Diphenylantimony(III) Thiocyanate: Unusual Thiocyanate Bridging

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The thiocyanate group can bond *via* sulphur or nitrogen or bridge between two centres, but in diphenylantimony thiocyanate, unusual bridging gives antimony atoms coordinated by, respectively, two sulphur atoms, two nitrogen atoms and one atom of each type, allowing development of a curious infinite 'triangular spiral' structure in the solid state.

Although antimony(III) and organoantimony(III) compounds contain a lone pair of electrons, they rarely behave as Lewis bases and their chemistry is dominated by the Lewis acid character consequent of their coordination unsaturation. For example, the halides are the basis of a number of anionic species, for example, $[SbX_4]^-$, $[SbX_5]^{2-}$, $[Sb_2X_9]^{3-}$, $[PhSbCl_3]^-$, $[PhSbCl_4]^{2-}$ and $[Ph_2SbCl_2]^-$.[1] In contrast, solid-state structures for both *p*-tolylantimony dibromide and dichloride and diphenylantimony bromide point to only weak intermolecular interactions.[2] In related antimony(V) compounds, where Lewis acidity is higher, intermolecular bonding is potentially stronger leading, in the case of Ph_2SbCl_3, to discrete dimers in the solid state.[3]

To investigate further the possibility of intermolecular interactions in substituted antimony(III) species, we have recently prepared diphenylantimony thiocyanate (m.p. 103 °C) by a metathesis reaction between Ph_2SbCl and potassium thiocyanate in acetonitrile. The ligand is ambidentate in which donation *via* either or both of the terminal atoms is well established spectroscopically and by X-ray crystallography.[4] The IR spectrum of the compound in the 2000 cm^{-1} region is complex, consisting of four absorptions at *ca.* 2055, 2065, 2094 and 2114 cm^{-1}. Spectra in chloroform become simpler on dilution, finally reducing to a sharp band at 2045 cm^{-1}. While this might suggest the presence of an *S*-bonded monomer, the ^{14}N NMR spectrum shows a single resonance at −260 (ppm) (rel. to external nitrate) usually considered diagnostic of *N*-bonding.[4]

An X-ray structure† reveals the reason for the complexity of the solid-state IR spectrum, and shows an infinite chain structure with a three molecule repeating unit (see Fig. 1 and 2). Each antimony is in pseudo-trigonal bipyramidal coordination with equatorial phenyl groups and axial thiocyanates.

Two features of this structure are, we think, unique. First, although the three independent thiocyanate groups all bridge between pairs of antimony atoms, they do so to give different coordination patterns about each of the antimony atoms. Sb(1) is coordinated to two nitrogen atoms (at 230.4 and 236.4 pm), Sb(2) to one nitrogen (227.3 pm) and one sulphur atom (283.1 pm), and Sb(3) to two sulphur atoms (at 270.0 and 284.2 pm), implying that primary bonding at Sb(1) and Sb(2) is to nitrogen but to sulphur at Sb(3). In all previously determined structures, the thiocyanate bridges have been regularly orientated.

The second feature is the 'triangular spiral' arrangement of the chain. The thiocyanate groups, as expected, are effectively linear [N–C–S 176.8(5), 178.8(6) and 178.6(6)°], but the angles at the coordinated nitrogen atoms are large [164.7, 150.4 and 174.9° for N(1), N(2) and N(3) respectively]. However, angles at the coordinated sulphur atoms, are much closer to 90° [85.7, 98.6 and 91.4° at S(1), S(2) and S(3), respectively]. These geometrical factors allow development of the 'triangular spiral' structure. The sides of the triangle are very unequal and comprise Sb(1) and the two *N*-bonded ligands, S(1) Sb(2) and an *N*-bonded group, and finally Sb(3) and two sulphur atoms.

Structures of a number of related compounds are available for comparison, among them trimethyl[5] and triphenyl[6] tin thiocyanates. Regularly bridging thiocyanate groups are present in both compounds, leading to infinite zig-zag chain structures. Coordination at the central atom in each case is close to trigonal bipyramidal, analogous to the pseudo-trigonal bipyramidal geometry at antimony in the present compound; tin–nitrogen distances are slightly shorter (215 and 222 pm respectively) but there are comparatively long tin–sulphur distances (313 and 292 pm respectively). Triphenyltellurium thiocyanate[7] is basically ionic, but both dimeric and tetrameric Ph_3TeNCS units can be identified where thiocyanate groups bridge between pairs of tellurium atoms (Te–N and Te–S contacts fall in the ranges 296.3–318.2 and 325.6–361.6 pm respectively). Basically ionic thiocyanate groups are also present in the two modifications of dimethylthallium thiocyanate, with alternate thallium atoms coordinated to four

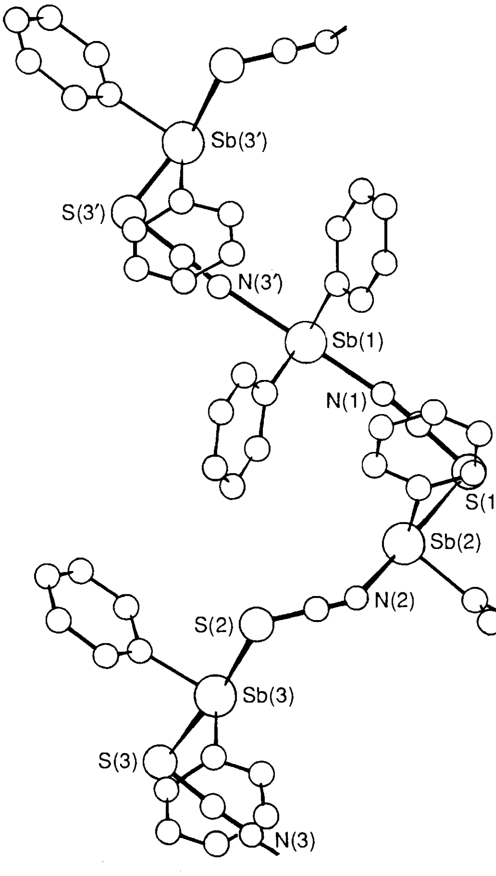

Fig. 1 Structure of Ph_2SbSCN, projected down the *c* axis

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† *Crystal data*: Ph_2SbSCN, $C_{13}H_{10}NSSb$, M = 333.8, triclinic, a = 321.7(3), b = 1327.2(3), c = 1288.9(3) pm, α = 91.82(4), β = 98.04(4), γ = 119.39(5)°; U = 1937.3 × 10^6 pm^3, Mo-Kα radiation (with graphite monochromator), space group $P\bar{1}$, D_c = 1.72 g cm^{-3}, Z = 6, μ = 22.8 cm^{-1}, R = 0.035, R_w = 0.043 for 4171 reflections with $I > 3\sigma(I)$; Hilger and Watts Y290 four-circle diffractometer, scanning range $0 < \theta < 22°$. Structure solved by Patterson methods and refined by full-matrix least-squares analysis with anisotropic thermal parameters for all non-hydrogen atoms; hydrogen atom positions were refined with isotropic thermal parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

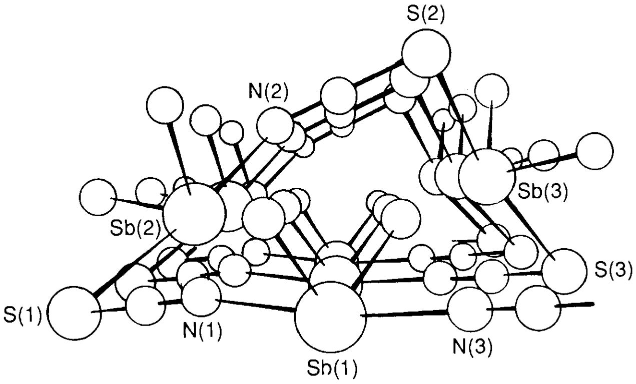

Fig. 2 Structure of Ph_2SbSCN, projected down the *b* axis (the phenyl groups are omitted for clarity)

nitrogen atoms at 277 pm and four sulphur atoms at 312 pm in the monoclinic modification and coordination of each thallium to two nitrogen (280 pm) and two sulphur atoms (311 pm) in the alternative orthorhomic form.[8]

This information makes it all the more difficult to offer any reasonable rationalisation for the antimony thiocyanate structure reported here. Clearly with central atoms of comparable size and hardness, regular structures can be obtained. We are left with considering two factors that may be important. In the first instance, the intermediate hardness of the diphenylantimony moiety means that there is probably no great preference for *N*-bonding over *S*-bonding. Secondly, the solid-state structure incorporating two effectively linear three-atom units, *i.e.* the thiocyanate groups and antimony atoms coordinated to axial thiocyanates generates the spiral structure as an efficient method of space filling.

It is interesting that triphenylantimony dithiocyanate[9] also contains three independent molecules in the asymmetric unit.‡ There are, however, no intermolecular interactions and the three molecules are trigonal bipyramidal with axial isothiocyanate groups. Molecular parameters of the three molecules differ basically in the angles at the coordinated nitrogen atoms, 151.0(7)–167.1(7)° and in the C–N bonds lengths, 106.7(9)–118.2(9) pm, but there is no strict parallel between these two parameters. The compound shows a single ^{14}N NMR signal at −237 (ppm).

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References

1 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, 1984; M. Hall and D. B. Sowerby, *J. Organomet. Chem.*, 1988, **347**, 59.
2 D. B. Sowerby and M. J. Begley, unpublished work.
3 J. Bordner, G. O. Doak and J. R. Peters, Jr., *J. Am. Chem. Soc.*, 1974, **96**, 6763.
4 A. M. Golub, H. Kohler and V. V. Skopenko, *Chemistry of Pseudohalides*, Elsevier, 1986.
5 R. A. Forder and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 1969, 1125.
6 A. M. Domingos and G. M. Sheldrick, *J. Organomet. Chem.*, 1974, **67**, 257.
7 J-S. Lee, D. D. Titus and R. F. Ziolo, *Inorg. Chem.*, 1977, **16**, 2487.
8 Y. M. Chow and D. Britton, *Acta Crystallogr. Sect. B*, 1975, **31**, 1922.
9 F. Challenger, A. L. Smith and F. J. Paton, *J. Chem. Soc.*, 1923, 1046.

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‡ *Crystal data:* $Ph_3Sb(NCS)_2$, $C_{20}H_{15}N_2S_2Sb$, $M = 468.8$, triclinic, $a = 1093.2(3)$, $b = 1760.4(3)$, $c = 1873.3(3)$ pm, $\alpha = 107.61(4)$, $\beta = 92.85(4)$, $\gamma = 116.72(5)°$; $U = 2995.3 \times 10^6$ pm^3, Mo-Kα radiation, space group $P\bar{1}$, $D_c = 1.56$ g cm^{-3}, $Z = 6$, $\mu = 16.0$ cm^{-1}, $R = 0.043$, $R_w = 0.049$ for 5538 reflections with $I > 3\sigma(I)$; processing as for Ph_2SbSCN, except that hydrogen atom positions were not refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.