Phenylantimony(III) Dithiocyanate and the Crystal Structure of K[SbPh(SCN)$_3$]†

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It is not possible to isolate phenylantimony dithiocyanate from phenylantimony dichloride (1 mol) and 2 equivalents of potassium thiocyanate in acetonitrile and a salt, K[SbPh(SCN)$_3$], is isolated instead. A tetrathiocyanate salt, K$_2$[SbPh(SCN)$_4$], has also been isolated and K[SbPh$_2$(SCN)$_2$] can be obtained from SbPh$_2$(SCN) and K(SCN). In K[SbPh(SCN)$_3$], X-ray diffraction shows that all the thiocyanate groups are S-bonded and the compound has an unusual polymeric structure in which the sulfur atom of one thiocyanate group bridges between pairs of antimony atoms. Co-ordination about antimony is square pyramidal with an apical phenyl group and sulfur atoms of two terminal (Sb–S 2.573, 2.595 Å) and two *cis* 1,1-sulfur bridging thiocyanate groups (Sb–S 2.938, 2.999 Å) forming the basal plane. All thiocyanate groups are orientated in the same fashion leading to distorted octahedral co-ordination about potassium.

We have previously described the preparation and curious 'spiral' structures of diphenylantimony[1] and diphenylbismuth[2] thiocyanates. Both compounds are polymeric with N,S-thiocyanate bridges between pairs of Group 15 atoms. In the former the orientation of every third bridging group is reversed giving a chain containing antimony atoms with three different co-ordination patterns. In the bismuth compound, the orientation of each alternate thiocyanate group is reversed, giving a chain with bismuth atoms co-ordinated to, respectively, two nitrogen atoms and two sulfurs. In this context it was of interest to investigate the preparation of phenylantimony(III) dithiocyanate as bonding in this compound might also be unusual. Decreasing the number of phenyl groups at antimony is expected to increase Lewis acidity at antimony, promoting bridging and reducing steric hindrance.

Experimental

Phenylantimony dichloride was prepared by reorganisation of a 1:2 mixture of triphenylantimony and antimony trichloride;[3] all reactions were carried out with dried solvents.

Preparation of Potassium Phenylantimony Trithiocyanate.—A solution of potassium thiocyanate (4.0 g, 0.04 mol) in dry acetonitrile was added with stirring to a solution of phenylantimony dichloride (5.0 g, 0.019 mol) in dry acetonitrile. After stirring for 24 h at ambient temperature, the solution was filtered to remove precipitated potassium chloride. The solvent was removed under vacuum to yield a yellow oil, which solidified on addition of dichloromethane. Recrystallisation from ethanol gave yellow plates, m.p. 146 °C (2.8 g, 6.8 mmol, 37%) (Found: C, 26.5; H, 1.4; K, 8.9; N, 9.8. Calc. for $C_9H_5KN_3S_3Sb$: C, 26.2; H, 1.2; K, 9.5; N, 10.2%).

Preparation of Potassium Phenylantimony Tetrathiocyanate.—A solution of potassium thiocyanate (0.3 g, 3.4 mmol) in acetonitrile was added with stirring to a solution of potassium phenylantimony trithiocyanate (1.4 g, 3.4 mmol) in acetonitrile. After stirring overnight the solvent was removed and the residue was recrystallised from ethanol to give potassium phenylantimony tetrathiocyanate, m.p. 140 °C (1.5 g, 3 mmol, 88%) (Found: C, 23.4; H, 1.0; K, 14.8; N, 10.8. Calc. for $C_{10}H_5K_2N_4S_4Sb$: C, 23.6; H, 1.0; K, 15.4; N, 11.0%).

Reactions with Silver Thiocyanate.—Silver thiocyanate was prepared from equimolar aqueous solutions of silver nitrate and potassium thiocyanate. The precipitate was filtered off, washed with water, ethanol and diethyl ether before drying in a vacuum desiccator over P_2O_5 in the dark. All reactions were performed in the dark. Reactions between phenylantimony dichloride and 2 mol equivalents of silver thiocyanate were carried out in a range of solvents, which included acetonitrile, diethyl ether, benzene, tetrahydrofuran and chloroform, for varying reaction times and temperatures ranging from ambient to reflux. Although IR spectroscopy of separated products indicated some incorporation of thiocyanate groups, this was far from complete with, for example, *ca.* 25% completion for a reaction refluxed in benzene for 24 h. Crystallisation of the reaction product, however, led only to isolation of unchanged phenylantimony dichloride.

Preparation of Potassium Diphenylantimony Dithiocyanate.—A solution of diphenylantimony thiocyanate (1.68 g, 5 mmol) in dry acetonitrile was added to a solution of potassium thiocyanate (0.49 g, 5 mmol) in dry acetonitrile. The mixture was stirred and warmed at 50 °C for 30 min after which the solvent was removed. The residue was recrystallised from boiling chloroform giving white crystals, m.p. 110 °C (1.66 g, 3.85 mmol, 77%) (Found: C, 38.7; H, 2.3; K, 8.6; N, 6.1. Calc. for $C_{14}H_{10}KN_2S_2Sb$: C, 39.0; H, 2.3; K, 9.1; N, 6.5%).

Crystal Structure of K[SbPh(SCN)$_3$].—Crystals suitable for X-ray diffraction were obtained by slow recrystallisation of solutions in ethanol.

Crystal data. $C_9H_5KN_3S_3Sb$, $M = 412.0$, orthorhombic, space group *Pbca*, $a = 7.954(3)$, $b = 33.301(9)$, $c = 11.208(3)$ Å, $U = 2968.7$ Å^3, Mo-Kα radiation (with graphite monochromator), $\lambda = 0.7107$ Å, $D_c = 1.84$ g cm^{-3}, $F(000) = 1584$, $Z = 8$, $\mu = 25.3$ cm^{-1}, crystal size 0.15 × 0.2 × 0.03 mm.

Structure determination. Intensity data were collected on a Hilger and Watts four-circle diffractometer in the range $0 < \theta < 25°$ ($0 < h < 10$, $0 < k < 39$, $0 < l < 13$) and 2116

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

Throughout this paper the thiocyanate group is written as SCN; except where specifically stated this is not to be taken as representing the true bonding pattern.

reflections with $I > 3\sigma(I)$ were considered observed. Corrections were made for Lorentz and polarisation effects and an empirical absorption correction was applied using DIFABS.[4] Crystallographic calculations used the CRYSTALS programs[4] and scattering factors for neutral atoms.[5]

The antimony position was obtained from a three-dimensional Patterson synthesis and the remaining atoms, including the hydrogens, were revealed by a series of full-matrix least-squares refinements and Fourier-difference syntheses. Anisotropic thermal parameters were assigned to the non-hydrogen atoms and after application of a four-coefficient Chebyshev weighting scheme, refinement was continued with isotropic thermal parameters for the hydrogen atoms. Final convergence occurred at $R = 0.0325$ ($R' = 0.0440$) for 174 parameters (max. shift/e.s.d. = 0.08, max. and min. residual electron densities 0.66 and −0.23 e Å^{-3}). The final atomic coordinates are collected in Table 1.

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

Table 1 Fractional atomic coordinates for K[SbPh(SCN)$_3$], with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb	0.026 39(4)	0.128 793(9)	0.073 25(3)
S(1)	0.318 4(2)	0.134 69(5)	−0.023 9(2)
S(2)	−0.126 3(2)	0.144 17(5)	−0.126 1(1)
S(3)	0.188 3(2)	0.125 60(4)	0.308 7(1)
K	0.440 0(2)	−0.009 12(5)	0.181 0(2)
C(1)	0.361 1(8)	0.086 2(2)	−0.011 0(5)
N(1)	0.392(1)	0.052 4(2)	−0.001 0(7)
C(2)	−0.150 9(9)	0.096 8(2)	−0.164 1(5)
N(2)	−0.166(1)	0.063 4(2)	−0.189 3(6)
C(3)	0.205 7(7)	0.076 2(2)	0.303 6(5)
N(3)	0.220 6(8)	0.041 6(2)	0.300 8(6)
C(11)	0.027 6(6)	0.192 3(1)	0.102 6(4)
C(12)	−0.043 5(6)	0.207 9(2)	0.206 2(4)
C(13)	−0.045 5(7)	0.249 0(2)	0.225 1(5)
C(14)	0.026 3(7)	0.274 9(2)	0.141 6(5)
C(15)	0.099 7(7)	0.259 3(2)	0.040 3(5)
C(16)	0.098 9(7)	0.218 2(1)	0.021 0(5)

Discussion

Preparations.—Reaction of phenylantimony dichloride with 2 mol equivalents of potassium thiocyanate in acetonitrile solution did not yield SbPh(SCN)$_2$, the expected product, and gave instead a low yield of the salt, K[SbPh(SCN)$_3$]; this compound was also obtained when ratios as low as 1:1 were used. Unreacted SbPhCl$_2$ was also present but was not isolated. Increasing the potassium thiocyanate ratio to 3:1 and 4:1 did not increase the yield but gave instead a tetrathiocyanate salt, K$_2$[SbPh(SCN)$_4$], which could also be obtained from equimolar quantities of K[SbPh(SCN)$_3$] and K(SCN). Products containing more than four thiocyanate groups could not be obtained even with higher ratios of potassium thiocyanate. Both salts are insoluble in chloroform and dichloromethane, but can be recrystallised as yellow plates from ethanol.

As an alternative preparative route to SbPh(SCN)$_2$, and to minimise the possibility of salt formation, silver thiocyanate was used in place of the potassium salt in a heterogeneous reaction with phenylantimony dichloride. Even though a large range of solvents, including acetonitrile, diethyl ether, dichloromethane, toluene, tetrahydrofuran, benzene and chloroform, was used and reaction times and temperatures were varied, no compound other than unchanged SbPhCl$_2$ was isolated. It is interesting in this connection that, although SbPh$_2$(O$_2$CMe)[6] and SbPh$_2$F[7] can both be isolated, the corresponding monophenyl derivatives, SbPh(O$_2$CMe)$_2$ and SbPhF$_2$, are unknown and, further, Bertazzi and Alonso[8] have observed only salt formation from reactions designed to produce antimony trithiocyanate unless a donor molecule is available to stabilise the Sb(SCN)$_3$ unit.

Potassium diphenylantimony dithiocyanate was also prepared from diphenylantimony thiocyanate and potassium thiocyanate in acetonitrile and can be crystallised from either chloroform, in which it is sparingly soluble, or ethanol. It was not possible to obtain anionic diphenylantimony thiocyanates containing more than two thiocyanate groups, even when an excess of thiocyanate was used.

It is possible to suggest structures for the three new anionic phenylantimony(III) thiocyanates by analogy with the known structures of related halides. These are based on the approach of successive halide ions *trans* to halogens in the parent halide and bonding *via* the low-lying Sb–halogen σ^* orbitals. Halide ions cannot approach *trans* to an organic group in the parent halide and that *trans* position is then effectively blocked. There is a further complication as co-ordination unsaturation at antimony can lead to further bonding *via* halogen bridging. In $[SbPh_2X_2]^-$ species, therefore, two potential acceptor sites are blocked and the monomeric pseudo-trigonal bipyramidal structure, predicted also by valence shell electron pair repulsion (VSEPR) arguments, is found in, for example, $[SbPh_2Cl_2]^-$.[9] The corresponding bismuth anions, $[BiPh_2Br_2]^-$ [10] and $[BiPh_2I_2]^-$ [11] have the same structure. One potential acceptor site is blocked in $[SbPhX_3]^-$ anions and, although monomers are possible, co-ordination unsaturation at antimony leads to halogen bridging and formation of square-pyramidal dimers, as in $[Sb_2Ph_2Cl_6]^{2-}$.[9,12] Again, there are parallels with related bismuth anions, *e.g.* $[Bi_2Ph_2Br_6]^{2-}$,[11] although in the corresponding iodide, $[Bi_2Ph_2I_6]^{2-}$,[10] the phenyl groups occupy *cis*, rather than *trans* positions, and the Bi$_2$Br$_6$ unit is not planar. Square-pyramidal geometry about antimony is also expected and found in monomeric $[SbPhCl_4]^{2-}$.[9]

On these arguments both K[SbPh$_2$(SCN)$_2$] and K$_2$[SbPh(SCN)$_4$] are expected to be monomers, the former with *trans* thiocyanate groups in a pseudo-trigonal bipyramidal arrangement about antimony and the latter with square-pyramidal geometry and an apical phenyl group. Either di- or poly-meric structures are expected for K[SbPh(SCN)$_3$]. Thiocyanate is, however, a well known ambidentate ligand and there is the problem of N- *versus* S-bonding. It is quite possible that there may be no strong preference for either type of bonding, as the phenylantimony(III) moiety is expected to be of intermediate hardness. This appears to be the situation with SbPh$_2$(SCN) where, although the group behaves as a bridge, it is possible to point to primary bonding *via* nitrogen in two of the formula units of the asymmetric unit and to sulfur in the third. Finally, although 1,3-bridging is the most widely observed type of bridging, there remains the possibility that bridging can be *via* either sulfur or nitrogen alone.

In some cases IR spectroscopy can give information on the type of thiocyanate co-ordination present in a compound,[13] but the ranges for each of the three major types of bonding, *i.e. via* nitrogen or sulfur or bridging *via* nitrogen and sulfur, often overlap. Further, thiocyanate shows an extremely versatile range of co-ordination modes and specific IR criteria are not available for each of these. Useful information can be obtained from nitrogen NMR spectroscopy[14] on the species in solution but, as secondary bonds to antimony are probably weak, the results will not necessarily be helpful in discussing solid-state structures. Similarly some information can be obtained from mass spectrometry but ultimately the nature of the solid can probably be determined only by X-ray diffraction studies.

K[SbPh(SCN)$_3$].—This compound shows an intense absorption in the C–N stretching region with components at 2128, 2056 and 2004 cm^{-1}, the deformation mode occurs at 479 cm^{-1}, but there was no band assignable to C–S stretching, presumably due to its intrinsic weakness. On usual criteria,[13] the 2128 and

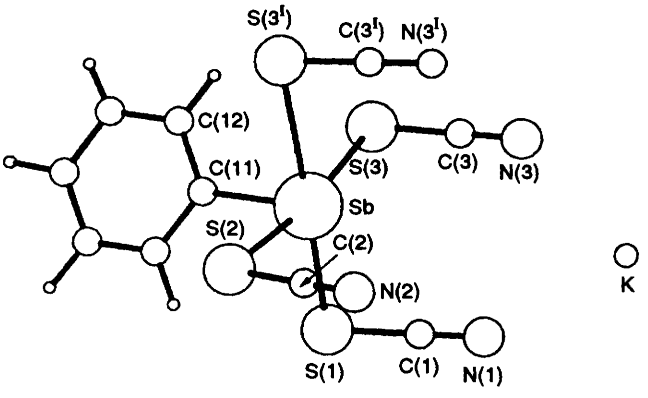

Fig. 1 The asymmetric unit for K[SbPh(SCN)$_3$] showing the atom numbering scheme

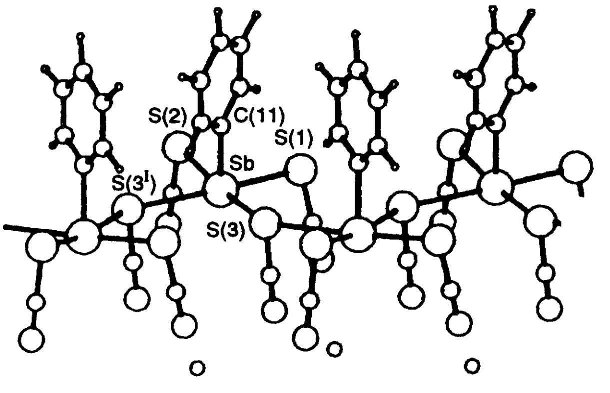

Fig. 2 The polymeric chain structure of K[SbPh(SCN)$_3$]

Table 2 Important bond lengths (Å) and angles (°) for K[SbPh(SCN)$_3$], with e.s.d.s in parentheses *

Sb–S(1)	2.573(1)	K–N(1^{II})	2.816(7)
Sb–S(2)	2.595(2)	K–N(2^{III})	2.836(8)
Sb–S(3)	2.938(2)	K–N(2^{IV})	2.933(9)
Sb–S(3^I)	2.999(1)	K–N(3)	2.776(7)
Sb–C(11)	2.139(4)	K–N(3^V)	2.807(6)
S(1)–C(1)	1.657(7)	C(1)–N(1)	1.156(8)
S(2)–C(2)	1.646(7)	C(2)–N(2)	1.152(9)
S(3)–C(3)	1.651(6)	C(3)–N(3)	1.158(7)
K–N(1)	2.917(8)		
S(2)–Sb–S(1)	92.47(6)	N(2^{IV})–K–N(1)	149.3(2)
S(3)–Sb–S(1)	89.26(5)	N(2^{IV})–K–N(1^{II})	75.5(2)
S(3)–Sb–S(2)	170.36(4)	N(2^{III})–K–N(2^{IV})	93.5(2)
S(3^I)–Sb–S(1)	177.41(5)	N(3)–K–N(1)	80.1(2)
S(3^I)–Sb–S(2)	88.13(5)	N(3)–K–N(1^{II})	163.0(2)
S(3)–Sb–S(3^I)	99.73(2)	N(3)–K–N(2^{III})	83.6(2)
C(11)–Sb–S(1)	89.2(1)	N(3^V)–K–N(1)	74.4(2)
C(11)–Sb–S(2)	86.5(1)	N(3^V)–K–N(1^{II})	89.1(2)
C(11)–Sb–S(3)	84.0(1)	N(3^V)–K–N(2^{III})	173.5(2)
C(11)–Sb–S(3^I)	88.4(1)	N(3)–K–N(2^{IV})	121.3(2)
C(1)–S(1)–Sb	94.2(2)	N(3^V)–K–N(2^{IV})	81.3(2)
C(2)–S(2)–Sb	95.1(2)	N(3)–K–N(3^V)	95.6(2)
Sb–S(3)–Sb^V	142.00(5)	N(1)–C(1)–S(1)	179.2(7)
C(3)–S(3)–Sb	92.4(2)	N(2)–C(2)–S(2)	178.7(7)
C(3)–S(3)–Sb^V	88.6(2)	N(3)–C(3)–S(3)	178.9(6)
N(1)–K–N(1^{II})	85.5(2)	C(12)–C(11)–Sb	119.8(3)
N(2^{III})–K–N(1)	111.8(2)	C(16)–C(11)–Sb	121.2(4)
N(1^{II})–K–N(2^{III})	93.5(2)		

* Symmetry operations: I $x - 0.5, y, 0.5 - z$, II $1 - x, -y, -z$, III $-x, -y, -z$, IV $0.5 - x, -y, 0.5 + z$, V $0.5 + x, y, 0.5 - z$.

2056 cm^{-1} bands can be assigned to terminal S- and N-bonded thiocyanates. The 2004 cm^{-1} band could arise from a second N-bonded group but, as the anion is most probably associated, it is perhaps more likely to be associated with a bridging group though its position is lower in energy than would be expected for normal 1,3 bridging. The 1,1-N and 1,1-S bridging modes are possible alternatives. The former has been proposed for [NMe$_4$][Sb(SCN)$_4$],[8] which shows a band at 1965 cm^{-1} (bands between 1950 and 2000 cm^{-1} in other compounds[15,16] known to have 1,1-N-bridges), while the latter, considered to be present in trimeric MEt$_2$(SCN) (M = Al, Ga or In) gives bands at 2075, 2150 and 2128 cm^{-1}, respectively.[17] From the relative positions of these bands, 1,1-S bonding seems a less likely source of the 2004 cm^{-1} band than the alternative 1,1-N bridging.

The EI mass spectrum shows peaks associated with the successive loss of thiocyanate groups from the parent, *i.e.* SbPh(SCN)$_3$ (relative intensity 2%), SbPh(SCN)$_2$ (5%), SbPh(SCN) (18%) and SbPh (84%). Loss of phenyl is represented by a low intensity peak for Sb(SCN)$_3$ (*ca.* 1%), and successive loss of thiocyanate from this species by peaks of intensities 1, 14 and 12%. Surprisingly the spectrum contains a number of peaks assigned to rearrangement ions such as SbPh$_3$(SCN), SbPh$_3$, SbPh$_2$ and Ph$_2$.

The ^{14}N NMR spectrum, measured in deuteriomethanol as the salt is insoluble in chloroform, showed a singlet at δ −198 (linewidth at half peak height = 15 ppm), substantially downfield from those for neutral antimony thiocyanates. This has also been observed with, for example, [SnPh$_3$(SCN)$_2$]$^-$ in methanol, where thiocyanate dissociation probably leads to a signal at δ −209, again significantly downfield from that for neutral SnPh$_3$(SCN) (δ −253).[18] From the above data, though, it is clear that conventional spectroscopic methods give an imperfect picture of the nature of the [SbPh(SCN)$_3$]$^-$ ion.

Crystals suitable for X-ray analysis were, however, available and structures of the asymmetric unit and the chain structure resulting from thiocyanate bridging are shown in Figs. 1 and 2, respectively. Important bond distances and angles are collected in Table 2. Fig. 2 shows that, in agreement with the analysis above, one of the thiocyanate groups in [SbPh(SCN)$_3$]$^-$ bridges between neighbouring antimony atoms to give a polymeric chain with antimony in five-fold, pseudo-octahedral co-ordination. The differences from prediction are that all the thiocyanate groups are S-bonded and bridging is rather unusually through the sulfur only (1,1-S bridging). This type is probably the least well established bridging mode but has been identified crystallographically in [AuOs$_3$(SCN)(CO)$_{10}$(PPh$_3$)],[19] in a copper(I) complex [Cu$_2$(SCN)L] of a macrocyclic Schiff base ligand L,[20] and in Ni(SCN)$_2$ itself.[21]

Sulfur atoms occupy the basal plane of the square pyramid about antimony with an apical phenyl group. All four C(11)–Sb(1)–S angles are less than 90°, ranging between 84.0(1) and 89.2(1)°, and the antimony atom lies some 0.14 Å below the plane of the four sulfur atoms [deviations from the best plane through these atoms are S(1) −0.09, S(2) 0.09, S(3) 0.08 and S(3^I) −0.08 Å]. The bridging sulfur atoms occupy *cis* positions in the antimony co-ordination sphere giving zigzag chains parallel to the *a* axis [Sb–S(3)–Sb 142.0, S(3)–Sb–S(3^I) 99.7° (for symmetry operations I and V, see footnote in Table 2)]; bridging is slightly asymmetric and the Sb–S distances alternate along the chain [Sb–S(3) 2.938(2), Sb–S(3^I) 2.999(1) Å]. All four Sb–S separations, in fact, differ [ranging between 2.573(1) and 2.999(1) Å] and show a *trans* influence with the shortest Sb–S separation *trans* to the longest. Rather surprisingly, even the short Sb–S separations here fall outside the 2.42–2.50 Å range for single antimony–sulfur bonds observed, for example, in compounds such as [Sb$_2$SX$_6$]$^{2-}$ (X = Cl, 2.415 and 2.427 Å;[22] X = Br, 2.450 and 2.499 Å[23]), 2-phenyl-1,3,6,2-trithiastibocane (2.428 and 2.471 Å),[24] antimony tris(monothioacetate) (2.451 Å),[25] and the tris(monothiobenzoate) (2.493 Å).[26] In passing, it should be noted that such solid-state structures almost invariably also show weak Sb ··· S secondary bonds.

The thiocyanate groups with mean C–S and C–N separations of 1.651 and 1.155 Å, respectively, are unexceptional but an interesting feature concerns their relative orientations. All four Sb–S–C angles are close to 90°, though bridging clearly closes the angles at S(3) to 92.4 and 88.6° compared with those at the two terminal thiocyanate groups (94.2 and 95.1°). Nevertheless, as shown in Figs. 1 and 2, their orientations are the same, providing a distorted-octahedral arrangement of nitrogen atoms involving N(1), N(3) and four other symmetry related atoms to accommodate the potassium counter ions. The $K \cdots N$ separations vary between 2.776 and 2.933 Å (mean 2.848 Å) and are a little shorter than those (2.808–3.012 Å) in *e.g.* the monopotassium salt of cyanoguanidine.[27] The extent of distorsion of the octahedron about potassium can be assessed by values of 149, 163 and 173° for the *trans* angles and values ranging between 74.4 and 121.3° (mean 90.4°) for *cis* angles.

In many ways this structural arrangement is quite understandable as the softer substituted antimony centre is co-ordinated by the softer sulfur end of the thiocyanate group while the harder nitrogen end is co-ordinated to harder potassium ions. It would be interesting to replace the potassium counter ion with either a softer cation or a cation such as tetraalkylammonium with no particular co-ordination properties to determine how much stabilisation of the all S-bonded structure can be traced to the availability of nitrogen in this arrangement for cation co-ordination.

$K_2[SbPh(SCN)_4]$.—In all probability, as mentioned above, this salt will be a square-pyramidal monomer with basal terminal thiocyanate groups, but there is still the problem of whether they are N- or S-bonded. The IR spectrum shows an intense absorption in the C–N stretching region with peaks at 2125, 2115 and 2055 cm^{-1}; the deformation mode was at 483 cm^{-1} but the C–S stretch was again not observed. In the initial assignment of the spectrum of $[SbPh(SCN)_3]^-$, the 2056 cm^{-1} band was assigned to an N-bonded thiocyanate but such an assignment is clearly not tenable in view of the structure determination above. It is tempting, therefore, to suggest that the four thiocyanate groups here are all also S-bonded as the hardness of the SbPh fragment is not expected to change markedly from that in the trithiocyanate. The multiplicity of peaks might then arise from coupling of vibrational modes. An all S-bonded structure would have some validity by providing a hard nitrogen co-ordination sphere for the potassium counter ions.

This compound, like the trithiocyanate above, gives a very broad ^{14}N NMR peak at δ -202 in methanol but there is again the possibility of dissociation. The EI mass spectrum shows peaks for neither $SbPh(SCN)_4$ nor $SbPh(SCN)_3$ and the highest mass peaks are associated with the rearrangement ions $SbPh_3(SCN)$ and $SbPh_3$. Medium-intensity peaks associated with $SbPh(SCN)_2$ and $Sb(SCN)_3$ and their subsequent fragments are, however, observed.

$K[SbPh_2(SCN)_2]$.—The IR spectrum of this compound, expected to have a monomeric pseudo-trigonal bipyramidal structure, was less complex in the C–N stretching region with bands at 2115 and 2055 cm^{-1}. The C–S mode was observed at 770 cm^{-1} and there were two components for thiocyanate deformation at 483 and 465 cm^{-1}. The band at 2055 cm^{-1} is intense and broad and closely resembles that found in compounds containing N-bonded thiocyanate groups. A deformation mode at 483 cm^{-1} is also expected in this case. The remaining bands at 2115, 770 and 465 cm^{-1} could then be assigned to vibrations of an S-bonded thiocyanate group, as such bands are much sharper than those for N-bonding. The presence of both N- and S-bonded thiocyanate groups in this ion would not perhaps be unusual in view of the different orientations of the thiocyanate groups in neutral diphenylantimony thiocyanate. Clearly, though, the same nitrogen environment found in the trithiocyanate structure and suggested for $[SbPh(SCN)_4]^-$, would not then be available for the potassium counter ion. Nitrogen-14 NMR spectroscopy showed the same broad signal at δ -196 (line width at half height = 18 ppm) in methanol solution as observed with the other compounds and, although the EI mass spectrum showed peaks for $SbPh_2(SCN)$ (19%), $SbPh(SCN)$ (3%) and $Sb(SCN)$ (13%), there was no fragment corresponding to $SbPh_2(SCN)_2$. Other peaks were assigned to SbPh (73%) and $SbPh_2$ (43%), indicating that loss of both thiocyanate groups is facile.

It is possible, therefore, to suggest reasonable structures for both $[SbPh(SCN)_4]^{2-}$ and $[SbPh_2(SCN)_2]^-$ but it looks certain that definitive structures for both compounds must await the results of X-ray structure determinations.

Acknowledgements

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