Some Group 15 Pseudo-halides and the Crystal Structure of Diphenylbismuth(III) Thiocyanate†

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A crystal structure determination showed that in diphenylbismuth thiocyanate the thiocyanate group bridges between pairs of bismuth atoms to give infinite chains in which alternate bismuth atoms are co-ordinated to either two nitrogen or two sulfur atoms. The conformation of the resulting chain is a 'rectangular spiral', in contrast to the 'triangular spiral' structure of the related diphenylantimony thiocyanate. Unstable diphenylantimony selenocyanate has also been prepared and the complexity in the C–N stretching region of the IR spectrum suggests a structure similar to that of the thiocyanate analogue. Diphenylarsenic thiocyanate is a liquid at room temperature and a conventional 1,3-thiocyanate-bridged structure is suggested from IR data.

We have recently shown that two diarylantimony(III) thiocyanates exhibit totally different crystal structures.[1] In diphenylantimony thiocyanate, the thiocyanate group bridges between pairs of antimony atoms to generate an infinite chain, while in bis(2,6-dimethylphenyl)antimony thiocyanate, steric effects from the two *o*-methyl substituents are sufficient to prevent thiocyanate bridging and the structure consists of discrete N-bonded monomers. Thiocyanate bridging in the diphenyl compound leads, however, to an unusual and probably unique structure type. The asymmetric unit consists of three molecules in which two of the independent thiocyanate groups can be considered as being primarily N-bonded while the orientation of the third is reversed and is primarily S-bonded. The bridging thiocyanate groups occupy axial positions in a pseudo-trigonal-bipyramidal arrangement about antimony and this in conjunction with angles of *ca.* 170° at nitrogen and *ca.* 90° at sulfur forces a 'triangular spiral' structure on the chains of molecules so generated.

Phenyl-substituted thiocyanates of two of the elements close to antimony in the Periodic Table, *i.e.* triphenyltin thiocyanate and triphenyltellurium thiocyanate, have more conventional structures. The former shows regular 1,3-thiocyanate bridging leading to infinite zigzag chains,[2] while in the latter, although the structure is basically ionic, there are di- and tetra-meric units in which thiocyanate groups bridge between pairs of tellurium atoms.[3] To examine further the parameters which may have a bearing on the unusual diphenylantimony thiocyanate structure, we have investigated the chemistry of analogues in which: (*a*) the central atom is either arsenic or bismuth and (*b*) in which antimony remains the central atom and the pseudo-halide is exchanged for either cyanate or selenocyanate.

Experimental

All reactions were carried out with dried and redistilled solvents under an atmosphere of nitrogen.

Preparation of Diphenylarsenic Thiocyanate.—**CAUTION**: Owing to the known hazards of phenylarsenic(III) halides (among others it causes severe skin ulceration on contact) and the likely hazards of the thiocyanate, all operations involved in the preparation and handling of both compounds were carried out with the greatest care in a fume cupboard using thick rubber gloves. Contaminated glassware was cleaned by soaking in alcoholic potassium hydroxide solution.

Diphenylarsenic chloride was prepared[4] by a high-temperature reorganisation of a mixture of $AsPh_3$ and $AsCl_3$ and purified by fractional distillation (Found: C, 54.4; H, 3.9. Calc. for $C_{12}H_{10}AsCl$: C, 54.5; H, 3.8%). A solution of dried potassium thiocyanate (2.25 g, 23.1 mmol) in dry acetonitrile was added slowly to a stirred solution of diphenylarsenic chloride (6.12 g, 23.1 mmol) and stirring was continued for 2 h. The resulting pale yellow solution was filtered to remove precipitated potassium chloride (1.52 g, 88%) and evaporated to dryness in a vacuum. The yellow oil which remained was then distilled under reduced pressure giving diphenylarsenic thiocyanate as a yellow liquid, b.p. 172 °C (0.12 Torr, *ca.* 16 Pa), yield 6.25 g, 22 mmol (93%) (Found: C, 54.5; H, 3.6; N, 4.6. Calc. for $C_{13}H_{10}AsNS$: C, 54.4; H, 3.5; N, 4.9%).

Attempted Preparation of Diphenylantimony Cyanate.—Silver cyanate was prepared in aqueous solution from silver nitrate and fresh potassium cyanate. The fine white precipitate was filtered off, washed with ethanol and diethyl ether, then dried in the dark over P_2O_5 for 2 d. Diphenylantimony chloride (4.9 g, 16 mmol) and silver cyanate (2.4 g, 16 mmol) were stirred together in dry ether in the dark for 1 week at room temperature. After filtration, the solution was concentrated and set aside in the freezer. A pale yellow oily solid (2.5 g) was collected (Found: C, 47.5; H, 3.4; N, 1.5. Calc. for $C_{13}H_{10}NOSb$: C, 49.1; H, 3.1; N, 4.4%). The product showed an IR band at 2208 cm^{-1}, consistent with the presence of N-bonded cyanate, but the low nitrogen content suggests that the product is contaminated, probably with unchanged $SbPh_2Cl$. All attempts at purification by fractional crystallisation from a range of solvents were unsuccessful, but the rearrangement product, triphenylantimony dicyanate, m.p. 114 °C (lit.,[5] 110 °C) was obtained from a tetrahydrofuran (thf) solution (Found: C, 55.0; H, 3.4; N, 6.3. Calc. for $C_{20}H_{15}N_2O_2Sb$: C, 55.0; H, 3.4; N, 6.4%).

Preparation of Diphenylantimony Selenocyanate.—A solution of potassium selenocyanate (0.97 g, 6.7 mmol) in dry acetone was added with stirring to a solution of diphenylantimony chloride (2.09 g, 6.7 mmol) in acetone. Stirring was continued for 24 h after which precipitated potassium chloride (0.65 g, 85%) was filtered off. The filtrate was evaporated to dryness in a vacuum without external heating to give a viscous yellow-orange oil. Crystallisation from dry ether gave yellow crystals,

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

m.p. 87 °C (2.1 g, 5.5 mmol, 82%) (Found: C, 40.3; H, 2.6; N, 3.3. Calc. for $C_{13}H_{10}NSbSe$: C, 41.0; H, 2.6; N, 3.7%).

Preparation of Diphenylbismuth Thiocyanate.—Triphenylbismuth was prepared from bismuth trichloride and phenyllithium and recrystallised from ethanol while thiocyanogen was obtained from lead thiocyanate and bromine in dichloromethane solution.[6] A solution of ice-cold, freshly prepared and standardised $(SCN)_2$ (0.8 g, 7 mmol) in dichloromethane was added with stirring to a solution of triphenylbismuth (3.1 g, 7 mmol) in dichloromethane at 0 °C. Stirring was continued for 1 h, when the solvent was evaporated in a vacuum to yield a yellow oil. Crystallisation from ethanol–light petroleum (b.p. 40–60 °C) (4:1 v/v) gave yellow, odourless crystals (1.4 g, 3.3 mmol, 48%), m.p. 123 °C (lit., 122,[7,8] 125 °C[9]) (Found: C, 36.9; H, 2.3; N, 3.3. Calc. for $C_{13}H_{10}BiNS$: C, 37.0; H, 2.4; N, 3.3%). Recrystallisation from a 1:1 v/v chloroform–hexane mixture gave yellow crystals of a chloroform hemi-solvate, $[BiPh_2(NCS)]_2 \cdot CHCl_3$ (m.p. 123 °C) (Found: C, 33.9; H, 2.2; N, 3.1. Calc. for $C_{27}H_{21}Bi_2Cl_3N_2S_2$: C, 33.7; H, 2.2; N, 2.9%).

Crystal Structure of $[BiPh_2(NCS)]_2 \cdot CHCl_3$.—Difficulties were experienced in growing crystals suitable for X-ray diffraction from chloroform–hexane mixtures and this clearly influenced the quality of the data and the final state of refinement of the structure.

Crystal data. $C_{27}H_{21}Bi_2Cl_3N_2S_2$, $M = 961.7$, monoclinic, space group $P2_1/c$, $a = 12.329(7)$, $b = 13.859(8)$, $c = 18.173(8)$ Å, $\beta = 99.58(2)°$, $U = 3061.9$ Å^3, Mo-Kα radiation (with graphite monochromator), $D_c = 2.09$ g cm^{-3}, $F(000) = 1784$, $Z = 4$, $\mu = 113.2$ cm^{-1}, crystal size 0.2 × 0.2 × 0.15 mm.

Structure determination. Intensity data were collected on a Hilger and Watts four-circle diffractometer for 3039 reflections in the range $0 < \theta < 25° (-11 < h < 11, 0 < k < 13, 0 < l < 17)$ of which 1556 with $I > 3\sigma(I)$ were considered observed. Corrections were made for Lorentz and polarisation effects. Density data indicated the presence of two independent bismuth atoms in the asymmetric unit. Crystallographic calculations used the CRYSTALS programs[10] and scattering factors for neutral atoms.[11]

Possible positions for the two bismuth atoms were obtained from a three-dimensional Patterson synthesis and the remaining non-hydrogen atoms were revealed by a series of full-matrix least-squares refinements and Fourier-difference syntheses. Owing to the quality of the data, refinement continued with anisotropic thermal parameters for bismuth, sulfur and chlorine atoms only. After application of a four-coefficient Chebyshev weighting scheme, the hydrogen atoms of the phenyl groups were place at their calculated positions [d(C–H) 1.0 Å]. These were not refined in the final cycles of refinement, which led to final convergence (180 least-squares parameters, maximum shift:e.s.d. 0.01, maximum and minimum residual electron densities 2.5 and −0.4 e Å^{-3}, with all peaks > 0.9 e Å^{-3} in the vicinity of the Bi, S or Cl atoms) at $R = 0.071$ ($R' = 0.088$). 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.

Discussion

Diphenylarsenic Thiocyanate.—This compound has not been described previously, but can be obtained in high yield and purity by a metathesis reaction between diphenylarsenic chloride and potassium thiocyanate in acetonitrile. Although the product is a liquid at room temperature, which can be purified by vacuum distillation, crystals do appear in acetone–hexane solutions stored in a freezer. Room-temperature X-ray diffraction is then clearly not an option for obtaining structural information.

An IR spectrum as a liquid film showed, in addition to the usual phenyl absorption modes, a very strong broad band at 2016 cm^{-1}. Broad bands in this region are often diagnostic of the presence of N-bonded thiocyanate groups and, indeed, its position is close to the range suggested for such groups.[12] However, there is considerable overlap between the ranges suggested for different thiocyanate co-ordination modes and it is not possible to rule out a bridging group on this evidence alone. Positions for the other two thiocyanate modes, *i.e.* ν(CS) and δ(NCS), could not be determined with certainty due to overlapping phenyl modes, but there was a poorly resolved shoulder on the phenyl y mode[13] at 476 cm^{-1} in the region expected for δ(NCS). However, it is anticipated that co-ordination unsaturation at arsenic will lead to bridging and, because arsenic(III) is a harder Lewis acid than antimony(III), this will be the normal 1,3-type giving a regular zigzag infinite-chain structure.

The electron impact (EI) mass spectrum of diphenylarsenic thiocyanate is very simple, showing an intense molecular ion peak (m/z 287, intensity 19%). As for the antimony analogue discussed previously,[1] of the two primary fragmentation processes, *i.e.* loss of phenyl or thiocyanate, it is the latter giving $AsPh_2$ (m/z 229, 100%) which is more favourable. Phenyl loss produces AsPh(NCS) (m/z 210, 1%) in much lower abundance and there is no evidence for As(NCS).

Although no ^{14}N NMR signal was observed in deuteriochloroform probably due to solubility problems, a single signal at δ −237 (linewidth at half peak height, 26 ppm) was observed in deuteriomethanol. This is downfield of signals for $SbPh_2$(NCS) and $Sb(C_6H_3Me_2)_2(NCS)$, *i.e.* δ −260 and −279 respectively, but is clearly in the range for N-bonded thiocyanate groups.[14]

Diphenylantimony Cyanate.—Pure samples of this compound could not be isolated and the heterogeneous reaction with silver cyanate is probably slow. All samples had low nitrogen contents, suggesting contamination with $SbPh_2Cl$ starting material. Attempts at purification from a range of solvents were unsuccessful and only triphenylantimony(V) dicyanate was isolated from dry thf. Clearly this compound can arise only as a result of both phenyl group reorganisation and oxidation. There was no evidence during the reaction for an antimony redox process and it is assumed that oxidation is by atmospheric oxygen. Air oxidation is known to occur with the related diphenylantimony bromide, but here the product is stable $(SbPh_2OBr)_2$.[15] Phenyl group reorganisation is also known in organoantimony chemistry with, for example, mixtures of triphenylantimony and either antimony trichloride or bromide yielding the mixed phenylantimony(III) halides.[16]

Diphenylantimony Selenocyanate.—This was prepared successfully as an unstable, foul-smelling yellow solid, which decomposes on exposure to heat, air, light and moisture. Decomposition products were red, implying separation of free selenium, with low nitrogen contents and no IR bands associated with the selenocyanate group. The initial preparative route used acetonitrile as solvent, but lower-boiling ether was substituted when it became obvious that the compound was thermally very sensitive. It is stable as a solid or in ether solution, if stored under nitrogen in a freezer in the dark. Crystals mounted in glass capillaries, however, decomposed rapidly and the compound was clearly too unstable for a structure determination at room temperature.

Its IR spectrum showed three sharp bands in the C–N stretching region at 2130, 2095 and 2060 cm^{-1}, with bands at 576 and 415 cm^{-1} assigned to ν(CSe) and δ(NCSe) respectively. The complexity of the spectrum in the region above 2000 cm^{-1} is reminiscent of that for the corresponding thiocyanate[1] and the general band positions are compatible with the presence of bridging selenocyanate groups.[12] As for correlations between the thiocyanate co-ordination mode and IR band positions, there is considerable overlap between different selenocyanate co-ordination modes, but it is not unreasonable to consider the presence of bridging selenocyanate groups in this compound. On balance, then, we suggest that the selenocyanate is isostructural with the corresponding thiocyanate and has the same 'triangular spiral' conformation of infinite $SbPh_2(SeCN)$ chains.

Diphenylbismuth Thiocyanate.—This compound was first prepared *via* the spontaneous decomposition of triphenylbismuth dithiocyanate,[7] but it can also be obtained by metathesis between diphenylbismuth(III) chloride and either aqueous sodium or potassium thiocyanate.[9] Its IR data have been interpreted in terms of a monomeric S-bonded unit in solution and a 1,3-bridged polymer in the solid,[8,9] but it is interesting that terminal N-bonded thiocyanate groups are considered to be present in $[BiPh_2(NCS)_2]^-$.[17]

In this work diphenylbismuth thiocyanate was prepared from triphenylbismuth dithiocyanate as an odourless yellow powder, but there were difficulties in crystallisation and only small crystals of a chloroform hemisolvate were obtained from chloroform–hexane mixtures.

In contrast to the complexity in the 2000 cm^{-1} region of the IR spectra of both $SbPh_2(NCS)$ and $SbPh_2(NCSe)$, a Nujol-mull spectrum of the bismuth compound showed a single ν(CN) band at 2085 cm^{-1}. Additionally, there was a weak band at 767 cm^{-1} [ν(CS)] with the deformation mode at 470 cm^{-1}. Previously reported spectra are very similar, except that a shoulder at 2102 cm^{-1} was reported on the main 2084 cm^{-1} band.[9] Raman spectra in acetone showed a single strong band at 2125 cm^{-1} together with bands at 724 and 438 cm^{-1}. From the usual correlations, these bands are consistent with either 1,3-bridging or terminal S-bonded thiocyanate groups but, as with all Group 15 thiocyanates in the +3 oxidation state, solid-state monomers are unlikely, in the absence of specific steric effects, as thiocyanate is an efficient bridging ligand and the central atom is co-ordinatively unsaturated. S-Bonded monomers, on the other hand, are possible in solution.

Support for bridging groups in $BiPh_2(NCS)$ comes from the IR spectrum of $[Bi(NCS)_3(bipy)_2]_2$ (bipy = 2,2'-bipyridyl), known from X-ray crystallography to contain both bridging and terminal N-bonded thiocyanates,[18] where bands at 2015 and 2080 cm^{-1} were assigned to terminal N-bonded and 1,3-bridging thiocyanate groups, respectively.

It was not possible to obtain information on the nature of the species in solution from ^{14}N NMR spectroscopy as saturated solutions in either deuteriochloroform or deuteriomethanol gave no signal, even with long acquisition times. This could result from low solubility of the compound, coupled with the general insensitivity of the ^{14}N nucleus and the high quadrupole moment of the bismuth. Alternatively, there could be rapid exchange between N- and S-linkage isomers with collapse of the signals into a single very broad peak.

The EI mass spectrum of diphenylbismuth thiocyanate was extremely simple. There was no parent ion and, indeed, no peaks containing both bismuth and thiocyanate were present. The most intense fragment was Bi (*m*/*z* 209, 100%) but peaks corresponding to both $BiPh_2$ and BiPh (*m*/*z* 363, 4.4% and 286, 67% respectively) were observed. The spectrum also showed a pattern of peaks at *m*/*z* 83, 85 and 87, associated with the $CHCl_2$ ion, confirming the presence of solvate chloroform.

Crystal Structure of Diphenylbismuth Thiocyanate.—Important bond lengths and angles for the compound are listed in Table 2 and the structure is illustrated by projection of the cell contents down the *c* and *b* axes in Figs. 1 and 2, respectively. The unit cell also contains four molecules of chloroform of solvation, one molecule for each pair of independent bismuth thiocyanate molecules.

As for the antimony analogue and, as expected from the IR spectrum, all thiocyanate groups bridge between pairs of bismuth atoms, but the 1,3-bridging is again not regular. Of the two independent bismuth atoms, one is co-ordinated to nitrogen atoms of two thiocyanates [Bi–N 2.53(6) and 2.52(5) Å, N–Bi–N 166.2(16)°], while the second is attached to two sulfurs [Bi–S 2.87(1) and 2.88(1) Å, S–Bi–S 177.0(4)°] to give infinite chains parallel to the *c* axis. The structure is related to that of diphenylantimony thiocyanate but, rather than having a three-molecule repeating pattern with antimony atoms co-ordinated to two nitrogen, one nitrogen and one sulfur and two sulfur atoms, respectively, here alternate bismuth atoms are co-ordinated to two nitrogen and two sulfur atoms, respectively. In the antimony case it was possible to recognise that, although all three independent thiocyanate groups were bridging, two were primarily N-bonded while the third was primarily S-bonded. In other words, in the infinite $SbPh_2(NCS)$ chains, the orientation of every third thiocyanate group was reversed. In the bismuth structure it is not possible to say which end of the

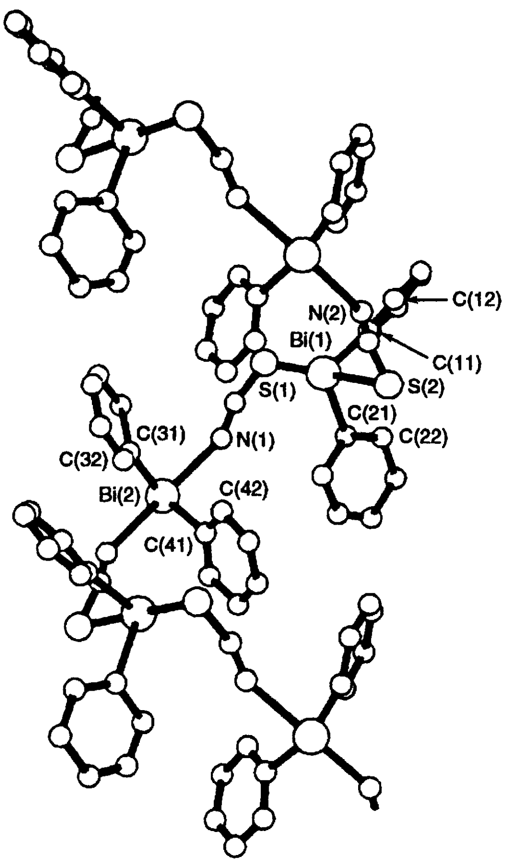

Fig. 1 Structure of $BiPh_2(NCS)\cdot0.5CHCl_3$ projected down the *c* axis

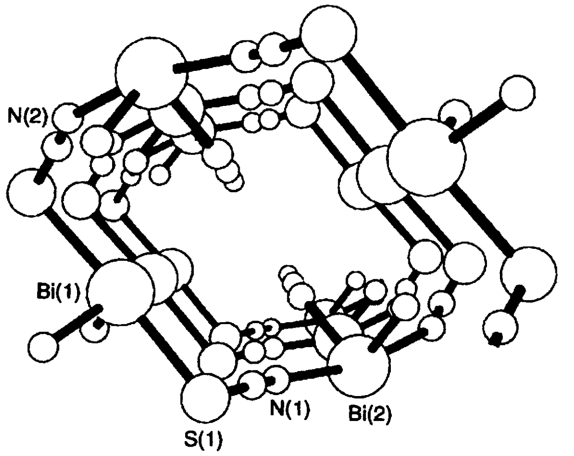

Fig. 2 Structure of $BiPh_2(NCS)\cdot0.5CHCl_3$ projected down the *b* axis (for clarity only the *ipso*-carbon atoms of the phenyl groups are shown)

thiocyanate group forms the primary bond, as the independent Bi–N and Bi–S distances are equal, but here the thiocyanate orientation reverses at each bismuth atom giving a two-molecule repeating unit.

Among the bismuth thiocyanate structures for comparison are those for $[Bi(NCS)_3(bipy)_2]_2$[18] and $[Bi(SCN)_6]^{3-}$.[19] Two of the six thiocyanate groups in the former are bridging with Bi–N (2.648 Å) and Bi–S distances (3.016 Å) which are longer, the latter substantially so, than those in the present compound. The remaining four thiocyanate groups are terminally N-bonded at substantially shorter Bi–N separations (2.453 and 2.408 Å). The hexa(thiocyanato)bismuthate(III) anion is known in two isomeric forms, the first with six terminally S-bonded ligands (Bi–S 2.819–2.832 Å) and the second with four S-bonded (Bi–S 2.812, 2.825 Å) and two N-bonded groups (Bi–N 2.34, 2.44 Å).

Table 1 Fractional atomic coordinates for $BiPh_2(NCS)\cdot0.5CHCl_3$, with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Bi(1)	0.2400(2)	0.2162(1)	0.2020(1)
Bi(2)	−0.1824(2)	−0.0433(1)	0.0612(1)
S(1)	0.091(1)	0.2450(8)	0.0647(7)
S(2)	0.399(1)	0.1868(8)	0.3352(7)
Cl(1)	0.807(2)	−0.018(2)	0.553(1)
Cl(2)	0.870(2)	0.006(2)	0.413(1)
Cl(3)	0.744(4)	0.151(2)	0.467(2)
C(1)	0.012(5)	0.152(4)	0.067(3)
N(1)	−0.030(4)	0.080(4)	0.065(3)
C(2)	0.348(5)	0.278(4)	0.382(3)
N(2)	0.325(4)	0.339(3)	0.410(3)
C(3)	0.812(9)	0.057(9)	0.477(6)
C(11)	0.361(3)	0.311(2)	0.154(2)
C(12)	0.427(3)	0.374(3)	0.205(2)
C(13)	0.496(4)	0.438(4)	0.171(3)
C(14)	0.506(4)	0.434(3)	0.103(3)
C(15)	0.443(3)	0.369(3)	0.050(2)
C(16)	0.368(4)	0.310(4)	0.081(3)
C(21)	0.294(3)	0.075(3)	0.161(2)
C(22)	0.393(4)	0.068(3)	0.128(3)
C(23)	0.431(4)	−0.016(3)	0.104(2)
C(24)	0.362(4)	−0.106(4)	0.109(3)
C(25)	0.276(4)	−0.090(4)	0.140(3)
C(26)	0.230(5)	−0.005(4)	0.165(3)
C(31)	−0.259(3)	0.058(3)	0.130(2)
C(32)	−0.277(5)	0.041(4)	0.203(3)
C(33)	−0.325(4)	0.108(3)	0.246(2)
C(34)	−0.348(4)	0.196(4)	0.216(3)
C(35)	−0.336(5)	0.219(5)	0.143(3)
C(36)	−0.291(5)	0.153(4)	0.098(3)
C(41)	−0.076(4)	−0.123(3)	0.158(3)
C(42)	−0.027(5)	−0.078(4)	0.224(3)
C(43)	0.039(5)	−0.136(5)	0.274(3)
C(44)	0.056(4)	−0.230(4)	0.261(3)
C(45)	0.012(5)	−0.275(5)	0.195(4)
C(46)	−0.060(4)	−0.219(4)	0.143(3)

Table 2 Important bond lengths (Å) and angles (°) for $BiPh_2(NCS)\cdot0.5CHCl_3$, with e.s.d.s in parentheses

Bi(1)–S(1)	2.87(1)	Bi(2)–C(31)	2.19(4)
Bi(1)–S(2)	2.88(1)	Bi(2)–C(41)	2.29(5)
Bi(1)–C(11)	2.27(3)	S(1)–C(1)	1.61(6)
Bi(1)–C(21)	2.23(4)	S(2)–C(2)	1.70(6)
Bi(2)–N(1)	2.53(6)	C(1)–N(1)	1.13(6)
Bi(2)–N(2)	2.52(5)	C(2)–N(2)	1.05(6)
S(1)–Bi(1)–S(2)	177.0(4)	Bi(1)–S(2)–C(2)	93(2)
S(1)–Bi(1)–C(11)	87.3(9)	S(1)–C(1)–N(1)	169(6)
S(1)–Bi(1)–C(21)	90.8(9)	Bi(2)–N(1)–C(1)	160(5)
S(2)–Bi(1)–C(11)	90.4(9)	Bi(2)–N(2)–C(2)	151(5)
S(2)–Bi(1)–C(21)	87.7(9)	S(2)–C(2)–N(2)	173(6)
C(11)–Bi(1)–C(21)	97.1(14)	Bi(1)–C(11)–C(12)	117(2)
N(1)–Bi(2)–N(2)	166.2(16)	Bi(1)–C(11)–C(16)	122(3)
N(1)–Bi(2)–C(31)	86.4(16)	Bi(1)–C(21)–C(22)	121(3)
N(1)–Bi(2)–C(41)	88.5(16)	Bi(1)–C(21)–C(26)	119(4)
N(2)–Bi(2)–C(31)	85.1(14)	Bi(2)–C(31)–C(32)	126(4)
N(2)–Bi(2)–C(41)	81.8(15)	Bi(2)–C(31)–C(36)	117(4)
C(31)–Bi(2)–C(41)	96.7(15)	Bi(2)–C(41)–C(42)	124(4)
Bi(1)–S(1)–C(1)	100(2)	Bi(2)–C(41)–C(46)	114(4)

Co-ordination about each central atom in $BiPh_2(NCS)$ is pseudo-trigonal bipyramidal, as in $SbPh_2(NCS)$, with axial thiocyanate and equatorial phenyl groups. The thiocyanate groups are effectively linear with angles at carbon of 169(6) and 173(6)° for C(1) and C(2), respectively, and although the estimated standard deviations (e.s.d.s) are relatively high, these angles are lower than those [177.3(8)°] at the bridging thiocyanates in $[Bi(NCS)_3(bipy)_2]_2$, suggesting perhaps greater strain. The C–N [1.13(6) and 1.05(6) Å] and C–S bond lengths [1.61(6) and 1.70(6) Å] here appear to show an interesting interrelationship, with the shorter C–N distance associated with the longer C–S distance and *vice versa*. This could be evidence for differentiation of the thiocyanate groups, but in view of the high e.s.d.s it must remain speculative. For comparison, in $[Bi(NCS)_3(bipy)_2]_2$, C–N and C–S distances in the bridging thiocyanates are 1.145(11) and 1.631(8) Å, respectively, and 1.154(12), 1.151(11) and 1.589(9), 1.593(9) Å, respectively, for the terminal N-bonded groups.

As in $SbPh_2(NCS)$, angles at the co-ordinated nitrogen atoms are large [160(5) and 151(5)°] compared with those at sulfur [100(2) and 93(2)°]. These values combined with the presence of axial thiocyanate groups lead to a new type of 'spiral' structure for the $BiPh_2(NCS)$ chains with a 'rectangular' repeating pattern (see Fig. 2), compared with the 'triangular' pattern in $SbPh_2(NCS)$.

We have previously proposed that the latter arises by

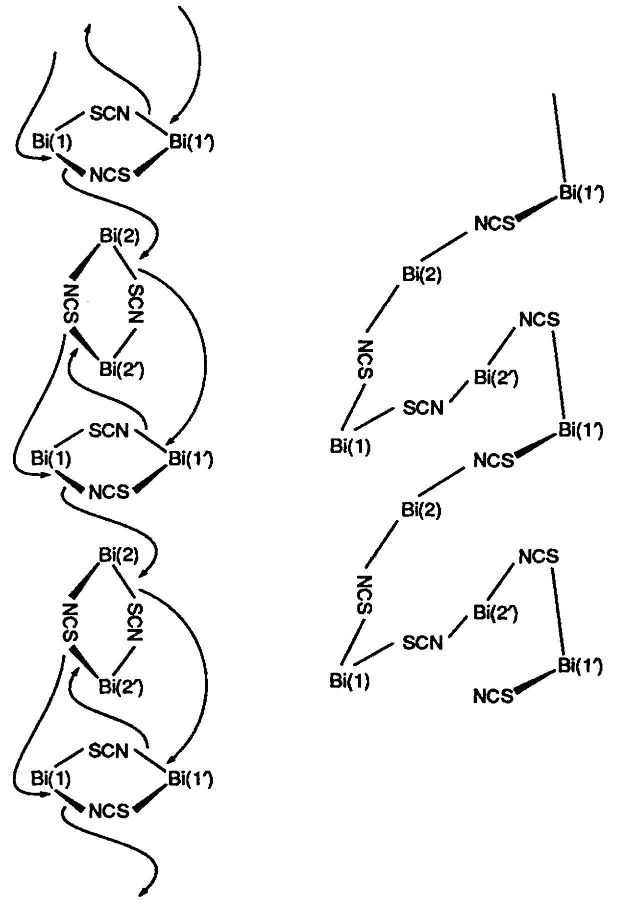

Fig. 3 Possible mechanism for formation of the rectangular spiral structure

insertion of an $SbPh_2(NCS)$ unit into one of the Sb–S bonds of a 1,3-thiocyanate-bridged dimer. The mechanism suggested in the present case is related to this and is summarised in Fig. 3. 1,3-Thiocyanate-bridged dimers, labelled Bi(1) and Bi(1′) and Bi(2) and Bi(2′), respectively, are again considered to be the starting point; for clarity the phenyl groups have been omitted and for convenience the Bi(2) dimer is rotated. The first steps are effectively cleavage of the two Bi–N and two Bi–S bonds in, respectively, Bi(1) and Bi(2) dimers. The chain structure then arises from: (*a*) insertion of a Bi(2′)–NCS unit into the Bi(1′)–NCS bond of a dimer, (*b*) formation of a bridge between two dimers by the Bi(2)–NCS unit, (*c*) co-ordination of the nitrogen atom of the upper Bi(1′)–SCN to Bi(2) and (*d*) co-ordination of the sulfur of Bi(2)–NCS to Bi(1) in the lower dimer.

Although these routes to the spiral structures are speculative, it is possible to see a pattern in the behaviour of thiocyanate as a bridging ligand. In the majority of cases, the ligand is regularly orientated as in $SnR_3(NCS)$ species, giving the well known infinite zigzag chain. If there is any ambiguity in the mode of attachment of the ligand, for reasons which could include, for example, the intermediate hardness of the central atom, it is possible to envisage other possibilities. For example, alternation of ligand orientation at each heavy atom would give the $BiPh_2(NCS)$ 'rectangular spiral' arrangement, while two thiocyanate groups in one orientation followed by a third which is reversed would give the 'triangular spiral' of $SbPh_2(NCS)$. It seems unlikely that other thiocyanate bridging patterns will be identified as the obvious alternatives, *e.g.* three groups in a given orientation followed by one in the reverse or two in a given orientation followed by two in the reverse, would be inefficient in space filling. However, it may be possible to stabilise discrete cyclic oligomers based on these patterns by incorporation of specific substituents in the aryl groups. One example of the effect of aryl group substitution is shown in the $Sb(C_6H_3Me_2\text{-}2,6)_2(NCS)$,[1] but the steric effects of the *o*-methyl groups are obviously too severe and the solid consists of N-bonded monomers.

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