

Tri- and di-arylantimony(V) thiocyanates and mixed halide thiocyanates; crystal structure of triphenylantimony(V) di-isothiocyanate

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Abstract

A series of triarylantimony(V) dithiocyanates has been prepared by oxidising the appropriate antimony(III) compound with thiocyanogen. IR and ^{14}N NMR spectroscopy indicate the presence of terminally N-bonded thiocyanate groups and this has been confirmed by a crystal structure determination for the $\text{SbPh}_3(\text{NCS})_2$. The asymmetric unit contains three independent trigonal bipyramidal molecules, which differ in the orientations of the axial N-bonded thiocyanates and the phenyl groups in the equatorial plane, and there may be weak C—H $\cdots$ S interactions.

Treatment of SbPh_2X_3 , where X = Br or Cl, with KSCN gave $\text{K}[\text{SbPh}_2(\text{NCS})_4]$ and attempts to prepare $\text{SbPh}_2(\text{NCS})_3$ and related diphenylantimony(V) mixed halide thiocyanates, $\text{SbPh}_2\text{X}_n(\text{NCS})_{3-n}$ where X = Br or Cl and $n = 0-2$, by treating appropriate diphenylantimony(III) precursors with thiocyanogen or thiocyanogen bromide or chloride gave products which in many cases underwent reorganisation during recrystallisation. Samples of $\text{SbPh}_2(\text{NCS})_3$, $\text{SbPh}_2\text{Br}(\text{NCS})_2$, $\text{SbPh}_2\text{Br}_2(\text{NCS})$ and $\text{SbPh}_2\text{Cl}_2(\text{NCS})$, and $\text{SbPh}_3\text{Br}(\text{NCS})$ have, however, been isolated as microcrystalline solids.

Keywords: Antimony; Crystal structure; Group 15; Thiocyanate; NMR spectroscopy; IR spectroscopy

1. Introduction

We have recently shown that it is possible to replace the halogen atom in SbPh_2X , where X = Br or Cl, with potassium thiocyanate to give $\text{SbPh}_2(\text{SCN})$ [1], but the corresponding monophenyl complex $\text{SbPh}(\text{SCN})_2$ cannot be isolated, even with a deficiency of potassium thiocyanate, and instead a salt $\text{K}[\text{SbPh}(\text{SCN})_3]$ is obtained [2]. Both $\text{SbPh}_2(\text{SCN})$ and $\text{K}[\text{SbPh}(\text{SCN})_3]$ have unusual structures. The former contains 1,3-bridging thiocyanate groups but the thiocyanate orientation is reversed at every third antimony atom to give an infinite chain which describes a 'triangular spiral'. The antimony(III) salt, which contains S-bonded thiocyanate groups, is also polymeric as one of the thiocyanate groups bridges via the sulphur atom to a symmetry-related antimony providing one of a small number of compounds in which 1,1-sulphur bridging has been authenticated.

Of the phenylantimony(V) thiocyanates, only $\text{SbPh}_3(\text{NCS})_2$ has been prepared [3–7] but related

methyl [4], *p*-tolyl [7], *p*-fluorophenyl [8] and *p*-chlorophenyl analogues are also known. The compounds are expected to have trigonal bipyramidal geometry and IR evidence points to the presence of N-bonded thiocyanate groups in agreement with the increased hardness of antimony(V). Our interest in these compounds is as precursors for diarylantimony(III) thiocyanates $\text{SbAr}_2(\text{NCS})$, via thermal decomposition [9], and in authentication of the structure of triphenylantimony dithiocyanate.

Diphenylantimony(V) trithiocyanate and the mixed halide thiocyanates, $\text{SbPh}_2\text{X}_n(\text{NCS})_{3-n}$ where X = Br or Cl and $n = 1$ or 2, are currently unknown and we describe here experiments designed to synthesise them. Related bromide chlorides, $\text{SbPh}_2\text{Br}_n\text{Cl}_{3-n}$ for $n = 1$ or 2, have been obtained previously as stable compounds by oxidising the appropriate diphenylantimony(III) halide with either bromine or chlorine [10]. Oxidation of diphenylantimony(III) fluoride, on the other hand, led to halogen reorganisation and in the case of chlorine the only compound isolated was SbPh_2Cl_3 . Reorganisation was slower in bromine oxidation and a series of mixed bromide fluorides, in addition to SbPh_2Br_3 , were iso-

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lated [11]. We have also noted [12] that oxidation of SbPh_2X with *t*-butyl hydroperoxide follows a different route for $\text{X} = \text{Br}$ or Cl , to give $(\text{SbPh}_2\text{OX})_2$ dimers, but reorganised tetramers, $\text{SbPh}_2\text{X}_2(\text{SbPh}_2\text{O})_2\text{SbPh}_2\text{X}_2$, for $\text{X} = \text{F}$ or SCN , and these observations suggest that any diphenylantimony(V) halide thiocyanate may be similarly susceptible to reorganisation.

2. Results and discussion

2.1. $\text{SbAr}_3(\text{NCS})_2$

2.1.1. Preparation and thermal decomposition

Triarylantimony(III) starting materials, with the exception of tris(*p*-fluorophenyl)antimony which was prepared via a Grignard reaction, were readily prepared in high yield from antimony(III) chloride and the appropriate aryl-lithium. Five dithiocyanates were then obtained in high yield and purity by oxidation with dithiocyanogen. With the exception of the *p*-fluoro derivative, which is an oil, they are stable crystalline solids, which can be recrystallised from diethyl ether. Chloroform, which appears to be retained in some samples crystallised from chloroform/hexane mixtures, can be removed by heating to ca. 50°C in a vacuum.

All the compounds were heated slowly under reduced pressure to ca. 20°C above their melting points, but only the 2,6-dimethyl derivative resulted in elimination of aryl thiocyanate to give a pure sample of the related antimony(III) compound, bis(2,6-dimethylphenyl)antimony thiocyanate [1]. Of the remaining thiocyanates, the two tolyl compounds were sufficiently stable to sublime partially; the others failed to decompose cleanly and are probably not suitable precursors for antimony(III) derivatives.

2.1.2. Infrared spectroscopy

IR spectra of all the compounds are complex owing to the presence of aryl groups but thiocyanate bands, particularly those in the 2000 cm^{-1} region, which often give information about the mode of bonding [13], are readily identified and are listed in Table 1. The antisymmetric stretch for all these dithiocyanates is broad and at relatively low energy, consistent with the presence of N-bonded thiocyanate and trigonal bipyramidal structures, as suggested previously. The trimesitylantimony dithiocyanate spectrum shows components at 2052 and 2030 cm^{-1} , probably the in-phase and out-of-phase components as previously observed for trimethylantimony dithiocyanate (2045 and 2015 cm^{-1}) [4]. The strong broad band at 2009 cm^{-1} for triphenylantimony dithiocyanate is intermediate between the previously reported values (2000 [4] and 2022 cm^{-1} [14]).

Although only limited data are available, the antisymmetric stretch appears to be sensitive to the elec-

Table 1
Thiocyanate group vibrations (cm^{-1}) for $\text{SbAr}_3(\text{NCS})_2$

Ar	$\nu(\text{CN})$	$\nu(\text{CS})$	$\delta(\text{NCS})$
mesityl	2052, 2030	750	473
2,6-dimethylphenyl	2049	767	453
<i>p</i> -tolyl	2040		
<i>o</i> -tolyl	2027		474
phenyl	2009		479
phenyl ^a	2022	865	495, 481
phenyl ^b	2000	843	470
<i>p</i> -fluorophenyl	2004	720	475
<i>p</i> -fluorophenyl ^c	2090 ^d		
methyl ^a	2016	848	490, 480
methyl ^b	2045, 2015	843	470
<i>p</i> -chlorophenyl ^c	2010	830	475

^a Ref. [14]. ^b Ref. [4]. ^c Ref. [8]. ^d Assignment questionable, perhaps as a result of a misprint.

tronic properties of the aryl group substituents, with electron-donating groups raising and electron-withdrawing groups lowering the energy.

2.1.3. Mass spectrometry

Electron impact (EI) mass spectra have been measured for all compounds except $\text{Sb}(\text{mesityl})_3(\text{NCS})_2$, for which an FAB spectrum was obtained. Important peaks are listed in Table 2. The parent ion was not observed in any of the EI spectra but $\text{SbAr}_3(\text{NCS})$, arising from thiocyanate loss, was present, except for the 2,6-dimethylphenyl derivative. It is perhaps significant that the most intense fragment in the spectrum of $(2,6\text{-Me}_2\text{C}_6\text{H}_3)_3\text{Sb}(\text{NCS})_2$, the only compound to undergo successful thermal decomposition, is $(2,6\text{-Me}_2\text{C}_6\text{H}_3)_3$, suggesting ready aryl group loss. Further peaks containing both antimony and thiocyanate occurred only with $\text{Sb}(\text{o-tolyl})_2(\text{NCS})$ (intensity < 1%) and a surprisingly intense SbNCS fragment (38.0%) in the $\text{Sb}(2,6\text{-Me}_2\text{C}_6\text{H}_3)_3(\text{NCS})_2$ spectrum. Loss of the second thiocyanate group is thus clearly also a favourable process and the resulting triarylantimony unit then fragments via stepwise loss of aryl groups.

The intensities of SbAr_3 , SbAr_2 , SbAr and Ar are approximately equal for $\text{Ar} = 4\text{-FC}_6\text{H}_4$, *o*-tolyl and *p*-tolyl, but there is a large variation in the intensities of the $\text{SbAr}_3(\text{NCS})$ fragments, i.e. 13.5%, 26.2% and 0.8% respectively, which cannot be correlated with

Table 2
Intensities of selected fragments in the EI mass spectra of $\text{SbAr}_3(\text{NCS})_2$

Ar	SbAr_3NCS	SbAr_3	SbAr_2	SbAr	Ar
phenyl	9.9	54.3	59.8	100.0	14.6
<i>p</i> -fluorophenyl	13.5	100.0	50.3	40.6	83.1
2,6-dimethylphenyl	—	80.5	60.4	62.6	100.0
<i>o</i> -tolyl	26.2	100.0	52.3	41.6	88.1
<i>p</i> -tolyl	0.8	100.0	52.3	39.5	78.1

either electronic or steric effects of the aryl group substituents.

The FAB spectrum of $\text{Sb}(\text{mesityl})_3(\text{NCS})_2$, on the other hand, showed a parent ion peak at 594 (intensity 2.0%), but the most intense peak, $\text{Sb}(\text{mesityl})_3(\text{NCS})$

(100%), corresponded to thiocyanate group loss. Subsequent fragmentation of this ion can involve loss of either mesityl or thiocyanate and, although the ions in the series $\text{Sb}(\text{mesityl})_2(\text{NCS})$ (1.9%), $\text{Sb}(\text{mesityl})(\text{NCS})$ (1.4%) and $\text{Sb}(\text{NCS})$ (3.8%) are observed, thiocyanate

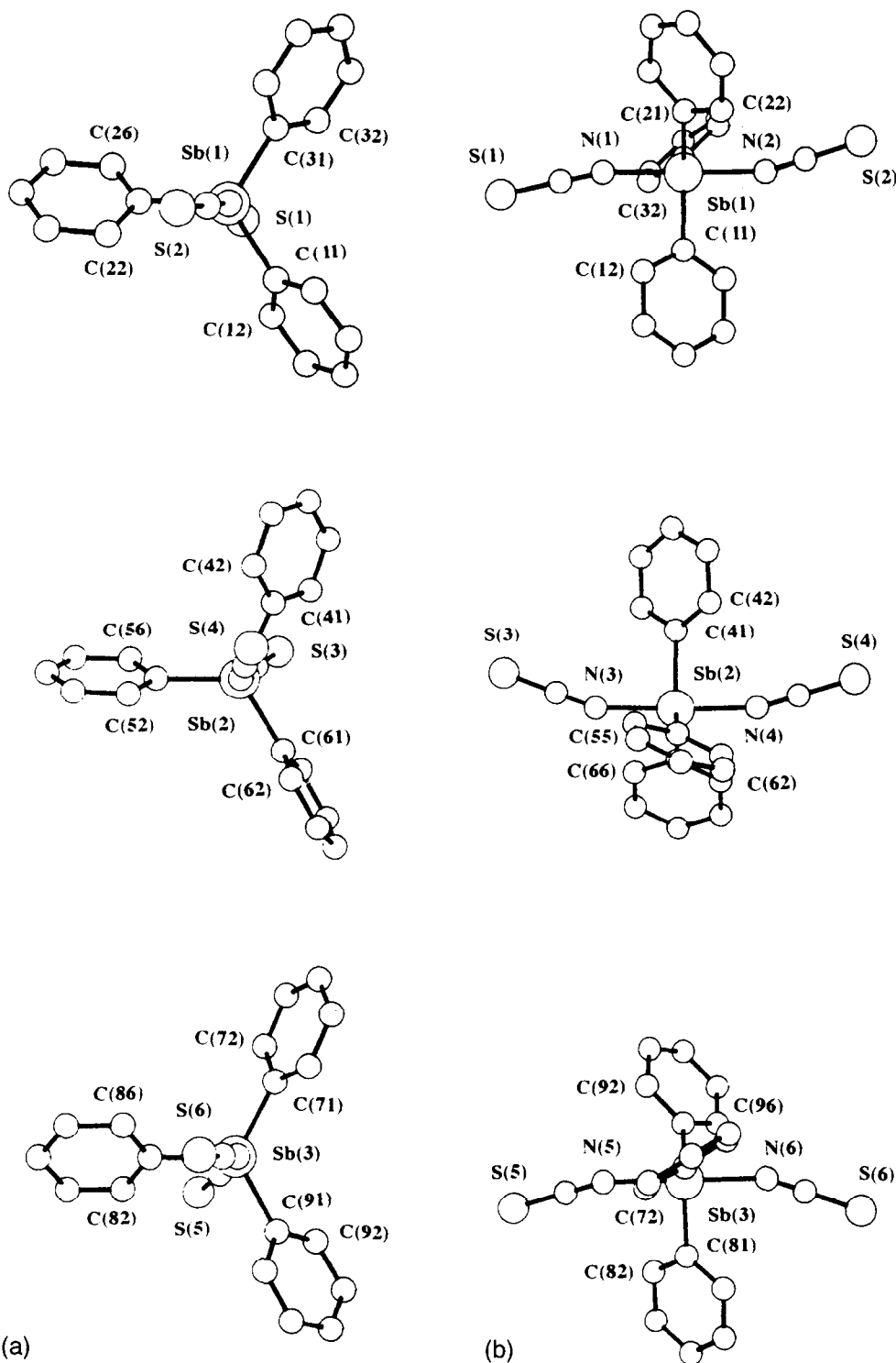


Fig. 1. Structures of the $\text{SbPh}_3(\text{NCS})_2$ molecules perpendicular to (a) the C_3Sb plane and (b) the N-Sb-N vector.

loss to give $\text{Sb}(\text{mesityl})_3$ (7.0%) and subsequently $\text{Sb}(\text{mesityl})_2$ (18.1%) and $\text{Sb}(\text{mesityl})$ (19.5%) is the more probable process.

2.1.4. ^{14}N NMR spectroscopy

Nitrogen-14 NMR spectra, recorded in deuteriochloroform and referenced to external nitrate, are listed in Table 3. Each compound showed a sharp singlet (half-peak line width, 1–2 ppm) between δ –226 and –237 ppm in the region expected for N-bonded thiocyanates [15]. The triphenyl derivative has the highest field signal and substitution in the 4-position with either methyl or fluorine leads to a small downfield shift. Substitution in the 2-position (*o*-tolyl, δ +10 ppm; *p*-tolyl, δ +5 ppm) has a greater effect on the signal position, suggesting that steric rather than electronic influences may be dominant. There is little further effect when the second 2-position is substituted and the mesityl shift (δ –229 ppm) is intermediate between those for the *p*-tolyl and 2,6-dimethylphenyl compounds. Sharp ^{14}N NMR signals appear to be characteristic of terminally N-bonded thiocyanate groups in axial positions about a trigonal bipyramidal antimony atom.

Although only the 2,6-dimethylphenyl derivative decomposed cleanly on heating, all thermolysis mixtures showed an extra broad upfield signal that could be assigned to the appropriate antimony(III) species, e.g. peaks at δ –270 and –259 ppm, respectively, for $\text{Sb}(\textit{o}$ -tolyl) $_2\text{NCS}$ and $\text{Sb}(\textit{p}$ -tolyl) $_2\text{NCS}$. Substitution in the *ortho* position again appears to promote larger shifts than *para* substitution but, contrary to the observation with the antimony(V) species, here the shift is upfield. The δ –259 ppm peak for the *p*-tolyl compound is virtually identical with that for SbPh_2SCN [1], showing that steric rather than electronic effects are again probably more important.

2.1.5. Structure of triphenylantimony di-isothiocyanate

Important bond distances and angles for this compound are listed in Table 4. The structure determination shows an asymmetric unit containing three independent molecules, with each antimony atom in trigonal bipyramidal geometry to equatorial phenyl and axial N-bonded thiocyanate groups. Any degree of thiocyanate bridging is ruled out by the absence of intermolecular $\text{Sb} \cdots \text{S}$

Table 4

Important bond lengths (Å) and angles (°) for $\text{SbPh}_3(\text{NCS})_2$ with estimated standard deviations in parentheses

Bond lengths			
$\text{Sb}(1)-\text{N}(1)$	2.128(7)	$\text{Sb}(2)-\text{C}(61)$	2.121(8)
$\text{Sb}(1)-\text{N}(2)$	2.142(7)	$\text{N}(3)-\text{C}(3)$	1.182(9)
$\text{Sb}(1)-\text{C}(11)$	2.099(7)	$\text{C}(3)-\text{S}(3)$	1.571(9)
$\text{Sb}(1)-\text{C}(21)$	2.097(7)	$\text{N}(4)-\text{C}(4)$	1.149(9)
$\text{Sb}(1)-\text{C}(31)$	2.085(7)	$\text{C}(4)-\text{S}(4)$	1.551(9)
$\text{N}(1)-\text{C}(1)$	1.142(9)	$\text{Sb}(3)-\text{N}(5)$	2.148(8)
$\text{C}(1)-\text{S}(1)$	1.593(9)	$\text{Sb}(3)-\text{N}(6)$	2.162(9)
$\text{N}(2)-\text{C}(2)$	1.145(9)	$\text{Sb}(3)-\text{C}(71)$	2.096(8)
$\text{C}(2)-\text{S}(2)$	1.583(9)	$\text{Sb}(3)-\text{C}(81)$	2.111(8)
$\text{Sb}(2)-\text{N}(3)$	2.126(7)	$\text{Sb}(3)-\text{C}(91)$	2.071(8)
$\text{Sb}(2)-\text{N}(4)$	2.147(7)	$\text{N}(5)-\text{C}(5)$	1.168(9)
$\text{Sb}(2)-\text{C}(41)$	2.110(7)	$\text{C}(5)-\text{S}(5)$	1.580(9)
$\text{Sb}(2)-\text{C}(51)$	2.109(8)	$\text{N}(6)-\text{C}(6)$	1.067(9)
		$\text{C}(6)-\text{S}(6)$	1.586(9)
Bond angles			
$\text{N}(1)-\text{Sb}(1)-\text{N}(2)$	179.0(3)	$\text{Sb}(2)-\text{N}(3)-\text{C}(3)$	153.8(7)
$\text{N}(1)-\text{Sb}(1)-\text{C}(11)$	90.5(3)	$\text{N}(3)-\text{C}(3)-\text{S}(3)$	178.5(9)
$\text{N}(1)-\text{Sb}(1)-\text{C}(21)$	89.8(3)	$\text{Sb}(2)-\text{N}(4)-\text{C}(4)$	164.1(7)
$\text{N}(1)-\text{Sb}(1)-\text{C}(31)$	89.9(3)	$\text{N}(4)-\text{C}(4)-\text{S}(4)$	179.3(8)
$\text{N}(2)-\text{Sb}(1)-\text{C}(11)$	90.5(3)	$\text{Sb}(2)-\text{C}(41)-\text{C}(42)$	118.4(6)
$\text{N}(2)-\text{Sb}(1)-\text{C}(21)$	89.5(3)	$\text{Sb}(2)-\text{C}(41)-\text{C}(46)$	120.4(6)
$\text{N}(2)-\text{Sb}(1)-\text{C}(31)$	90.0(3)	$\text{Sb}(2)-\text{C}(51)-\text{C}(52)$	120.6(6)
$\text{C}(11)-\text{Sb}(1)-\text{C}(21)$	123.3(3)	$\text{Sb}(2)-\text{C}(51)-\text{C}(56)$	119.2(7)
$\text{C}(11)-\text{Sb}(1)-\text{C}(31)$	116.0(3)	$\text{Sb}(2)-\text{C}(61)-\text{C}(62)$	120.1(6)
$\text{C}(21)-\text{Sb}(1)-\text{C}(31)$	120.7(3)	$\text{Sb}(2)-\text{C}(61)-\text{C}(66)$	120.3(6)
$\text{Sb}(1)-\text{N}(1)-\text{C}(1)$	167.1(7)	$\text{N}(5)-\text{Sb}(3)-\text{N}(6)$	178.9(3)
$\text{N}(1)-\text{C}(1)-\text{S}(1)$	178.7(9)	$\text{N}(5)-\text{Sb}(3)-\text{C}(71)$	90.5(3)
$\text{Sb}(1)-\text{N}(2)-\text{C}(2)$	154.8(6)	$\text{N}(5)-\text{Sb}(3)-\text{C}(81)$	90.9(3)
$\text{N}(2)-\text{C}(2)-\text{S}(2)$	179.0(8)	$\text{N}(5)-\text{Sb}(3)-\text{C}(91)$	89.7(3)
$\text{Sb}(1)-\text{C}(11)-\text{C}(12)$	121.1(6)	$\text{N}(6)-\text{Sb}(3)-\text{C}(71)$	89.3(3)
$\text{Sb}(1)-\text{C}(11)-\text{C}(16)$	117.5(6)	$\text{N}(6)-\text{Sb}(3)-\text{C}(81)$	90.1(3)
$\text{Sb}(1)-\text{C}(21)-\text{C}(22)$	119.3(6)	$\text{N}(6)-\text{Sb}(3)-\text{C}(91)$	89.5(3)
$\text{Sb}(1)-\text{C}(21)-\text{C}(26)$	118.5(6)	$\text{C}(71)-\text{Sb}(3)-\text{C}(81)$	117.2(3)
$\text{Sb}(1)-\text{C}(31)-\text{C}(32)$	119.8(6)	$\text{C}(71)-\text{Sb}(3)-\text{C}(91)$	123.2(3)
$\text{Sb}(1)-\text{C}(31)-\text{C}(36)$	120.6(5)	$\text{C}(81)-\text{Sb}(3)-\text{C}(91)$	119.6(3)
$\text{N}(3)-\text{Sb}(2)-\text{N}(4)$	178.2(3)	$\text{Sb}(3)-\text{N}(5)-\text{C}(5)$	151.0(7)
$\text{N}(3)-\text{Sb}(2)-\text{C}(41)$	89.4(3)	$\text{N}(5)-\text{C}(5)-\text{S}(5)$	176.6(8)
$\text{N}(3)-\text{Sb}(2)-\text{C}(51)$	91.3(3)	$\text{Sb}(3)-\text{N}(6)-\text{C}(6)$	159.3(9)
$\text{N}(3)-\text{Sb}(2)-\text{C}(61)$	91.5(3)	$\text{N}(6)-\text{C}(6)-\text{S}(6)$	178.9(8)
$\text{N}(4)-\text{Sb}(2)-\text{C}(41)$	88.8(3)	$\text{Sb}(3)-\text{C}(71)-\text{C}(72)$	119.6(6)
$\text{N}(4)-\text{Sb}(2)-\text{C}(51)$	89.2(3)	$\text{Sb}(3)-\text{C}(71)-\text{C}(76)$	119.3(7)
$\text{N}(4)-\text{Sb}(2)-\text{C}(61)$	89.8(3)	$\text{Sb}(3)-\text{C}(81)-\text{C}(82)$	120.1(6)
$\text{C}(41)-\text{Sb}(2)-\text{C}(51)$	113.1(3)	$\text{Sb}(3)-\text{C}(81)-\text{C}(86)$	118.3(6)
$\text{C}(41)-\text{Sb}(2)-\text{C}(61)$	125.7(3)	$\text{Sb}(3)-\text{C}(91)-\text{C}(92)$	120.5(7)
$\text{C}(51)-\text{Sb}(2)-\text{C}(61)$	121.1(3)	$\text{Sb}(3)-\text{C}(91)-\text{C}(96)$	119.6(7)

Table 3

Nitrogen-14 chemical shifts (δ , ppm) and line widths at half-height ($\Delta\delta$, ppm)

Compound	Shift	Line width
$\text{Sb}(\text{mesityl})_3(\text{NCS})_2$	–229	1
$\text{Sb}(2,6\text{-Me}_2\text{C}_6\text{H}_3)_3(\text{NCS})_2$	–226	1
$\text{Sb}(\textit{p}$ -tolyl) $_3(\text{NCS})_2$	–232	1
$\text{Sb}(\textit{o}$ -tolyl) $_3(\text{NCS})_2$	–227	1
$\text{SbPh}_3(\text{NCS})_2$	–237	2
$\text{Sb}(\textit{p}$ -FC $_6\text{H}_4$) $_3(\text{NCS})_2$	–234	2

interactions within 4.1 Å. Fig. 1 shows the atom numbering scheme and views of the independent molecules perpendicular to (a) the trigonal plane and (b) the N–Sb–N vector; the relative orientations of the three molecules are shown in Fig. 2.

The data in Table 4 show that there are clear differences between the three molecules, particularly in respect of the thiocyanate distances and angles and these are highlighted in Table 5. In each molecule, for example, there is one short and one long Sb–N bond distance and the two Sb–N–C angles are different. No simple relationship between the Sb–N bond length and Sb–N–

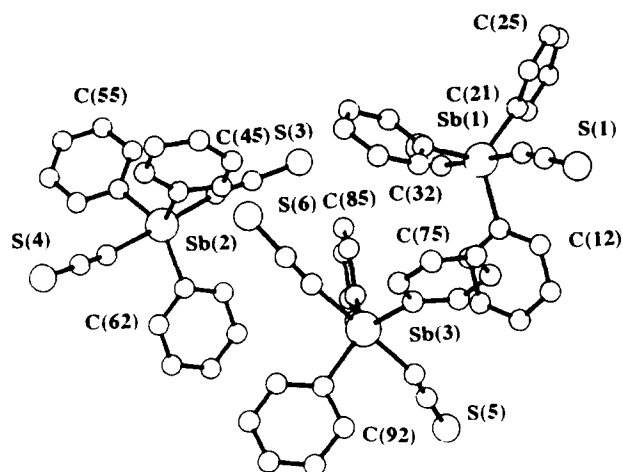
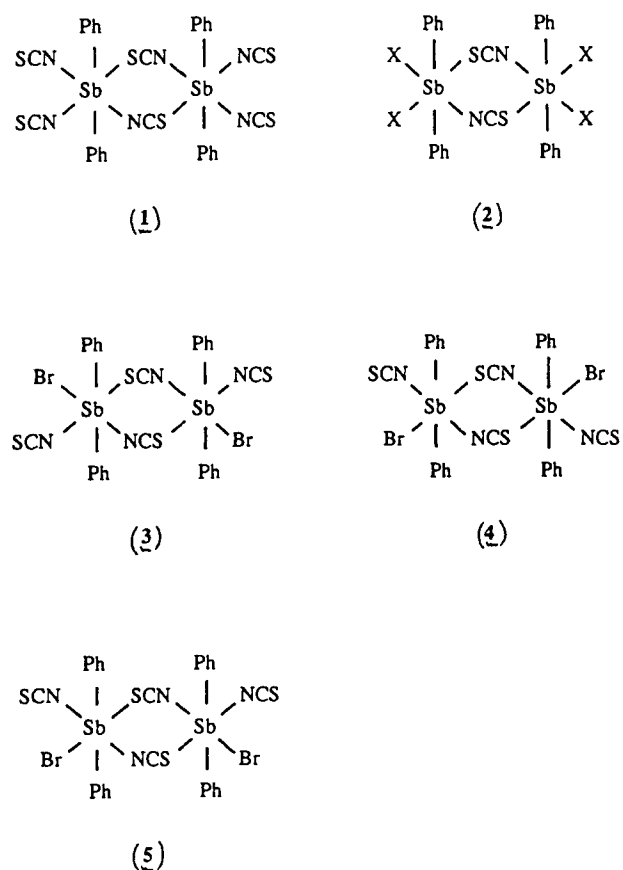


Fig. 2. Relative orientations of the three molecules in the unit cell.



C bond angle could be established as, for example, bonds to N(2), N(4) and N(5) are very similar (2.142, 2.147 and 2.148 Å) but the corresponding nitrogen angles (154.8, 164.1 and 151.0°, respectively) are markedly different. The mean Sb–N bond length (2.14 Å) is slightly longer than that in diphenylantimony oxide thiocyanate (2.10 Å) [12] as perhaps may be expected from the decrease in Lewis acidity on replacing oxygen by the less electronegative phenyl group. The thiocyanate groups are effectively linear, with an average angle at the carbon atom of 178.5°, and, as expected, the N–Sb–N angles between the axial thiocyanate groups are also close to 180°, at 179.0(3)°, 178.2(3)° and 178.9(3)° at Sb(1), Sb(2) and Sb(3), respectively.

For comparison, in the related di-isocyanate, $\text{SbPh}_3(\text{NCO})_2$, angles at nitrogen are 145.4° and 152.2°, with C–N bond lengths of 1.146 and 1.111 Å [16]. Bond lengths to antimony are effectively equal (2.125 and 2.122 Å) and the N–Sb–N angle is 178.5°.

The present structure, however, shows curious differences between the three molecules, particularly in the details of the phenyl and thiocyanate group arrangements. In all cases, even though the sum of the angles between the phenyl groups in the equatorial plane is 360°, indicating planarity of the SbC_3 systems, only one of the angles at each antimony is 120°. The spread at Sb(1) is from 116.0° to 123.3°, at Sb(2) from 113.1° to 125.7° and from 117.2° to 123.2° at Sb(3). Deviations of equatorial angles from 120° could result from inter- or intra-molecular interactions as in SbPh_4OAc [17] and $\text{SbPh}_3(\text{OAc})_2$ [18], but there are no antimony contacts within 4.1 Å, and this type of interaction cannot be the cause of deviations here.

Torsion angles representing the relative orientations of the phenyl groups at each antimony atom are given in the upper part of Table 6 and show that the groups at Sb(1) and Sb(3) are in a propeller arrangement (three torsion angles approximately equal with the same sign) while one of the groups at Sb(2) is oppositely oriented (one torsion angle with opposite sign to the other two). These arrangements are also shown in Fig. 1(a). Different phenyl group orientation are not unknown in other triphenylantimony(V) derivatives, as shown by a propeller arrangement in the dichloride [19] and the same orientation as in molecule 2 in the corresponding dibromide [19] and di-isocyanate [16].

The orientation of the thiocyanate ligand with respect to the equatorial atoms varies at each antimony atom as shown by the lower set of torsion angles in Table 6. One group at each antimony is effectively coincident with one of the Sb–phenyl bonds, i.e. thiocyanate 2 with Sb(1)–C(21), thiocyanate 4 with Sb(2)–C(41) and thiocyanate 6 with Sb(3)–C(81), while the second group takes up a variable, intermediate orientation. The differences can be seen from Fig. 1(b) which also shows that

Table 5
Thiocyanate bond lengths (Å) and angles (°)

Sb	NCS groups	Bond lengths			Bond angles	
		Sb–N	N–C	C–S	Sb–N–C	N–C–S
Sb(1)	N(1)C(1)S(1)	2.128	1.142	1.593	167.1	178.7
Sb(1)	N(2)C(2)S(2)	2.142	1.145	1.583	154.8	179.0
Sb(2)	N(3)C(3)S(3)	2.126	1.182	1.571	153.8	178.5
Sb(2)	N(4)C(4)S(4)	2.147	1.149	1.551	164.1	179.3
Sb(3)	N(5)C(5)S(5)	2.148	1.168	1.580	151.0	176.6
Sb(3)	N(6)C(6)S(6)	2.162	1.067	1.596	159.3	178.9

Table 6
Selected torsion angles (°)

C(21)–Sb(1)–C(11)–C(12)	63.3
C(11)–Sb(1)–C(21)–C(22)	51.0
C(11)–Sb(1)–C(31)–C(32)	51.9
C(51)–Sb(2)–C(41)–C(42)	46.0
C(41)–Sb(2)–C(51)–C(56)	67.3
C(41)–Sb(2)–C(61)–C(66)	–84.6
C(81)–Sb(3)–C(71)–C(72)	–59.6
C(71)–Sb(3)–C(81)–C(86)	–49.7
C(71)–Sb(3)–C(91)–C(96)	–53.3
C(21)–Sb(1)–N(1)–C(1)	–138.6
C(21)–Sb(1)–N(2)–C(2)	8.1
C(41)–Sb(2)–N(3)–C(3)	37.3
C(41)–Sb(2)–N(4)–C(4)	8.1
C(81)–Sb(3)–N(5)–C(5)	–45.9
C(81)–Sb(3)–N(6)–C(6)	–0.5

the two groups on both Sb(2) and Sb(3) bend in the same direction to give a pseudo-*cis* arrangement of terminal sulphur atoms, while those on Sb(1) bend in 'opposite directions' and the sulphur atoms adopt a pseudo-*trans* arrangement.

This structure, with three independent molecules differing in both phenyl and thiocyanate orientations, is rather surprising. Clearly the reasons for the unexpected structure of the di-isothiocyanate are associated with weak 'crystal packing' effects but, as noted above, there are no antimony–sulphur interactions within 4.1 Å that might have influenced the structure. There are, however, three S...S interactions within 4.1 Å [S(1)...S(5), 4.00 Å; S(2)...S(3), 3.73 Å; and S(3)...S(6), 4.09 Å], but it is difficult to see what influence these might have, and there is a series of contacts between the six thiocyanate sulphur atoms and C–H bonds of neighbouring phenyl groups. These distances (within an arbitrary upper limit of 3.2 Å), to-

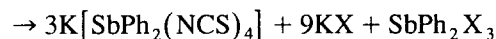
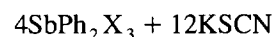
gether with the corresponding C...S separations and C–H...S and H...C–S angles, are listed in Table 7.

In recent years, detailed analysis of many solid-state structures has revealed the presence of weak intra- and inter-molecular interactions which influence crystal packing. Among these are weak contacts between C–H bonds and, in particular, oxygen or nitrogen atoms; C...O separations, for example, are ca. 3.5 Å [20]. Even weaker interactions would be expected between C–H bonds and sulphur and the S...C separations listed in Table 7 fall between 3.62 and 3.95 Å (the corresponding H...S separations are between 2.75 and 3.17 Å). In the absence of any other close contacts, we suggest that at least some of the differences between the three molecules in this structure may be a consequence of these very weak contacts.

2.2. $\text{SbPh}_2\text{X}_n(\text{NCS})_{3-n}$ where X = NCS, Br or Cl and $n = 0-2$

2.2.1. Preparations

Diphenylantimony(V) trithiocyanate could not be prepared by treating either diphenylantimony trichloride or tribromide with 3 mol of potassium thiocyanate in acetonitrile, and potassium diphenylantimony tetrathiocyanate was obtained instead.



(where X = Cl or Br)

This salt, together with unchanged trihalide, was also obtained even with reactant ratios much lower than 1:3 and clearly neither the trithiocyanate nor the mixed halide thiocyanates, $\text{SbPh}_2\text{X}_n(\text{NCS})_{3-n}$, can be pro-

Table 7
Short S...C and S...H contacts (Å and °)

x	y	S(x)...C(y)	S(x)...H(y)	S(x)...H(y)–C(y)	H(y)...S(x)–C(x)
1	53 ^a	3.76	2.99	130	167
1	54 ^b	3.88	3.12	131	78
1	92 ^c	3.93	3.05	141	114
2	33 ^d	3.82	3.17	124	146
2	43 ^b	3.81	3.14	123	138
2	55 ^e	3.95	2.98	154	138
3	33 ^d	3.95	3.20	132	128
3	35 ^b	3.79	3.13	123	73
3	84	3.83	2.95	144	94
4	13 ^f	3.74	3.05	124	144
4	83 ^g	3.84	2.90	151	86
5	15	3.84	3.11	129	66
5	53 ^g	3.87	3.00	141	84
6	95 ^h	3.62	2.75	139	98

Symmetry codes:

^a 1 + x, y, z. ^b 1 – x, 1 – y, 1 – z. ^c 1 – x, –y, –z. ^d x – 1, y, z. ^e –x, 1 – y, 1 – z. ^f x, y, 1 + z. ^g –x, –y, 1 – z. ^h 1 – x, –y, 1 – z.

duced by this type of reaction. A similar problem was observed previously with thiocyanate substitution in SbPh_2X_2 for $\text{X} = \text{Br}$ or Cl , when again a salt, $\text{K}[\text{SbPh}(\text{SCN})_3]$, was obtained instead of the neutral dithiocyanate [2]. In both cases halide replacement must be rapid, giving a high Lewis acidity product which, even with a deficiency of potassium thiocyanate, immediately forms the salt.

Alternative approaches to mixed halide thiocyanate synthesis are (a) oxidation of SbPh_2SCN with halogens, (b) oxidation of SbPh_2X (where $\text{X} = \text{Cl}$ or Br) with dithiocyanogen and (c) oxidation of SbPh_2X (where $\text{X} = \text{SCN}$, Cl or Br) with thiocyanogen bromide or chloride.

(a) Treatment of diphenylantimony thiocyanate with 1 mol of bromine gave SbPh_2Br_3 and, even though new thiocyanate bands appeared in the spectra of products from reactions with lower ratios of bromine, microanalysis pointed to the presence of mixtures of SbPh_2Br_3 and $\text{SbPh}_2\text{Br}_2(\text{NCS})$. On successive recrystallisations the nitrogen content dropped and eventually pure SbPh_2Br_3 was isolated. Because reorganisation is clearly occurring, corresponding reactions with chlorine were not carried out.

(b) Oxidation of SbPh_2X (where $\text{X} = \text{Br}$, Cl or NCS) with dithiocyanogen gave initial products with analyses close to those of the expected products, $\text{SbPh}_2\text{X}(\text{NCS})_2$, with IR spectra showing one sharp and one broad, lower energy, IR band in the antisymmetric NCS stretching region. Problems from ligand scrambling again arose during conventional recrystallisations and in all cases only triphenylantimony dithiocyanate and SbPh_2X_3 for $\text{X} = \text{Br}$ or Cl were isolated. Recrystallisations at ca. 0°C were successful in producing pure trithiocyanate, $\text{SbPh}_2(\text{NCS})_3$, as a pale yellow microcrystalline solid, but crystals suitable for X-ray diffraction could not be obtained. The trithiocyanate is stable at room temperature and reacts, as expected, with potassium thiocyanate to give potassium diphenylantimony tetrathiocyanate. Mixed halide thiocyanates remained elusive and, even at low temperature, products with progressively decreasing nitrogen content were obtained on attempts at recrystallisation until finally pure SbPh_2X_3 was isolated.

(c) Thiocyanogen bromide reacted smoothly with SbPh_2Br , $\text{SbPh}_2(\text{SCN})$ and SbPh_3 giving $\text{SbPh}_2\text{Br}_2(\text{NCS})$, $\text{SbPh}_2\text{Br}(\text{NCS})_2$ and $\text{SbPh}_3\text{Br}(\text{NCS})$, respectively, in high yields and purity. Probably because of this high initial purity, they could all be recrystallised rapidly from cold solvents giving microcrystalline material but unsuitable for X-ray crystallography.

Related reactions with thiocyanogen chloride were not as successful and, although IR spectra of the initial products were similar to those above, only pure $\text{SbPh}_2\text{Cl}_2(\text{NCS})$ was always obtained. Reorganisation during recrystallisation is certainly more rapid in this chloride system and, for example, triphenylantimony

Table 8
Thiocyanate group vibrations (cm^{-1})

Compound	$\nu_{\text{as}}(\text{NCS})$		$\nu_{\text{s}}(\text{NCS})$	$\delta(\text{NCS})$
	sharp	broad		
$\text{SbPh}_3\text{Br}(\text{NCS})$		2024	775	477
$\text{SbPh}_3(\text{NCS})_2$		2009	775	479
$\text{SbPh}_2\text{Br}_2(\text{NCS})$	2100		785	475, 465
$\text{SbPh}_2\text{Cl}_2(\text{NCS})$	2106		790, 770	
$\text{SbPh}_2\text{Br}(\text{NCS})_2$	2092	1993	770	465
$\text{SbPh}_2(\text{NCS})_3$	2120	2000	785	463
	2105			
$\text{K}[\text{SbPh}_2(\text{NCS})_4]$		2010	760	463
		2002		

chloride thiocyanate gave mixtures of the dichloride and dithiocyanate while $\text{SbPh}_2\text{Cl}(\text{NCS})_2$ gave the more stable dichloride, $\text{SbPh}_2\text{Cl}_2(\text{NCS})$.

2.2.2. Infrared spectra

Bands due to thiocyanate vibrations are collected in Table 8. Potassium diphenylantimony tetrathiocyanate, which is expected to have octahedral geometry with *trans* phenyl groups, showed a broad absorption with maxima at 2010 and 2002 cm^{-1} (cf. 1990 cm^{-1} [21]), most probably associated with in-phase and out-of-phase components of terminal N-bonded thiocyanate groups. We prefer to assign the weak band at 760 cm^{-1} to the symmetric stretch in contrast to its earlier assignment to a band at 860 cm^{-1} . Bands at 860 cm^{-1} are found in a range of phenylantimony(V) derivatives and are probably better assigned as phenyl ($w + y$) combination modes [22].

Single sharp bands at 2100 and 2106 cm^{-1} , respectively, in the region associated with either 1,3-bridging or terminal S-bonded thiocyanate groups are found for $\text{SbPh}_2\text{Br}_2(\text{NCS})$ and $\text{SbPh}_2\text{Cl}_2(\text{NCS})$ but the hardness of Sb^{V} makes the latter assignment unlikely. Substitution of a second thiocyanate group giving $\text{SbPh}_2\text{Br}(\text{NCS})_2$ leads to an additional broad band at 1993 cm^{-1} , indicative of a terminally N-bonded thiocyanate, and there is a similar additional broad band at 2000 cm^{-1} in the spectrum of $\text{SbPh}_2(\text{NCS})_3$. In this spectrum, the sharp bridging thiocyanate absorption is split into components at 2105 and 2120 cm^{-1} .

In both $(\text{SbPh}_2\text{Cl}_3)_2$ [23] and $[\text{SbPh}_2\text{X}_4]^-$ [24] phenyl groups occupy *trans* positions about octahedrally coordinated antimony atoms and this is the basis for the dimeric structures suggested below for $\text{SbPh}_2(\text{NCS})_3$, $\text{SbPh}_2\text{Br}(\text{NCS})_2$ and $\text{SbPh}_2\text{X}_2(\text{NCS})$, where $\text{X} = \text{Br}$ or Cl . There must always be one bridging thiocyanate group giving structures **1** and **2** for $\text{SbPh}_2(\text{NCS})_3$ and $\text{SbPh}_2\text{X}_2(\text{NCS})$, respectively. For $\text{SbPh}_2\text{Br}(\text{NCS})_2$, there are three possible dimeric alternatives where bromine is *trans* to either N-bonded thiocyanates (**3**) or to S-bonded thiocyanates (**4**) or to

Table 9

Nitrogen-14 chemical shifts (δ , ppm) and line widths at half-height ($\Delta\delta$, ppm)

Compound	Shift	Line width
$\text{SbPh}_3(\text{NCS})_2$	– 237	2
$\text{SbPh}_3\text{Br}(\text{NCS})$	– 226	2
	– 233 ^a	2
$\text{SbPh}_2(\text{NCS})_3$	– 239	24
	– 233 ^a	2
$\text{SbPh}_2\text{Br}(\text{NCS})_2$	– 229	16
$\text{SbPh}_2\text{Br}_2(\text{NCS})$	– 223	14

^a Signal due to $\text{SbPh}_3(\text{NCS})_2$ from reorganisation.

one N- and one S-bonded thiocyanate (5). More highly polymeric structures are, of course, also possible.

2.2.3. Mass spectrometry

None of the compounds showed a parent ion peak and in all cases loss of thiocyanate groups is a highly probable process. For example, in the case of both $\text{SbPh}_2(\text{NCS})_3$ and $\text{K}[\text{SbPh}_2(\text{NCS})_4]$, with the exception of a high intensity SbPh_3NCS rearrangement ion, the only antimony–thiocyanate species were low intensity $\text{SbPh}_2(\text{NCS})_2$, $\text{SbPh}(\text{NCS})_3$ and $\text{SbPh}(\text{NCS})_2$ peaks, and somewhat more intense peaks associated with SbPhNCS (ca. 10%) and SbNCS (ca. 8%). Broadly the same picture is observed for the mixed halide thiocyanates but here the highest mass peak arose by complete loss of the thiocyanate group. Subsequent fragmentation then involves loss of either halogen (more probable) or phenyl groups.

2.2.4. ¹⁴N NMR spectroscopy

Probably owing to poor solubility, no signal was observed in either deuteriochloroform or deuteromethanol solution for $\text{K}[\text{SbPh}_2(\text{NCS})_4]$, but signals for the tri- and di-phenyl compounds in deuteriochloroform (see Table 9) are in the region for N-bonded thiocyanate groups. Our sample of triphenylantimony bromidethiocyanate showed two sharp resonances (δ – 226 and – 233 ppm; half-peak line width, 2 ppm) in the ratio 2:1, which can be assigned, respectively, to the compound itself and to its reorganisation product, $\text{SbPh}_3(\text{NCS})_2$. These assignments are supported by (a) the rapid reorganisation of the corresponding chloride, $\text{SbPh}_3\text{Cl}(\text{NCS})$, which always gave mixtures of $\text{SbPh}_3(\text{NCS})_2$ and SbPh_3Cl_2 , and (b) the appearance after 24 h standing of signals at δ – 233 ppm in the spectra of $\text{SbPh}_2(\text{NCS})_3$ and $\text{SbPh}_2\text{Br}(\text{NCS})_2$, which are known to give $\text{SbPh}_3(\text{NCS})_2$ on recrystallisation at normal temperatures. The sharpness of the signal also points to the presence of thiocyanate groups occupying axial positions in a trigonal bipyramidal arrangement about antimony.

Broad signals, on the other hand, were observed for $\text{SbPh}_2(\text{NCS})_3$ (δ – 239 ppm), $\text{SbPh}_2\text{Br}_2(\text{NCS})$ (δ

– 223 ppm) and $\text{SbPh}_2\text{Br}(\text{NCS})_2$ (δ – 229 ppm). Although all compounds are considered to be at least dimeric in the solid, dissolution will break any thiocyanate bridges and fluxionality between axial and equatorial thiocyanate groups is a possible source of line broadening. Long acquisition times were required to obtain these spectra and as the compounds are known to reorganise in solution it was difficult to obtain definitive spectra.

These data point to a downfield shift of the nitrogen resonance in the order $\text{SbPh}_2(\text{NCS})_3 > \text{SbPh}_3(\text{NCS})_2 > \text{SbPh}_2\text{Br}(\text{NCS})_2 > \text{SbPh}_3\text{Br}(\text{NCS}) > \text{SbPh}_2\text{Br}_2(\text{NCS})$, with shielding at nitrogen influenced by the antimony substituents in the order $\text{NCS} > \text{Ph} > \text{Br}$.

3. Experimental details

3.1. Preparation of SbAr_3

Triphenylantimony (Aldrich) was used as received. With the exception of the *p*-fluorophenyl which was obtained via a Grignard reaction with antimony(III) chloride, the other triarylantimony derivatives were prepared from the appropriate lithium aryl and antimony(III) chloride. Analytical data are summarised in Table 10.

3.2. Oxidation of SbAr_3 with dithiocyanogen

Dithiocyanogen solutions in dichloromethane were obtained by treating lead(II) thiocyanate with bromine [25] and standardised by titrating the iodine liberated from aqueous potassium iodide with standard sodium thiosulphate solution.

In general, an ice-cold, freshly prepared and standardised solution of dithiocyanogen in dichloromethane was added with stirring to an ice-cold equimolar solution of the appropriate SbAr_3 in dichloromethane at 0°C. After being stirred for 30 min at 0°C, the solution was concentrated in a vacuum and placed in the freezer. The resulting crystals were collected and recrystallised from either diethyl ether or a 1:1 mixture of chloroform and hexane. Analytical data for solvent-free samples, obtained either directly from ether or by heating the

Table 10

Analytical data for SbAr_3

Ar	M.p. (°C)	Analysis (%): Found (calc.)	
		C	H
<i>o</i> -tolyl	100	64.3 (63.8)	5.4 (5.3)
<i>p</i> -tolyl	127	62.8 (63.8)	5.3 (5.3)
2,6-dimethylphenyl	120	65.5 (65.9)	6.3 (6.2)
mesityl	131	66.6 (67.7)	6.8 (6.9)
<i>p</i> -fluorophenyl	81	52.9 (53.1)	2.9 (3.0)

Table 11
Analytical data for $\text{SbAr}_3(\text{NCS})_2$

Ar	M.p. (°C)	Analysis (%): Found (calc.)		
		C	H	N
phenyl	111	51.1 (51.2)	3.2 (3.2)	5.9 (6.0)
<i>o</i> -tolyl	245	54.0 (54.0)	4.1 (4.1)	5.6 (5.5)
<i>p</i> -tolyl	238	54.0 (54.0)	4.0 (4.1)	5.4 (5.5)
2,6-dimethylphenyl	250	64.3 (63.8)	5.4 (5.3)	4.8 (5.1)
mesityl	240	57.7 (58.5)	5.5 (5.6)	4.6 (4.7)
<i>p</i> -fluorophenyl	oil	43.9 (45.9)	2.2 (2.3)	5.0 (4.6)

chloroform products to 50°C in a vacuum are summarised in Table 11.

3.3. Thermal decomposition of triarylantimony dithiocyanates

Each of the dithiocyanates was heated slowly to ca. 25°C above the melting point under reduced pressure on a vacuum frame fitted with a nitrogen bleed [9] and held there for ca. 1 h. The cooled residue was dissolved in chloroform, stirred with charcoal and recrystallised from a chloroform hexane mixture. Only for tris(2,6-dimethylphenyl)antimony dithiocyanate did we isolate a pure sample of the decomposition product, bis(2,6-dimethylphenyl)antimony thiocyanate. M.p. 149°C (Analysis: Found: C, 52.3; H, 4.7; N, 3.6%. $\text{C}_{17}\text{H}_{18}\text{NSSb}$ calc.: C, 52.3; H, 4.6; N, 3.6%).

3.4. Crystal structure of $\text{SbPh}_3(\text{NCS})_2$

Crystals suitable for X-ray diffraction were grown slowly from chloroform hexane mixtures and mounted in glass capillaries.

3.4.1. Crystal data

$\text{SbPh}_3(\text{NCS})_2$; $\text{C}_{20}\text{H}_{15}\text{N}_2\text{S}_2\text{Sb}$; M, 468.8; triclinic; $a = 10.932(3)$, $b = 17.604(3)$, $c = 18.733(3)$ Å, $\alpha = 107.61(4)$, $\beta = 92.85(4)$, $\gamma = 116.72(5)^\circ$; $U = 2995.3$ Å³; Mo K α radiation (with graphite monochromator); space group $P\bar{1}$; $D_c = 1.56$ g cm⁻³; $Z = 6$; $\mu = 16.0$ cm⁻¹, for 5538 reflections with $I > 3\sigma(I)$; Hilger & Watts Y290 four-circle diffractometer, scanning range $0^\circ < \theta < 22^\circ$.

3.4.2. Structure determination

Intensity data were collected on a Hilger & Watts Y290 diffractometer for 7357 independent reflections in the range $0^\circ < \theta < 22^\circ$ ($-13 < h < 13$, $-19 < k < 19$, $0 < l < 20$) of which 5538 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 [26] programs and neutral atom scattering factors [27]. Density data suggested the pres-

ence of six antimony atoms in the triclinic unit cell and possible positions for the three independent atoms in the asymmetric unit were obtained from a three-dimensional Patterson synthesis. The remaining non-hydrogen atoms were located following a series of full-matrix least-squares refinements (each molecule in a separate block) and difference Fourier syntheses. After convergence with anisotropic thermal parameters, the hydrogen atoms were placed at their calculated positions [$d(\text{C}-\text{H})$ 1.0 Å] but not refined in further cycles. Application of a four-coefficient Chebyshev weighting scheme led to final convergence (677 parameters, max. shift: esd = 0.02, max. and min. residual electron densities 0.70 and -0.22 e Å⁻³) at $R = 0.0425$ ($R_w = 0.0490$).

The final atomic coordinates are listed in Table 12. Tables of bond lengths and angles, anisotropic thermal parameters and calculated hydrogen atom positions have been deposited with the Cambridge Crystallographic Data Centre.

3.5. Reaction of potassium thiocyanate with diphenylantimony trichloride

A solution of potassium thiocyanate (3.17 g, 0.033 mol) in dry acetonitrile was added with stirring to one of diphenylantimony trichloride (4.15 g, 0.011 mol) in dry acetonitrile. After being stirred at room temperature for 24 h, the solution was filtered to remove precipitated potassium chloride and evaporated to dryness in a vacuum to give a yellow oil, which on recrystallisation from toluene gave yellow crystals of potassium diphenylantimony tetrathiocyanate (2.33 g, 37%). M.p. 156°C (Analysis: Found: C, 34.7; H, 1.8; N, 10.1; K, 6.3%. $\text{C}_{16}\text{H}_{10}\text{KN}_4\text{S}_4\text{Sb}$ calc.: C, 35.1; H, 1.8; N, 10.2; K, 7.2%. $\text{SbPh}_2(\text{NCS})_3$ ($\text{C}_{15}\text{H}_{10}\text{N}_3\text{S}_3\text{Sb}$) calc.: C, 40.0; H, 2.2; N, 9.3%).

Even in the presence of a deficiency of potassium thiocyanate, only the potassium salt was isolated together with unchanged diphenylantimony trichloride. Identical results were obtained with diphenylantimony tribromide, but when silver thiocyanate replaced potassium thiocyanate, there was no reaction and diphenylantimony trihalide was recovered quantitatively.

3.6. Oxidation of SbPh_2X ($\text{X} = \text{SCN}$, Br and Cl) with dithiocyanogen

3.6.1. Diphenylantimony thiocyanate

An ice-cold solution of dithiocyanogen (containing 2.3 g, 20 mmol) was added with stirring at 0°C to a solution of diphenylantimony thiocyanate (6.6 g, 19.8 mmol) in dry dichloromethane (50 ml). After being stirred at 0°C for 15 min, the solution was reduced to one-third of its original volume in a vacuum and allowed to crystallise in the freezer. The precipitate so formed was then rapidly recrystallised from a chilled

Table 12

Fractional atomic coordinates for $\text{SbPh}_3(\text{NCS})_2$ with estimated standard deviations in parentheses

Atom	x	y	z	U_{eq}
Sb(1)	0.46101(5)	0.35026(3)	0.14394(3)	0.0584
N(1)	0.6278(8)	0.3589(5)	0.0870(4)	0.0775
C(1)	0.703(1)	0.3460(5)	0.0516(5)	0.0667
S(1)	0.8063(4)	0.3274(2)	0.0006(2)	0.1096
N(2)	0.2948(8)	0.3440(5)	0.2021(4)	0.0746
C(2)	0.2098(8)	0.3621(5)	0.2199(5)	0.0644
S(2)	0.0935(3)	0.3878(2)	0.2462(2)	0.1059
C(11)	0.3379(8)	0.2115(5)	0.0750(4)	0.0587
C(12)	0.3574(9)	0.1772(6)	0.0028(5)	0.0754
C(13)	0.278(1)	0.0837(6)	−0.0390(5)	0.0866
C(14)	0.183(1)	0.0273(6)	−0.0080(6)	0.0832
C(15)	0.1644(9)	0.0626(6)	0.0628(6)	0.0804
C(16)	0.2409(8)	0.1555(5)	0.1062(5)	0.0704
C(21)	0.4604(9)	0.4559(5)	0.1144(4)	0.0593
C(22)	0.333(1)	0.4517(6)	0.0933(5)	0.0788
C(23)	0.338(1)	0.5263(8)	0.0779(6)	0.0943
C(24)	0.464(2)	0.6005(7)	0.0853(6)	0.0891
C(25)	0.586(1)	0.6020(6)	0.1051(5)	0.0801
C(26)	0.5875(9)	0.5291(5)	0.1194(4)	0.0696
C(31)	0.5872(8)	0.3791(5)	0.2462(4)	0.0610
C(32)	0.6759(8)	0.3425(5)	0.2450(5)	0.0704
C(33)	0.7566(9)	0.3593(6)	0.3137(6)	0.0801
C(34)	0.7521(9)	0.4147(6)	0.3809(6)	0.0808
C(35)	0.667(1)	0.4538(6)	0.3830(5)	0.0771
C(36)	0.5839(9)	0.4358(5)	0.3159(5)	0.0682
Sb(2)	0.09721(5)	0.23984(3)	0.62587(3)	0.0625
N(3)	0.0439(7)	0.3000(5)	0.5556(5)	0.0860
C(3)	0.0519(9)	0.3257(6)	0.5036(5)	0.0797
S(3)	0.0650(4)	0.3625(2)	0.4362(2)	0.1060
N(4)	0.1579(8)	0.1815(5)	0.6968(4)	0.0792
C(4)	0.2209(8)	0.1637(5)	0.7335(5)	0.0645
S(4)	0.3044(4)	0.1384(2)	0.7824(2)	0.1214
C(41)	0.3069(8)	0.3052(5)	0.6143(4)	0.0606
C(42)	0.4130(9)	0.3452(5)	0.6787(4)	0.0674
C(43)	0.5512(9)	0.3958(6)	0.6747(6)	0.0790
C(44)	0.580(1)	0.4036(7)	0.6058(7)	0.0917
C(45)	0.475(1)	0.3612(8)	0.5423(6)	0.0963
C(46)	0.3359(9)	0.3121(6)	0.5457(5)	0.0813
C(51)	0.0573(8)	0.3179(5)	0.7221(5)	0.0659
C(52)	0.0359(9)	0.2929(6)	0.7845(5)	0.0776
C(53)	0.017(1)	0.3473(8)	0.8481(6)	0.0956
C(54)	0.020(1)	0.4254(8)	0.8503(7)	0.1010
C(55)	0.042(1)	0.4509(6)	0.7901(8)	0.0930
C(56)	0.0625(9)	0.3984(6)	0.7235(6)	0.0826
C(61)	−0.0615(8)	0.1073(5)	0.5537(4)	0.0667
C(62)	−0.0925(9)	0.0342(6)	0.5753(5)	0.0800
C(63)	−0.200(1)	−0.0510(6)	0.5301(7)	0.0944
C(64)	−0.277(1)	−0.0635(7)	0.4632(8)	0.1016
C(65)	−0.245(1)	0.0085(9)	0.4406(6)	0.1101
C(66)	−0.137(1)	0.0948(6)	0.4867(6)	0.0936
Sb(3)	0.40244(6)	0.02014(4)	0.23987(3)	0.0713
N(5)	0.2540(8)	−0.0729(5)	0.1333(4)	0.0791
C(5)	0.139(1)	−0.1232(5)	0.0982(5)	0.0684
S(5)	−0.0154(3)	−0.1878(2)	0.0476(2)	0.0986
N(6)	0.5535(9)	0.1121(6)	0.3470(6)	0.1034
C(6)	0.6014(8)	0.1661(6)	0.4017(5)	0.0558
S(6)	0.6744(5)	0.2479(2)	0.4822(2)	0.1283
C(71)	0.5576(8)	0.0738(5)	0.1804(5)	0.0702
C(72)	0.5197(9)	0.0765(6)	0.1102(5)	0.0781
C(73)	0.625(1)	0.1207(6)	0.0754(5)	0.0843
C(74)	0.764(1)	0.1595(6)	0.1102(7)	0.0882
C(75)	0.799(1)	0.1522(7)	0.1772(7)	0.0971

Table 12 (continued)

Atom	x	y	z	U_{eq}
C(76)	0.6976(9)	0.1116(6)	0.2146(5)	0.0841
C(81)	0.2794(9)	0.0843(5)	0.2696(4)	0.0667
C(82)	0.1353(9)	0.0328(6)	0.2540(5)	0.0792
C(83)	0.0570(9)	0.0762(7)	0.2748(6)	0.0924
C(84)	0.122(1)	0.1701(7)	0.3102(6)	0.0915
C(85)	0.266(1)	0.2204(6)	0.3250(5)	0.0827
C(86)	0.3475(9)	0.1787(6)	0.3058(4)	0.0717
C(91)	0.3687(8)	−0.0893(6)	0.2718(5)	0.0685
C(92)	0.347(1)	−0.1709(7)	0.2177(6)	0.0940
C(93)	0.331(1)	−0.2403(8)	0.2432(9)	0.1058
C(94)	0.325(1)	−0.2317(9)	0.317(1)	0.0983
C(95)	0.342(1)	−0.154(1)	0.3693(7)	0.1033
C(96)	0.3645(9)	−0.0818(7)	0.3469(6)	0.0838

dichloromethane/hexane mixture to give $\text{SbPh}_2(\text{NCS})_3$ as a microcrystalline yellow solid (5.5 g, 62%). M.p. 127°C. (Analysis: Found: C, 40.2; H, 2.2; N, 9.6%. $\text{C}_{15}\text{H}_{10}\text{N}_3\text{S}_3\text{Sb}$ calc.: C, 40.0; H, 2.2; N, 9.3%.)

This compound readily reorganised to $\text{SbPh}_3(\text{NCS})_2$ when solution in chloroform, toluene, ether or dichloromethane were allowed to stand, and only by using chilled solvents and minimising the time in solution were consistent analyses obtained. Crystals suitable for X-ray crystallography could not be obtained.

3.6.2. Diphenylantimony bromide and chloride

These reactions were carried out as described above and, although microanalyses of the crude products indicated that the oxidised compounds $\text{SbPh}_2\text{X}(\text{NCS})_2$ for X = Br or Cl had probably been produced, inconsistent analyses were obtained after attempted recrystallisations.

3.7. Reaction of diphenylantimony trithiocyanate with potassium thiocyanate

A solution of potassium thiocyanate (0.15 g, 1.5 mmol) in dry acetonitrile (20 ml) was added to one of diphenylantimony trithiocyanate (0.7 g, 1.6 mmol) in dry acetonitrile (20 ml) and the mixture was stirred at room temperature for 24 h. The solution was then evaporated to dryness and the solid recrystallised from dichloromethane/hexane to give potassium diphenylantimony tetrathiocyanate (0.6 g, 68%). M.p. 156°C. (Analysis: Found: C, 34.5; H, 1.8; N, 10.2; K, 6.8%. $\text{C}_{16}\text{H}_{10}\text{KN}_4\text{S}_4\text{Sb}$ calc.: C, 35.1; H, 1.8; N, 10.2; K, 7.2%.)

3.8. Oxidation of $\text{Ph}_2\text{Sb}(\text{SCN})$ with bromine

A solution of bromine (1.3 g, 8.4 mmol) in dry dichloromethane was added with stirring at 0°C to one of diphenylantimony thiocyanate (2.8 g, 8.4 mmol) in

dry dichloromethane. The bromine colour disappeared. The solution was concentrated in a vacuum and deposited crystals of SbPh_2Br_3 . M.p. 170°C (lit. value [11]: 171°C). (Analysis: Found: C, 28.0; H, 2.0%. $\text{C}_{12}\text{H}_{10}\text{Br}_3\text{Sb}$ calc.: C, 27.9; H, 1.9%. $\text{C}_{13}\text{H}_{10}\text{Br}_2\text{NSSb}$ calc.: C, 31.6; H, 2.0; N, 2.8%.)

Identical results were obtained when the reaction was repeated at -78°C , but a low-temperature reaction with a 20% deficiency of bromine gave material with good analyses for $\text{SbPh}_2\text{Br}_2(\text{NCS})$. (Analysis: Found: C, 32.6; H, 2.1; N, 3.1%. $\text{C}_{13}\text{H}_{10}\text{Br}_2\text{NSSb}$ calc.: C, 31.6; H, 2.0; N, 2.8%.) Attempted recrystallisations gave products with decreasing nitrogen content until pure SbPh_2Br_3 was obtained.

3.9. Oxidation with thiocyanogen bromide

Because of its instability, thiocyanogen bromide was freshly prepared for each experiment by adding the stoichiometric amount of bromine at 0°C to an ice-cold solution of dithiocyanogen in dichloromethane [28]. The brick red solution was stirred at 0°C for 30 min before use.

3.9.1. Diphenylantimony thiocyanate

A solution of thiocyanogen bromide (containing 1.4 g, 10 mmol) in dry dichloromethane was added with stirring to one of diphenylantimony thiocyanate (3.5 g, 10 mmol) in dry dichloromethane (30 ml) at 0°C . After being stirred for 15 min, the solution was concentrated to ca. 20 ml in a vacuum and cooled in a freezer to give a yellow solid. Recrystallisation from a chilled dichloromethane/hexane mixture gave $\text{SbPh}_2\text{Br}(\text{NCS})_2$ as a yellow powder (2.8 g, 59%). M.p. 97°C . (Analysis: Found: C, 35.6; H, 2.1; N, 5.1%. $\text{C}_{14}\text{H}_{10}\text{BrN}_2\text{S}_2\text{Sb}$ calc.: C, 35.6; H, 2.1; N, 5.9%.)

3.9.2. Diphenylantimony bromide

The reaction was carried out as above with diphenylantimony bromide (4.6 g, 13 mmol) in dichloromethane (50 ml) and a thiocyanogen bromide solution (containing 1.79 g, 13 mmol). Recrystallisation from chilled dichloromethane/hexane gave a pale yellow powder (4.0 g, 74%). M.p. 138°C . (Analysis: Found: C, 31.6; H, 1.8; N, 2.9%. $\text{C}_{13}\text{H}_{10}\text{Br}_2\text{NSSb}$ calc.: C, 31.6; H, 2.0; N, 2.8%.)

3.9.3. Triphenylantimony

As described above, triphenylantimony (5.0 g, 14 mmol) in dichloromethane (50 ml) was treated with a thiocyanogen bromide solution (containing 1.97 g, 14 mmol) to give after recrystallisation $\text{SbPh}_3\text{Br}(\text{NCS})$ as a pale yellow powder (5.5 g, 81%). M.p. 129°C . (Analysis: Found: C, 46.8; H, 3.0; N, 2.5%. $\text{C}_{19}\text{H}_{15}\text{BrN}(\text{NCS})\text{Sb}$ calc.: C, 46.5; H, 3.0; N, 2.9%.)

3.10. Oxidation with thiocyanogen chloride

A golden yellow solution of thiocyanogen chloride in dichloromethane was prepared at 0°C by mixing equimolar quantities of standardised dichloromethane solutions of chlorine and dithiocyanogen [28,29]; the solution was used immediately.

3.10.1. Diphenylantimony chloride

A thiocyanogen chloride solution (containing 0.75 g, 8 mmol) was added with stirring to an ice-cold solution of diphenylantimony chloride (2.5 g, 8 mmol) in dry dichloromethane (30 ml). The solution was stirred for 10 min at 0°C , then concentrated and placed in a freezer. The resulting pale yellow solid was recrystallised from dry diethyl ether to give $\text{SbPh}_2\text{Cl}_2(\text{NCS})$ (1.2 g, 37%). M.p. 128°C . (Analysis: Found: C, 39.2; H, 2.3; N, 3.9%. $\text{C}_{13}\text{H}_{10}\text{Cl}_2\text{NSSb}$ calc.: C, 38.5; H, 2.5; N, 3.5%.)

3.10.2. Diphenylantimony thiocyanate and triphenylantimony

A similar reaction with diphenylantimony thiocyanate gave an immediate product, which analysis suggested was impure $\text{SbPh}_2\text{Cl}(\text{NCS})_2$. During recrystallisation both the IR spectrum and the microanalysis changed and finally a sample of pure diphenylantimony dichloride thiocyanate was isolated. The corresponding reaction with triphenylantimony did not yield $\text{SbPh}_3\text{Cl}(\text{NCS})$ and fractional crystallisation of the initial reaction product gave pure samples of both SbPh_3Cl_2 and $\text{SbPh}_3(\text{NCS})_2$. These results show that reorganisation in solution is again faster for the chloride thiocyanate species than for the bromide analogues.

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