a curious 'triangular spiral' structure for the polymeric chains.

Organoantimony halides with the stoichiometries SbR_2X and $SbRX_2$ are well known for a range of both alkyl and aryl groups and structures have been reported recently for $SbRX_2$ (R = Ph, X = Cl, Br or I;[1] R = *p*-tolyl, X = Cl or Br[2]) and $SbPh_2Br$.[2] As expected for each class of compound, the basic unit is pyramidal but for the dihalides there are both intermolecular halide bridges, which link the molecules into infinite chains, and weak contacts between the aromatic group and antimony. In the case of $SbPh_2Br$ there are no intermolecular halide bridges, though molecules are linked by weak arene–antimony contacts. The absence of halide bridging here is probably a function of the lower electronegativity of bromine, as in the related (biphenyl-2,2′-diyl)antimony chloride[2] loose chloride-bridged dimers are formed in addition to the same weak arene–antimony contacts.

The related organoantimony thiocyanates are not known, but they are of interest not only because the intermediate hardness of the substituted antimony(III) centre leads to ambiguity about whether primary bonding at antimony will be to nitrogen or sulfur, but also because co-ordination unsaturation at antimony(III) could promote thiocyanate bridging. Bridging between substituted antimony(III) centres has, for example, been observed with both diphenylantimony fluoride[3] and acetate.[4] We have therefore prepared diphenylantimony thiocyanate and determined its crystal structure and for comparison have also investigated the related hindered 2,6-dimethylphenyl analogue, $Sb(C_6H_3Me_2\text{-}2,6)_2(SCN)$. A preliminary report on the structure of diphenylantimony thiocyanate has already been published.[5]

Little is actually known about antimony(III) thiocyanates but the following compounds have been prepared and their IR spectra reported: $[NMe_4][Sb(NCS)_4]$, the adducts $Sb(NCS)_3{\cdot}tptz$ and $3Sb(NCS)_3{\cdot}2dqp$, where tptz = 2,4,6-tris(2′-pyridyl)-1,3,5-triazine and dqp = 2,6-bis(2-quinolyl)pyridine,[6] $K_2[SbCl_3(SCN)_2]$, $Sb(SCN)(C_5H_5)_2$, $SbCl(NCS)_2$ and $Sb(NCS)_2(C_5H_5)$.[7]

Experimental

Acetonitrile was dried over P_2O_5 and distilled under nitrogen while hexane and toluene were dried over sodium wire. Potassium thiocyanate was dried in a vacuum desiccator over P_2O_5 for 2 d before use. Diphenylantimony chloride and bromide were prepared by reorganisation of mixtures of triphenylantimony (2 mol) and resublimed antimony trihalide (1 mol).[8]

Preparations.—Diphenylantimony thiocyanate. A solution of potassium thiocyanate (3.1 g, 0.032 mol) in dry acetonitrile was added slowly with stirring to a solution of diphenylantimony chloride (10.0 g, 0.032 mol) in the same solvent and the mixture stirred at ambient temperature for 24 h. Precipitated potassium chloride (1.65 g, 0.023 mol, 69%) was filtered off and the filtrate evaporated to dryness under reduced pressure to give a pale yellow viscous oil. This was taken up in dry toluene and residual potassium chloride was filtered off. Concentrating the toluene solution to dryness under reduced pressure yielded a yellow oil, which was recrystallised from chloroform–hexane (50 : 50 v/v) as colourless needles. Yield 9.0 g, 0.027 mol, 84%, m.p. 103 °C (Found: C, 46.7; H, 3.0; N, 4.0. Calc. for $C_{13}H_{10}NSSb$: C, 46.7; H, 3.0; N, 4.2%). The compound can be prepared similarly from diphenylantimony bromide.

Tris(2,6-dimethylphenyl)antimony. A solution of bromo-2,6-dimethylbenzene (18.5 g, 0.1 mol) in dry diethyl ether (50 cm^3) was added dropwise with stirring over a period of 45 min to a stirred suspension of lithium metal slivers (1.39 g, 0.2 mol) in dry ether (150 cm^3) at 0 °C under an argon atmosphere. Stirring was continued for 2 h after which a solution of antimony trichloride (7.63 g, 0.033 mol) in dry ether (100 cm^3) was added dropwise over 30 min. After 90 min more of stirring, the reaction vessel was allowed to warm to room temperature and the mixture filtered on to crushed ice. The two layers were then separated and the aqueous layer extracted three times with ether (50 cm^3 portions). The combined ether fractions were dried over anhydrous magnesium sulfate and evaporated to dryness giving a pale yellow solid. Recrystallisation from ethanol gave white crystals. Yield: 9.61 g, 0.022 mol, 66%, m.p. 120 °C (Found: C, 65.5; H, 6.3. Calc. for $C_{24}H_{27}Sb$: C, 65.9; H, 6.2%).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Bis(2,6-*dimethylphenyl*)*antimony bromide*. A mixture of tris(2,6-dimethylphenyl)antimony (4.00 g, 0.009 mol) and antimony tribromide (1.81 g, 0.005 mol) was heated at 85 °C in the absence of solvent for 48 h, as described previously for the related mesityl system.[9] Carbon tetrachloride–pentane (50 : 50 v/v, 80 cm^3) was then added and any insoluble material filtered off. The solution was set aside overnight in the freezer and precipitated (2,6-dimethylphenyl)antimony dibromide filtered off. The filtrate was evaporated to dryness in a vacuum, and the residue on trituration with pentane gave bis(2,6-dimethylphenyl)antimony bromide as a yellow solid, m.p. 80 °C. Yield 6.7 g, 15.2 mmol, 81% (Found: C, 46.3; H, 4.3. Calc. for $C_{16}H_{18}BrSb$ requires C, 46.6; H, 4.4%).

Bis(2,6-*dimethylphenyl*)*antimony thiocyanate*. (*a*) *From bis*(2,6-*dimethylphenyl*)*antimony bromide*. This compound was prepared from potassium thiocyanate (0.5 g, 5.1 mmol) and bis(2,6-dimethylphenyl)antimony bromide (2.0 g, 5 mmol) in dry acetonitrile as described above for diphenylantimony thiocyanate. Recrystallisation from chloroform–hexane (50 : 50 v/v) gave yellow crystals. Yield 0.6 g, 1.5 mmol, 31%, m.p. 145 °C (Found: C, 52.2; H, 4.7; N, 3.4. Calc. for $C_{17}H_{18}NSSb$: C, 52.3; H, 4.6; N, 3.6%).

(*b*) *From tris*(2,6-*dimethylphenyl*)*antimony dithiocyanate*. An ice-cold solution of freshly prepared and standardised dithiocyanogen, $(SCN)_2$ (0.29 g, 2.5 mmol) in dichloromethane was added with stirring to a solution of tris(2,6-dimethylphenyl)antimony (1.1 g, 2.5 mmol) in dichloromethane at 0 °C. After 30 min the solution was concentrated and set aside in a freezer for crystallisation. The resulting solid was recrystallised from chloroform–hexane (50 : 50 v/v) giving tris(2,6-dimethylphenyl)antimony dithiocyanate as white crystals, m.p. 250 °C. Yield 1.0 g, 1.8 mmol, 72% (Found: C, 55.9; H, 4.8; N, 4.8. Calc. for $C_{26}H_{27}N_2S_2Sb$: C, 56.4; H, 4.8; N, 4.8%). The product was then heated under reduced pressure,[9] raising the temperature slowly to prevent charring, until melting occurred. Maintaining the temperature at 270 °C for 1 h completed loss of (2,6-dimethylphenyl)thiocyanate. After cooling, the residue was dissolved in chloroform and the solution filtered and treated with charcoal. Addition of a small amount of hexane followed by cooling gave crystals of the required compound. Yield 0.2 g, 0.5 mmol, 25%.

Crystal Structure Determinations.—*Diphenylantimony thiocyanate*. Crystals suitable for X-ray investigation were grown from a chloroform–hexane mixture and mounted in 0.3 mm glass capillaries.

Crystal data. $C_{13}H_{10}NSSb$, $M = 333.8$, triclinic, space group $P\bar{1}$, $a = 13.217(3)$, $b = 13.272(3)$, $c = 12.889(3)$ Å, $\alpha = 91.82(4)$, $\beta = 98.04(4)$, $\gamma = 119.39(5)°$, $U = 1937.3$ Å^3, Mo-Kα radiation (with graphite monochromator), $\lambda = 0.710\ 69$ Å, $Z = 6$, $D_c = 1.72$ g cm^{-3}, $\mu = 22.8$ cm^{-1}, crystal size 0.3 × 0.4 × 0.1 mm.

Intensity data were collected on a Hilger and Watts Y290 four-circle diffractometer for 4738 reflections in the range $0 \leqslant \theta \leqslant 22°$ $(-13 < h < 13, -13 < k < 13, 0 < l < 13)$ of which 4171 with $I > 3\sigma(I)$ were considered to be observed. Corrections were made for Lorentz and polarisation effects, but an absorption correction was not considered necessary. Crystallographic calculations used the CRYSTALS programs[10] and neutral atom scattering factors.[11] Positions for the three independent antimony atoms were obtained from a three-dimensional Patterson synthesis and the remaining non-hydrogen atoms revealed by a series of Fourier-difference syntheses and full-matrix least-squares refinements (each formula unit constituting a separate block). After further refinement with anisotropic thermal parameters, a Fourier-difference synthesis gave the hydrogen-atom positions, which were refined with isotropic thermal parameters. Application of a four-coefficient Chebyshev weighting scheme then led to final convergence (maximum shift/e.s.d. = 0.09, 554 least-squares parameters) at $R = 0.0355$ ($R' = 0.0430$). Except close to the heavy atoms, there were no peaks in a final Fourier-difference synthesis with intensities > 0.3 e Å^{-3}. The final atomic coordinates are listed in Table 1.

Bis(2,6-*dimethylphenyl*)*antimony thiocyanate*. Suitable crystals were obtained by slow recrystallisation from a chloroform–hexane mixture and mounted on a glass fibre.

Crystal data. $C_{17}H_{18}NSSb$, $M = 389.8$, orthorhombic, space group $Pna2_1$, $a = 13.843(4)$, $b = 10.433(3)$, $c = 11.319(4)$ Å, $U = 1633.7$ Å^3, $Z = 4$, $D_c = 1.58$ g cm^{-3}, $F(000) = 776$, Mo-Kα radiation (with graphite monochromator), $\lambda = 0.710\ 69$ Å, $\mu = 19.8$ cm^{-1}, crystal size 0.6 × 0.25 × 0.1 mm.

Data were collected as described above in the range $0 \leqslant \theta \leqslant 25°$ $(0 < h < 16, 0 < k < 12, 0 < l < 13)$ for 1693 reflections of which 1195 with $I > 3\sigma(I)$ were considered observed. The structure was solved essentially as described above and converged (maximum shift/e.s.d. = 0.09, 252 least-squares parameters) at $R = 0.0306$ ($R' = 0.0403$) with anisotropic thermal parameters for the non-hydrogen atoms, isotropic thermal parameters for the hydrogen atoms and application of a four-coefficient Chebyshev weighting scheme. The final atomic coordinates are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Discussion

Preparations.—As antimony trithiocyanate is not known, diphenylantimony thiocyanate cannot be prepared by the $SbPh_3$–SbX_3 reorganisation reaction that is successful for the corresponding chloride and bromide.[8] The compound can however be obtained in high yield and purity by a simple metathesis reaction between either diphenylantimony chloride or the corresponding bromide and potassium thiocyanate in acetonitrile solution. It is stable in the solid but sensitive to oxidation in solution. It is a mild lachrymator and, like the corresponding fluoride, may cause sneezing and headaches after exposure. It is soluble in a range of organic solvents, including ethanol, toluene and chloroform, but can best be recrystallised from chloroform–hexane (1 : 1 v/v). Rather surprisingly, it can also be recrystallised unchanged from pyridine and it is similarly not possible to complex the compound with triphenylphosphine in chloroform solution.

Reorganisation of 2 : 1 mixtures of tris(2,6-dimethylphenyl) antimony and antimony tribromide to give the precursor, $Sb(C_6H_3Me_2\text{-}2,6)_2Br$, does not proceed as cleanly as in the phenyl system and it is necessary to separate first the dibromide which is also produced.[9] Metathesis with potassium thiocyanate then proceeds smoothly to give $Sb(C_6H_3Me_2\text{-}2,6)_2(NCS)$ as stable pale yellow crystals. An alternative preparative route depends on the thermal decomposition of tris(2,6-dimethylphenyl)antimony dithiocyanate, obtained by oxidising the triarylantimony with dithiocyanogen in dichloromethane solution.

Infrared Spectroscopy.—Infrared spectroscopy often gives information on the type of thiocyanate bonding present in a compound.[12] For example, sharp bands in the 2085–2130 cm^{-1} region together with bands at 700–760 and 430–470 cm^{-1} normally indicate *S*-bonding. For *N*-bonding the corresponding ranges are 2050–2100, 820–870 and 475–485 cm^{-1} and for 1,3 bridging they are 2065–2165, 750–800 and 440–470 cm^{-1}.

The infrared spectrum of diphenylantimony thiocyanate as a Nujol mull is unusual as it shows, in addition to bands associated with the phenyl groups attached to antimony, a series of four sharp bands in the C–N stretching region at *ca*. 2055, 2065, 2094 and 2114 cm^{-1}; C–S stretching can be assigned to a weak band at 740 cm^{-1} and the bending mode, δ(NCS), to a shoulder on the phenylantimony vibration at 450 cm^{-1}.[13]

It is clear from the multiplicity of bands in the C–N stretching region that there are probably a number of thiocyanate environments but it is difficult to be much more specific at this stage. As antimony(III) species are Lewis acids and thiocyanate is a well known bridging group, it is highly probable that bridging occurs and the complexity in the 2000 cm^{-1} region might arise from different types of bridging groups.

Spectra in chloroform or toluene solutions are much less complicated around 2000 cm^{-1} showing a single broad band centred at 2020 cm^{-1} at concentrations greater than 0.01 mol dm^{-3}. On dilution to 0.01 mol dm^{-3} a sharp band begins to separate on the high-energy side (2045 cm^{-1}) of the broad band which increases in intensity at the expense of the broad band at 2020 cm^{-1} until at 0.001 mol dm^{-3} only the sharp band at 2045 cm^{-1} remains. Solvent absorptions obscure the C–S stretching region and no further information is available from the solution spectra. The simplification of the spectra on dilution can be correlated with cleavage of the intermolecular bridges considered to be present in the solid state, and the single band at 2045 cm^{-1} in the most dilute solutions can probably be assigned to a monomer with an *N*-bonded thiocyanate group. Its sharpness does give rise to some ambiguity as normally *S*-bonded thiocyanates give sharp bands while *N*-bonding generally produces broad bands.

The IR spectrum of bis(2,6-dimethylphenyl)antimony thiocyanate as a Nujol mull is completely different from that of the phenyl analogue, showing a single band in the C–N stretching region at 2031 cm^{-1}, *i.e.* the region associated with terminal *N*-bonding. The corresponding deformation mode is at 475 cm^{-1} while the C–S stretch is assigned to a weak, broad band at 755 cm^{-1}. This is outside the accepted range (820–870 cm^{-1}) for *N*-bonding leading to ambiguity in deciding the co-ordination mode.

Mass Spectrometry.—The electron-impact (EI) mass spectra for the two compounds each showed the molecular ion, at *m*/*z* 333 (22%) for $SbPh_2(NCS)$ and 389 (3%) for $Sb(C_6H_3Me_2\text{-}2,6)_2(NCS)$ (relative intensities in parentheses), and, although the fragmentation patterns for the compounds are very similar, the most intense peaks (100% intensity) are $SbPh_2$ for the former and $Me_2C_6H_3$ for the latter. The primary fragmentation could be loss of either a thiocyanate or an aryl group but, although both processes are observed, thiocyanate loss is clearly more important for both compounds. This is shown by the SbR : SbR(NCS) (R = Ph or $C_6H_3Me_2$-2,6) peak ratios of *ca.* 20 : 1 and 1.4 : 1, respectively, for fragmentation of the molecular ion and SbR : Sb(NCS) ratios of 2.5 : 1 and 1.6 : 1, respectively, for fragmentation of the SbR(NCS) ion for $SbPh_2(NCS)$ and $Sb(C_6H_3Me_2\text{-}2,6)_2(NCS)$. Aryl group loss, on the other hand, is relatively more important for the 2,6-dimethyl-substituted compound as shown by SbR_2 : SbR(NCS) (20 : 1 and 1.4 : 1) and SbR_2 : SbR (1.4 : 1 and 0.8 : 1) intensity ratios for the phenyl and substituted phenyl compounds respectively. This may be a consequence of Sb–C bond weakening by steric hindrance by the *o*-methyl groups.

The FAB mass spectrum of $SbPh_2(NCS)$ is more revealing, showing $Sb_2Ph_n(NCS)_m$ fragments with n = 2–4 and m = 1 or 2, although with the exception of $Sb_2Ph_4(NCS)$ (*m*/*z* 608, 7.8%) the peak intensities were less than 1%. Fragments containing more than two antimony atoms were not observed, but diantimony fragments are consistent with the presence of bridging thiocyanate groups. A low-intensity peak corresponding to $Sb_2Ph(NCS)_3$ was also observed, which may indicate the presence of units greater than dimers.

^{14}N *NMR Spectroscopy.*—The ^{14}N NMR spectra of the two compounds in $CDCl_3$ solution showed broad singlets at δ −260 (linewidth 12 ppm at half peak height) and −279 (linewidth 10 ppm at half peak height), respectively for $SbPh_2(NCS)$ and $Sb(C_6H_3Me_2\text{-}2,6)_2(NCS)$, consistent with the presence of *N*-bonded thiocyanate groups[14] and supporting the evidence from solution IR spectroscopy.

Structure of Diphenylantimony Thiocyanate.—Important bond lengths and angles are listed in Table 3 and projections of the unit-cell contents down the *c* and *b* axes are shown in Figs. 1 and 2 respectively. The asymmetric unit contains three independent diphenylantimony thiocyanate molecules linked together by bridging thiocyanate groups and generating an infinite polymeric structure. The most unusual and probably unique features of the structure lie in the 'triangular spiral' arrangement so generated and the different orientations of the bridging thiocyanate groups and consequently the co-ordination patterns at the three antimony atoms. Atom Sb(1), for example, is co-ordinated to two nitrogen atoms [at 2.304(5) and 2.364(6) Å], Sb(2) to one nitrogen [2.273(6) Å] and one sulfur atom [2.831(2) Å], while Sb(3) is attached to two sulfur atoms [at 2.700(2) and 2.842(2) Å], implying that, while primary bonding is to nitrogen at Sb(1) and Sb(2), the primary bond is to sulfur at Sb(3). The sides of the triangle are, however, very unequal in size and comprise: (*a*) Sb(1) and two *N*-bonded

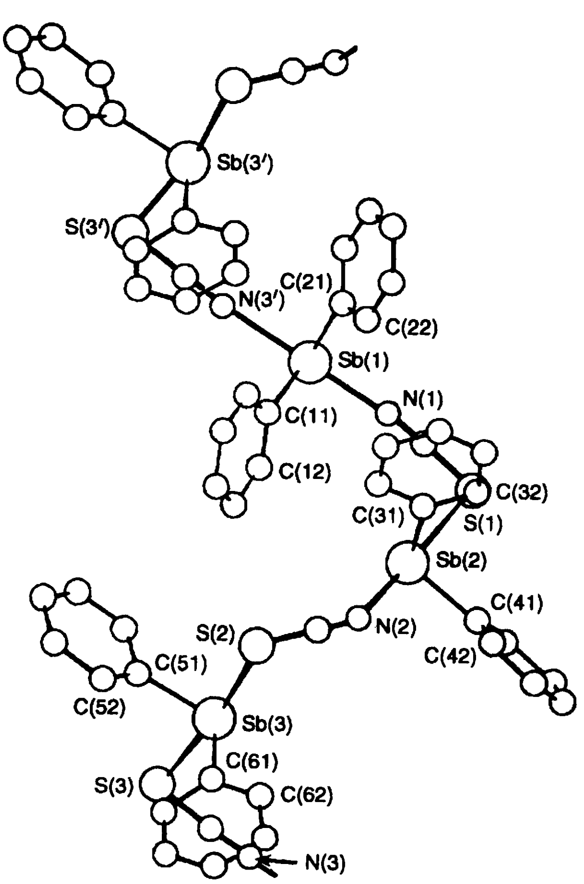

Fig. 1 Structure of $SbPh_2(NCS)$ projected down the *c* axis, showing the atom numbering scheme

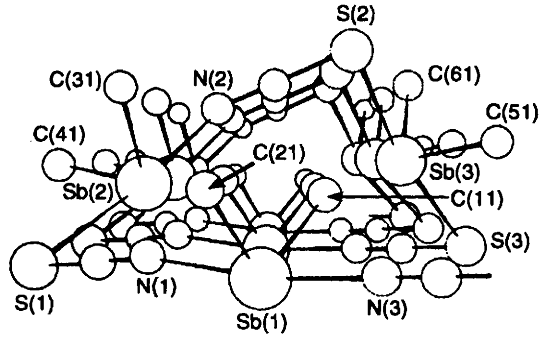

Fig. 2 Structure of $SbPh_2(NCS)$ projected down the *b* axis (for clarity only the *ipso*-carbon atoms of the phenyl groups are shown)

Table 1 Fractional atomic coordinates for $\mathrm{SbPh_2(NCS)}$, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	0.030 52(4)	0.254 69(3)	0.057 02(3)
N(1)	0.195 8(5)	0.237 0(4)	0.100 8(4)
C(1)	0.270 0(5)	0.217 0(5)	0.099 9(4)
S(1)	0.373 3(1)	0.181 5(2)	0.102 0(1)
C(11)	−0.056 1(5)	0.116 0(5)	0.149 6(5)
C(12)	−0.076 3(6)	0.007 0(6)	0.116 3(5)
C(13)	−0.130 9(7)	−0.085 6(6)	0.172 5(6)
C(14)	−0.169 0(6)	−0.070 8(6)	0.262 4(6)
C(15)	−0.149 4(8)	0.036 1(8)	0.296 0(8)
C(16)	−0.096 2(6)	0.129 9(6)	0.239 8(6)
C(21)	0.110 8(5)	0.396 3(5)	0.179 9(5)
C(22)	0.160 0(6)	0.386 7(6)	0.279 8(6)
C(23)	0.214 8(8)	0.479 0(8)	0.356 9(8)
C(24)	0.221 8(9)	0.584 9(8)	0.333(1)
C(25)	0.174 1(8)	0.594 9(7)	0.237(1)
C(26)	0.118 9(7)	0.501 4(6)	0.158 6(7)
Sb(2)	0.222 21(3)	−0.016 98(3)	0.193 62(3)
N(2)	0.114 8(5)	−0.164 2(5)	0.286 5(5)
C(2)	0.026 6(6)	−0.226 5(5)	0.311 3(5)
S(2)	−0.097 6(1)	−0.313 0(1)	0.348 6(1)
C(31)	0.258 7(5)	0.097 7(5)	0.331 7(4)
C(32)	0.372 8(6)	0.180 6(6)	0.379 7(5)
C(33)	0.390 0(8)	0.255 6(6)	0.465 9(6)
C(34)	0.297 0(8)	0.248 2(7)	0.504 3(6)
C(35)	0.184 9(8)	0.168 2(8)	0.457 6(6)
C(36)	0.166 0(7)	0.093 8(7)	0.371 1(6)
C(41)	0.365 0(5)	−0.048 9(5)	0.236 9(5)
C(42)	0.388 7(6)	−0.076 0(6)	0.337 3(7)
C(43)	0.471 8(7)	−0.108 3(7)	0.364 5(9)
C(44)	0.531 7(9)	−0.115 3(7)	0.291(1)
C(45)	0.513 3(8)	−0.088 5(9)	0.190(1)
C(46)	0.427 0(7)	−0.056 3(7)	0.162 5(7)
Sb(3)	−0.195 42(3)	−0.493 10(3)	0.177 62(3)
N(3)	−0.138 9(5)	−0.725 5(5)	0.044 0(5)
C(3)	−0.215 9(6)	−0.707 2(5)	0.037 0(5)
S(3)	−0.324 5(2)	−0.679 2(2)	0.030 0(1)
C(51)	−0.349 8(5)	−0.481 7(5)	0.187 8(5)
C(52)	−0.418 2(6)	−0.524 6(6)	0.263 9(6)
C(53)	−0.510 8(6)	−0.504 6(7)	0.268 8(7)
C(54)	−0.533 3(7)	−0.439 3(7)	0.200 1(7)
C(55)	−0.466 1(8)	−0.396 9(9)	0.124 0(8)
C(56)	−0.373 5(6)	−0.416 4(7)	0.118 2(6)
C(61)	−0.206 7(5)	−0.610 4(5)	0.292 9(4)
C(62)	−0.104 1(6)	−0.584 5(5)	0.359 4(5)
C(63)	−0.103 8(7)	−0.659 4(6)	0.430 4(5)
C(64)	−0.205 8(8)	−0.758 6(7)	0.436 1(6)
C(65)	−0.308 0(7)	−0.786 2(6)	0.369 3(6)
C(66)	−0.309 5(6)	−0.713 3(5)	0.297 8(5)

Table 2 Fractional atomic coordinates for $\mathrm{Sb(C_6H_3Me_2\text{-}2,6)_2(NCS)}$, with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb	−0.004 38(3)	0.040 91(4)	0
N	0.031 5(6)	0.231 4(7)	−0.014(1)
C(1)	0.019 1(5)	0.336 (1)	−0.035 4(8)
S	0.003 5(2)	0.483 3(3)	−0.069 8(5)
C(11)	0.114 4(5)	−0.028 3(7)	0.108 3(7)
C(12)	0.095 6(6)	−0.138 8(7)	0.172 2(8)
C(13)	0.167 0(8)	−0.194(1)	0.243 5(9)
C(14)	0.256(1)	−0.138(2)	0.247(1)
C(15)	0.278 2(7)	−0.031(1)	0.180(1)
C(16)	0.207 3(6)	0.026 6(8)	0.109 7(9)
C(17)	−0.001(1)	−0.207(1)	0.166(2)
C(18)	0.237 4(9)	0.139(1)	0.034(1)
C(21)	−0.107 2(6)	0.079 0(8)	0.141 5(8)
C(22)	−0.199 9(7)	0.022 0(8)	0.126(1)
C(23)	−0.269 8(8)	0.048(1)	0.213(1)
C(24)	−0.249(1)	0.123(1)	0.307(2)
C(25)	−0.161 0(9)	0.178(1)	0.319(1)
C(26)	−0.087 1(6)	0.157 5(8)	0.238 2(8)
C(27)	−0.226 3(9)	−0.065(1)	0.025(1)
C(28)	0.008 5(9)	0.222(1)	0.258(1)

Table 3 Important bond lengths (Å) and angles (°) for $\mathrm{SbPh_2(NCS)}$, with e.s.d.s in parentheses

Sb(1)–N(1)	2.304(5)	Sb(1)–C(11)	2.139(6)
Sb(1)–C(21)	2.133(6)	Sb(1)–N(3′)	2.364(6)
N(1)–C(1)	1.137(7)	C(1)–S(1)	1.647(6)
Sb(2)–N(2)	2.273(6)	Sb(2)–S(1)	2.831(2)
Sb(2)–C(31)	2.141(6)	Sb(2)–C(41)	2.135(6)
N(2)–C(2)	1.149(8)	C(2)–S(2)	1.628(7)
Sb(3)–S(2)	2.842(2)	Sb(3)–S(3)	2.700(2)
Sb(3)–C(51)	2.140(5)	Sb(3)–C(61)	2.152(5)
N(3)–C(3)	1.150(8)	C(3)–S(3)	1.641(7)
N(1)–Sb(1)–C(11)	87.5(2)	N(1)–Sb(1)–C(21)	86.6(2)
N(1)–Sb(1)–N(3′)	170.0(2)	C(11)–Sb(1)–C(21)	98.5(2)
C(11)–Sb(1)–N(3′)	86.2(2)	C(21)–Sb(1)–N(3′)	86.6(2)
Sb(1)–N(1)–C(1)	164.7(5)	Sb(1)–N(3′)–C(3′)	174.9(6)
N(1)–C(1)–S(1)	176.8(5)	Sb(1)–C(11)–C(12)	118.5(5)
Sb(1)–C(11)–C(16)	123.0(4)	Sb(1)–C(21)–C(22)	121.4(5)
Sb(1)–C(21)–C(26)	119.2(6)	S(1)–Sb(2)–N(2)	173.0(2)
S(1)–Sb(2)–C(31)	87.7(2)	S(1)–Sb(2)–C(41)	89.4(2)
N(2)–Sb(2)–C(31)	86.3(2)	N(2)–Sb(2)–C(41)	87.9(2)
C(31)–Sb(2)–C(41)	97.1(2)		
Sb(2)–S(1)–C(1)	85.7(2)	Sb(2)–N(2)–C(2)	150.4(5)
N(2)–C(2)–S(2)	178.9(6)	Sb(2)–C(31)–C(32)	122.7(5)
Sb(2)–C(31)–C(36)	118.8(5)	Sb(2)–C(41)–C(42)	120.9(5)
Sb(2)–C(41)–C(46)	120.6(5)	S(2)–Sb(3)–S(3)	169.62(5)
S(2)–Sb(3)–C(51)	81.6(2)	S(2)–Sb(3)–C(61)	87.2(2)
S(3)–Sb(3)–C(51)	89.8(2)	S(3)–Sb(3)–C(61)	88.8(2)
C(51)–Sb(3)–C(61)	100.7(2)	N(3)–C(3)–S(3)	178.6(6)
Sb(3)–S(2)–C(2)	98.6(2)	Sb(3)–S(3)–C(3)	91.4(2)
Sb(3)–C(51)–C(52)	124.4(5)	Sb(3)–C(51)–C(56)	116.1(5)
Sb(3)–C(61)–C(62)	117.4(4)	Sb(3)–C(61)–C(66)	123.2(4)

Atoms carrying a prime are related to unprimed atoms by the symmetry operation *x*, 1 + *y*, *z*.

ligands, (*b*) S(2), Sb(2) and an *N*-bonded ligand and (*c*) Sb(3) with the two remaining sulfur atoms.

The geometry at each antimony atom is best described as pseudo-trigonal bipyramidal with thiocyanate groups in axial positions and two phenyl groups and the antimony lone pair of electrons in the equatorial sites. From the observed structure, antimony in this compound is clearly of intermediate hardness, implying that there is no great energy difference between primary *N*- and *S*-bonding and adoption of the 'spiral' structure could be a consequence of efficient space filling. Weak antimony–arene interactions of the type found previously in phenylantimony mono- and di-halides[1,2] are, however, not observed in this structure.

The thiocyanate groups, as expected, are effectively linear with angles at C(1), C(2) and C(3) of 176.8(5), 178.9(6) and 178.6(6)° respectively. The C–N bond lengths are all short [1.137(7), 1.149(8) and 1.150(8) Å] and appear to be triple bonds (*cf.* C≡N 1.16 and C=N 1.30 Å[15]), while the C–S bond lengths, 1.647(6), 1.628(7) and 1.641(7) Å, are closer to those observed for C=S double bonds (*ca.* 1.55 Å) than for single bonds (*ca.* 1.82 Å).[15]

Angles at the co-ordinated nitrogen are all large but significantly different, *i.e.* 164.7(5), 150.4(5) and 174.9(6)° for N(1), N(2) and N(3) respectively, while those at sulfur are close to 90°, *i.e.* 85.7(2), 98.6(2) and 91.4(2)° at S(1), S(2) and S(3) respectively. These values, in conjunction with the linearity of the thiocyanate groups in the axial positions in the antimony co-ordination polyhedron, impose constraints on the structure,

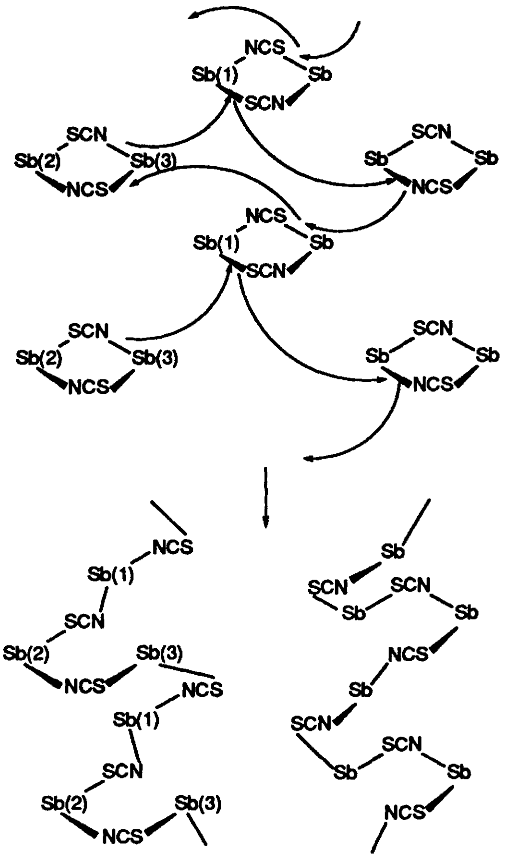

Fig. 3 Possible mechanism for the formation of the triangular spiral structure (for clarity the phenyl substituents have been omitted)

which lead to the polymeric chain adopting the unusual 'triangular spiral' structure shown in Fig. 1.

It is interesting that organometallic thiocyanates of elements close to antimony in the Periodic Table have more conventional structures. In $SnMe_3(NCS)$ [16] and $SnPh_3(NCS)$,[17] for example, the thiocyanate groups form regular bridges between trigonal-bipyramidal tin atoms leading to infinite zigzag chains. The primary Sn–N bonds (2.15 and 2.22 Å, respectively) are somewhat shorter than the Sb–N distances here (2.304 and 2.273 Å) but the bonds to sulfur are slightly longer (3.13 and 2.92 Å) than those in $SbPh_2(NCS)$ [2.831(2) and 2.842(2) Å]. The primary bond to S(3) in $SbPh_2(NCS)$ [2.700(2) Å] is shorter yet and is obviously accompanied on bridging by a longer Sb–N bond [2.364(6) Å].

Triphenyltellurium thiocyanate, on the other hand, is basically ionic, but di- and tetra-metric units with thiocyanate groups bridging between pairs of tellurium atoms can be identified (Te–N and Te–S contacts fall in the ranges 2.963–3.182 and 3.256–3.611 Å respectively).[18] Finally in dimethylthallium thiocyanate[19] there are basically ionic thiocyanate groups present in both the monoclinic and orthorhombic modifications. Alternate thallium atoms co-ordinate to four nitrogen atoms at 2.77 Å and four sulfur atoms at 3.12 Å in the monoclinic modification, while each thallium atom is co-ordinated by two nitrogens at 2.80 Å and two sulfurs at 3.11 Å in the orthorhombic form.

Thiocyanate-bridged systems are thus quite widespread and a survey of the observed structural types shows that in the majority of cases bridging is regular giving an infinite zigzag chain. In a few cases bridging occurs between two specific monomers leading to an eight-membered $M(NCS)_2M$ ring. This is found, for example, in $[\{Bi(NCS)_3(bipy)_2\}_2]$[20] (bipy = 2,2′-bipyridyl) where the ring adopts a distorted chair conformation, and a similar intermediate has been proposed in the interconversion of the linkage isomers of $[\{Pd(AsPh_3)(NCS)_2\}_2]$.[21]

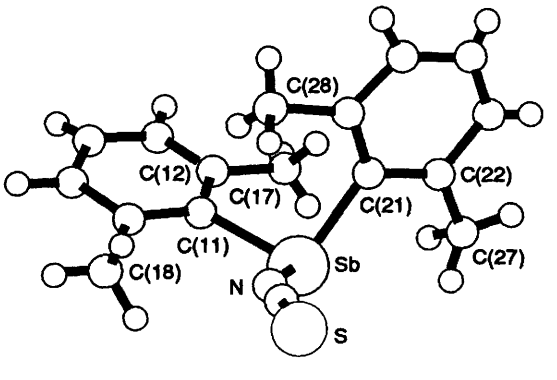

Fig. 4 Structure of $Sb(C_6H_3Me_2\text{-}2,6)_2(NCS)$, showing the atom numbering scheme

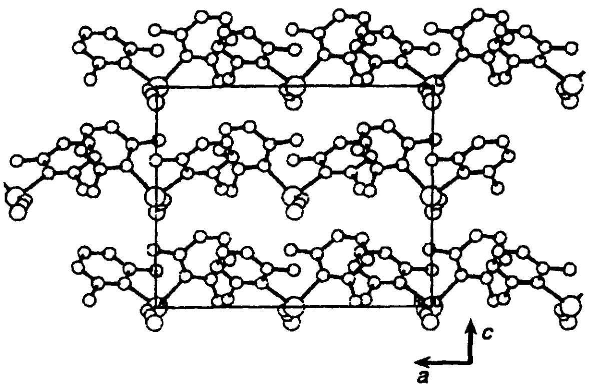

Fig. 5 Structure of $Sb(C_6H_3Me_2\text{-}2,6)_2(NCS)$ projected down the *b* axis

It is interesting to speculate on how the unusual diphenylantimony thiocyanate structure arises and why the third thiocyanate group is oppositely orientated from the other two. Spectroscopic evidence suggests that in monomeric diphenylantimony thiocyanate the thiocyanate group is *N*-bonded and it is difficult to see how the final structure could arise from simple aggregation of such units. The starting point for a possible mechanism is therefore the formation of 1,3-bridged dimers, as shown in Fig. 3. The next step requires Sb–S bond cleavage in one in every three dimers to give *N*-bonded monomers, each of which inserts into Sb-N bonds of two adjacent dimers. The result then is an infinite-chain structure, containing a sequence of three antimony atoms co-ordinated to, respectively, two nitrogens, one nitrogen and one sulfur and two sulfur atoms, as observed experimentally.

Structure of Bis(2,6-*dimethylphenyl*)*antimony Thiocyanate*.—The structure determination shows that, in complete contrast to the situation with diphenylantimony thiocyanate, the thiocyanate group here is terminal and the solid consists of simple pyramidal monomers. Two of the sites are occupied by aryl ligands and the third by an *N*-bonded thiocyanate group. Important bond lengths and angles are listed in Table 4 and the monomeric structure and cell packing are shown in Figs. 4 and 5, respectively. The Sb–N bond length [2.055(8) Å] is substantially shorter than those for the primarily *N*-bonded but bridging thiocyanates in $SbPh_2(NCS)$ and also shorter than the Sn–N separations in $SnPh_3(NCS)$ (2.15 and 2.22 Å),[17] where again primarily *N*-bonded thiocyanates bridge pairs of tin atoms. Even in $SbPh_3(NCS)_2$[5,22] where the thiocyanate groups are terminally bonded, the Sb–N distances fall between

Table 4 Important bond lengths (Å) and angles (°) for Sb(C$_6$H$_3$Me$_2$-2,6)$_2$(NCS), with e.s.d.s in parentheses

Sb–N	2.055(8)	N–C(1)	1.13(1)
Sb–C(11)	2.174(8)	C(1)–S	1.60(1)
Sb–C(21)	2.179(8)		
N–Sb–C(11)	100.6(4)	Sb–C(11)–C(16)	124.2(6)
N–Sb–C(21)	92.3(4)	C(12)–C(11)–C(16)	120.2(8)
C(11)–Sb–C(21)	98.0(3)	Sb–C(21)–C(22)	115.1(7)
Sb–N–C(1)	156.1(9)	Sb–C(21)–C(26)	123.7(6)
N–C(1)–S	177.8(9)	C(22)–C(21)–C(26)	121.2(8)
Sb–C(11)–C(12)	115.4(6)		

2.13 and 2.16 Å. The 2.06 Å reported for the Sn–N separation in [SnMe$_2$(NCS)]$_2$O[23] is shorter still and comparable with the distance here.

The N–C and C–S bond distances [1.13(1) and 1.60(1) Å respectively] are normal for *N*-bonded thiocyanates[24] and the thiocyanate group is again effectively linear [S–C–N 177.8(9)°]. The Sb–N–C angle [156.1(9)°] is comparable with those (151–157°) to the terminal thiocyanate groups in SbPh$_3$(NCS)$_2$.

The Sb–C bond lengths, 2.174(8) and 2.179(8) Å, are shorter than those for tris(2,6-dimethylphenyl)antimony (2.191, 2.188 and 2.192 Å),[25] probably a consequence of the greater electronegativity of thiocyanate compared with a third aryl group. A similar decrease in Si–C bond lengths from 1.87 to 1.85 Å was noted for a series of SiPh$_3$X compounds with increasing electronegativity of X.[26] The angles at Sb between the carbon atoms of the aryl groups in Sb(C$_6$H$_3$Me$_2$-2,6)$_3$ are 98.7, 109.5 and 106.0°.[25] The corresponding angle in Sb(C$_6$H$_3$Me$_2$-2,6)$_2$(NCS) is 98.0(3)° with angles at antimony between nitrogen and the carbon of the aryl groups of 100.6(4) and 92.3(4)°. Distortion as a result of intramolecular steric effects is common in Group 15 triaryl compounds[27] and variation in angles at antimony is not unusual. However, as would be expected for the sterically less demanding *N*-bonded thiocyanate group, the mean angle for Sb(C$_6$H$_3$Me$_2$-2,6)$_2$(NCS) (97.3°) is much smaller than the mean angle for Sb(C$_6$H$_3$Me$_2$-2,6)$_3$ (104.7°) and is identical with that for the sterically unhindered Sb(C$_6$H$_4$Me-4)$_3$ (97.3°).[27]

The absence of thiocyanate briding in this compound is very surprising. The closest Sb $\cdots$ S intermolecular contact is, in fact, at 5.87 Å and represents an interaction with the antimony atom translated one unit-cell dimension in the *y* direction. Incorporating methyl groups in the *ortho* positions of the aryl groups was expected to produce a small influence on thiocyanate co-ordination, perhaps promoting the more usual 1,3 end-to-end bridging. However it is clear that steric hindrance by the two *o*-methyl groups is sufficient to prevent approach of the free end of the thiocyanate and this, rather than electronic effects, is considered to be the major reason for monomer formation. Although not directly comparable, steric hindrance by the two *o*-methyl groups in both Sb(C$_6$H$_2$Me$_3$-2,4,6)$_3$ and Sb(C$_6$H$_3$Me$_2$-2,6)$_3$ is thought to be responsible for formation of triarylantimony dihydroxides,[28] rather than the expected dimeric triarylantimony oxides, *e.g.* (SbR$_3$O)$_2$, when these two antimony(III) compounds are oxidised by *tert*-butyl hydroperoxide. The tin and tellurium analogues of the present compound, *i.e.* Sn(C$_6$H$_3$Me$_2$-2,6)$_3$(NCS) and Te(C$_6$H$_3$Me$_2$-2,6)$_3$(NCS), are currently unknown but it would be interesting to know whether steric effects would lead to monomer formation in these cases also.

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