Complexes of 2,5,7,9-Tetrathiabicyclo[4.3.0]non-1(6)-ene-8-thione (L^1). Part 1. Synthesis and Antimony-121 Mössbauer Spectroscopic Characterisation of SbCl$_3$(L^1)$_{1.5}$, Crystal and Molecular Structures of SbCl$_3$(L^1)$_{1.5}$ and Uncomplexed L^1 *

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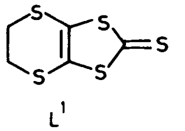
The preparation, crystal structure, and Mössbauer spectroscopic studies of SbCl$_3$(L^1)$_{1.5}$ are reported {L^1 = 2,5,7,9-tetrathiabicyclo[4.3.0]non-1(6)-ene-8-thione}. The structure is polymeric with each antimony centre bonded to three chlorine atoms [Sb–Cl 2.305(14), 2.385(13), and 2.381(9) Å] and also linked to three different L^1 ligands through their terminal (C=S) sulphur atoms. Each ligand is in turn bridging two antimony centres. The potential sulphur donors on the ligand rings do not participate in co-ordination; Sb–S distances of 3.085(15), 3.112(4), and 3.407(16) Å reflect a weak type of interaction and this is confirmed by the lack of change in the ^{1}H and ^{13}C n.m.r. spectra of the ligand on complexation. Mössbauer spectroscopy shows that the lone pair on the antimony is stereochemically active, operating through the plane formed by the three sulphurs. The structure of the free ligand L^1 is almost planar which is consistent with a delocalised π-electron system.

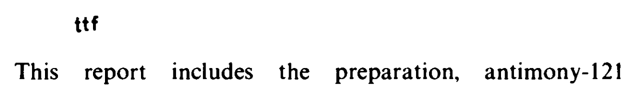
Our interest in the co-ordination behaviour of 'thio' ligands towards Group 5B metal halides has previously been focused on the comparison of co-ordination properties of S- *versus* N-donor sites on *N,N'*-disubstituted dithio-oxamides [RHNC(S)C(S)NHR, R = Me, Et, Pr^i, Bu^n, cyclohexyl, or CH$_2$Ph] [1–3] and *N,N'*-disubstituted dithiomalonamides [RHNC(S)CH$_2$C(S)NHR, R = Me, Et, Pr^i, Bu^n, or cyclohexyl] [4] and the choice between chelation and bridging of the metal centres. All ligands invariably employ their S-donor sites. In the case of *N,N'*-disubstituted dithio-oxamides, while S,S-chelation was observed for BiCl$_3$,[3] the S,S-bridging mode was found to prevail with SbX$_3$ (X = Cl or Br) complexes.[1,2] However, *N,N'*-disubstituted dithiomalonamides did form chelates with SbCl$_3$,[4] in which the lone pair of electrons occupied an antimony co-ordination site.

For complexes of SbX$_3$(X = Cl, Br) with bridging ligands, any suggestion of lone-pair stereochemical activity lacked supporting evidence in the absence of further studies. In this work, Mössbauer spectroscopy has been employed to provide evidence for such lone-pair activity. The scope of the work has also been expanded by investigating the co-ordination ability of a terminal 'thio' (C=S) group, as found in the above ligands, compared with that of an ether-type group (C–S–C), as found in 1,4-dithiane,[5] for example, towards SbCl$_3$, by forming its complex with L^1, a ligand containing both such groups. The choice of L^1 as a ligand has been greatly influenced by the current interest in the synthesis and electron-transfer properties of inorganic complex-based materials.[6]



L^1

Since tetrathiafulvalene (ttf) was known to possess semiconductor properties as well as the ability to form the unusually stable electron-conducting organic radical cation complexes,[7–9] other ligands with the tetrathioethylene unit seem attractive.



ttf

This report includes the preparation, antimony-121 Mössbauer spectroscopic study, and the crystal and molecular structure of SbCl$_3$(L^1)$_{1.5}$. The crystal structure of neat L^1 is also described. Mössbauer spectroscopic evidence reveals that the lone pair is stereochemically active in SbCl$_3$(L^1)$_{1.5}$. The structure of SbCl$_3$(L^1)$_{1.5}$ shows that the preferred co-ordination is through the terminal 'thioketonic' (C=S) sulphur atom and not through any of the other four 'cyclic thioether' (C–S–C) sulphur atoms. This is also the first observation of a C=S group bridging two main-group metal centres through the sulphur.

Experimental

All manipulations were conducted under an inert atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were routinely dried prior to use. Microanalyses were performed in the Microanalytical Laboratory of the Chemistry Department at Manchester University. Antimony(III) chloride (AnalaR) was used as commercially supplied and was kept under nitrogen in a Schlenk tube. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier-transform spectrophotometer over the range 4 000—400 cm^{-1}. Data were obtained from KBr pellets. Proton (300 MHz) and ^{13}C (75 MHz) n.m.r. spectra were obtained for C$_6$D$_6$ solutions using a Varian XL 300 instrument. The residual methine peak at δ 7.30 in the solvent was used as the internal reference for ^{1}H

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue, 1, pp. xvii—xx.

Table 1. Details of cell constants, data collection, and refinement

	(1)	L^1
Formula	SbCl$_3$(L^1)$_{1.5}$	$C_5H_4S_5$
M	564.7	224.4
F(000)	2 184	456
Class	Monoclinic	Monoclinic
Space group	*I*2/*c* (no. 15)	*P*2$_1$/*n*
a/Å	10.349(12)	10.76(1)
b/Å	11.640(12)	5.880(5)
c/Å	28.050(22)	13.42(1)
β/°	95.0(1)	92.5(1)
U/Å^3	3 366.1	848.3
Z	8	4
D_m/g cm^{-3}	Too soluble	1.74
D_c/g cm^{-3}	2.23	1.76
μ(Mo-K_α radiation)/cm^{-1}	29.9	12.3
2θ(max.)	50	50
Rotation axis	a	b
No. of independent data measured	2 967	1 537
No. of data used in refinement	910 [$I > 2\sigma(I)$]	1000 [$I > 4\sigma(I)$]
No. of parameters	134	92
R	0.097	0.052
R'	0.102	0.054

Table 2. Atomic co-ordinates (× 10^4) for compound (**1**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Sb(1)	490(4)	1 065(2)	1 455(1)
Cl(1)	−1 304(15)	−40(9)	1 572(4)
Cl(2)	1 922(16)	−357(10)	1 813(4)
Cl(3)	676(17)	333(9)	671(4)
S(1)	−1 640(15)	2 840(10)	1 153(4)
C(2)	−673(50)	3 792(31)	957(14)
S(3)	508(15)	3 552(9)	622(4)
C(4)	930(47)	4 898(26)	542(11)
S(5)	2 269(18)	5 074(1)	178(4)
C(6)	2 639(76)	6 434(50)	250(23)
C(7)	2 080(92)	7 229(63)	485(30)
S(8)	716(20)	7 190(8)	779(5)
C(9)	553(49)	5 706(30)	794(13)
S(10)	−751(15)	5 256(9)	1 107(4)
S(21)	0*	1 715(13)	2 500*
C(22)	0*	3 097(66)	2 500*
S(23)	−1 029(18)	3 892(10)	2 796(4)
C(24)	−582(55)	5 257(34)	2 659(15)
S(25)	−1 150(22)	6 427(11)	2 907(5)
C(26)	−247(112)	7 561(62)	2 687(25)

* Fixed parameter.

Table 3. Atomic co-ordinates (× 10^4) for L^1 with e.s.d.s in parentheses.

Atom	*x*	*y*	*z*
S(1)	9 589(2)	6 383(5)	6 838(2)
S(3)	9 449(2)	3 202(4)	8 536(2)
S(5)	8 654(2)	1 433(4)	10 459(2)
S(8)	6 814(2)	6 343(5)	10 445(2)
S(10)	7 945(2)	7 217(4)	8 511(2)
C(2)	9 026(7)	5 693(14)	7 907(6)
C(4)	8 553(7)	3 598(14)	9 565(5)
C(6)	7 572(9)	2 346(18)	11 364(6)
C(7)	6 435(8)	3 557(17)	10 931(7)
C(9)	7 858(8)	5 492(15)	9 563(6)

n.m.r. spectra. The ^{121}Sb Mössbauer spectrum was obtained as described previously [10] with the source and sample immersed in liquid helium.

2,5,7,9-Tetrathiabicyclo[4.3.0]non-1(6)-ene-8-thione (L^1) was prepared by 1,2-dibromoethane treatment of the product from the reaction of potassium metal with carbon disulphide in dimethylformamide, as described previously,[11] and characterised by microanalysis and spectroscopic methods (Found: C, 26.8; H, 1.7; S, 71.6. Calc. for $C_5H_4S_5$: C, 26.75; H, 1.75; S, 71.45%). I.r. (KBr): 2 364, 1 477, 1 290, 1 127, 1 061, 1 041, 1 020, 925, and 870 cm^{-1}. N.m.r. (C_6D_6): ^{1}H, δ 2.18 (s,CH_2); ^{13}C, δ 208.0 (C=S), 122.9 (C=C), and 29.5 (CH_2).

Preparation of SbCl$_3$(L^1)$_{1.5}$ (**1**).—Benzene (25 cm^3) was added to a mixture of SbCl$_3$ (0.54 g, 2.37 mmol) and L^1 (0.53 g, 2.36 mmol) under nitrogen. Some of the benzene (3 cm^3) was evaporated from the resulting solution *in vacuo* to degas the system and create a partial vacuum. The Schlenk tube was then sealed and heated at 90 °C with stirring overnight (**CAUTION**: possibility of explosion). There was a subtle colour change from yellow to brownish orange. The solution was allowed to cool to room temperature before evaporating the benzene *in vacuo* until the onset of crystallisation. The system was then allowed to stand to facilitate crystal growth. When crystallisation was complete, nitrogen was introduced into the system and the rest of the supernatant solution syringed off leaving orange-brown needles of SbCl$_3$(L^1)$_{1.5}$ which were pumped dry at room temperature. Yield 60% (Found: C, 16.15; H, 1.0; Cl 19.2; S, 43.5. Calc. for SbCl$_3$($C_5H_4S_5$)$_{1.5}$: C, 15.95; H, 1.05; Cl, 18.85; S, 42.55%). I.r. (KBr): 2 371, 1 469, 1 457, 1 407, 1 289, 1 258, 1 127, 1 060, 1 035, 1 015, 918, and 873 cm^{-1}. N.m.r. (C_6D_6): ^{1}H, δ 2.18 (s,CH_2); ^{13}C, δ 208.0 (C=S), 123.1 (C=C), and 29.6 (CH_2).

Structure Determinations.—The crystals were prepared as described above. Precession photographs established the preliminary cell constants and space groups. The crystals were then transferred to a Stoe STADI-2 diffractometer equipped with a graphite monochromator. Precise determination of lattice constants was carried out from the accurate setting angles of a number of axial reflections. The scan speed was 0.033° s^{-1} with a scan width of (1.5 + 0.5 sin μ/tan θ) and the background was measured at the ends the ω scan for 20 s. Measurement of standard reflections showed no deterioration. Details of the cell constants, data collection, and refinement are given in Table 1.

In both structures, the Patterson function was used to determine the positions of the heaviest atoms. The positions of the remaining atoms were located from Fourier maps and refined by full-matrix least squares. For compound (**1**) the data were of poor quality and only the antimony, sulphur, and chlorine atoms were refined anisotropically with carbon atoms being refined isotropically. One ligand was in a general position, and the other was imposed upon the two-fold axis. There is good evidence from the Fourier difference map (and indeed from the anisotropic thermal parameters) that this ligand may be disordered about the two-fold axis but we were unable to refine a satisfactory model. For L^1 all non-hydrogen atoms were refined anisotropically. For both (**1**) and L^1 the methylene hydrogen atoms were included in calculated positions with a common refined thermal parameter. The weighting scheme used in both structures was $w = 1/[\sigma^2(F) + 0.003F^2]$. The final Fourier difference maps showed no important features and in the final cycles of refinement no shift/error ratio was greater than 0.10. Calculations were carried out using SHELX 76 [12] and some of our own programs on the Amdahl V7 computer at the University of Reading. Atomic parameters are given in Tables 2 and 3, bond lengths and angles in Tables 4 and 5.

Results and Discussion

Stirring L^1 with SbCl$_3$ (1:1 molar ratio) in dry benzene under a solvent-vapour blanket in a sealed Schlenk tube at 90 °C

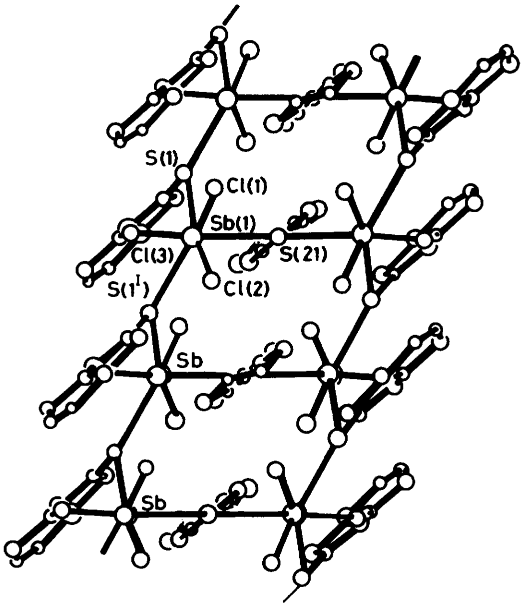


Figure 1. The crystal structure of $SbCl_3(L^1)_{1.5}$

overnight gave an orange solution from which brownish orange crystals of $SbCl_3(L^1)_{1.5}$ were isolated in 60% yield. A similar product was obtained by treating L^1 with $SbCl_3$ in molar ratios of 1:2 and 1:3 ($SbCl_3$:L^1) under the same conditions. Any attempt to perform the reaction in dry tetrahydrofuran (thf) always resulted in a complex which analysed as $SbCl_3(L^1)_{1.5}$ but turned from brownish orange to purple when all the thf was pumped off. Complexes isolated from benzene were more stable to solvent removal.

The ^1H n.m.r. spectrum of the ligand L^1 in C_6D_6 shows the expected singlet at δ 2.18 due to the CH_2 protons. There is no noticeable shift of this peak on complexation. The ^{13}C n.m.r. spectrum (C_6D_6) of the complex is again almost identical with that of the ligand. There is no shift of the C=S peak at δ 208.0 on complexation. The more likely explanation is that this complex is unstable towards dissociation in solution, a phenomenon that has already been encountered in *N,N'*-disubstituted dithiooxamide complexes of $SbCl_3$.[1–3]

The i.r. spectra of the ligand and the complex are almost identical except for a few trivial shifts in the ν(CS) region (870—1 130 cm^{-1}).[13] The main change is the splitting of the ligand-perturbed ν(C=S) stretching mode at 1 477 cm^{-1} (ref. 14) into three bands at 1 469, 1 457, and 1 407 cm^{-1}.

The structure of $SbCl_3(L^1)_{1.5}$ is shown in Figure 1 with the atomic numbering scheme. It is polymeric with the terminal sulphur atom of each ligand bridging two separate antimony centres. To our knowledge this is the first terminal >C=S group to bridge two antimony centres through the sulphur atom. There are however many examples of such bridges for transition metals. A search of the Cambridge Data Centre files revealed over 40 structural studies involving such ligands as thioacetamide and thiourea. It is curious that none of these molecules contained the $X^2(X^1)C{=}SM_2$ (M = transition metal) fragment, with $X^1 = X^2 = C$. Most of them had at least $X^1 = N$.

In the present structure the antimony environment may be described as a distorted octahedron formed by three chlorine and three sulphur atoms from three different ligands. One of the Sb–Cl distances is shorter than the others [Sb(1)–Cl(1) 2.305(14) *vs.* Sb(1)–Cl(2) 2.385(13) and Sb(1)–Cl(3) 2.381(9) Å]. This short Sb–Cl distance is *trans* to the longest of the three Sb-S interactions [Sb(1)–S(1^I)] which is 3.407(16) compared to Sb(1)–S(1) 3.085(15) and Sb(1)–S(21) 3.112(4) Å. The Sb–S distances in themselves reflect fairly weak interactions, a phenomenon that has been observed in a whole range of $SbCl_3$ complexes with S-donor ligands.[1,2,5,15,16] In such complexes the ligands are attached only loosely to the metal and hence are unstable towards dissociation to free ligand and $SbCl_3$ in solution. This is further supported by ^{13}C n.m.r. spectra of $SbCl_3(L^1)_{1.5}$ where no shift is observed in the δ(C=S) resonance at δ 208 on complexation.

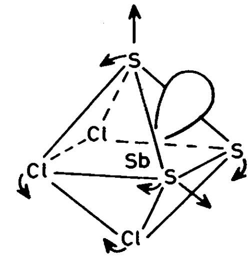
Table 4. Molecular dimensions (distances in Å, angles in °) in the metal co-ordination sphere of compound (**1**)

Sb(1)–Cl(1)	2.305(14)	Sb(1)–S(1)	3.085(15)
Sb(1)–Cl(2)	2.385(13)	Sb(1)–S(21)	3.112(4)
Sb(1)–Cl(3)	2.381(9)	Sb(1)–S(1^I)	3.407(16)
Cl(1)–Sb(1)–Cl(2)	91.82(49)	Cl(1)–Sb(1)–S(1^I)	167.08(37)
Cl(1)–Sb(1)–Cl(3)	93.61(45)	Cl(2)–Sb(1)–S(1^I)	80.85(43)
Cl(2)–Sb(1)–Cl(3)	92.48(47)	Cl(3)–Sb(1)–S(1^I)	76.23(45)
Cl(1)–Sb(1)–S(1)	81.24(42)	S(1)–Sb(1)–S(1^I)	107.38(35)
Cl(2)–Sb(1)–S(1)	169.54(35)	S(21)–Sb(1)–S(1^I)	111.10(26)
Cl(3)–Sb(1)–S(1)	95.75(46)	Sb(1)–S(1)–C(2)	96.0(17)
Cl(1)–Sb(1)–S(21)	78.61(32)	Sb(1)–S(1)–Sb(1^{II})	143.1(4)
Cl(2)–Sb(1)–S(21)	85.30(37)	C(2)–S(1)–Sb(1^{II})	113.9(17)
Cl(3)–Sb(1)–S(21)	171.81(42)	Sb(1)–S(21)–C(22)	104.1(27)
S(1)–Sb(1)–S(21)	85.66(31)	Sb(1)–S(21)–Sb(1^{III})	151.8(5)

Symmetry operations: I $\frac{1}{2} + x, \frac{1}{2} - y, z$; II $-\frac{1}{2} + x, \frac{1}{2} - y, z$; III $-x, y, \frac{1}{2} - z$.

The polymeric nature of this complex is intriguing in that although each antimony atom is bonded to three sulphur atoms from three different ligands, the resulting polymer can be described as a two-dimensional system where two zigzag polymeric chains are connected by additional ligands *via* their antimony centres. A somewhat similar situation is found in the complex $SbCl_3(L^2)_{1.5}$,[1] formed by the bidentate ligand EtHNC(S)C(S)NHEt (L^2), where each sulphur atom is bonded to only one antimony centre while in the present $SbCl_3(L^1)_{1.5}$ every sulphur atom is bonded to two $SbCl_3$ centres.

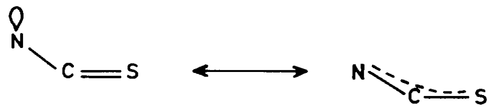
There is no obvious indication from the structure that the lone pair is stereochemically active. However a brief comparison of Sb–S distances found in compound (**1**) with those in the structures of 1:1 complexes of $SbCl_3$ with EtHNC(S)-CH_2C(S)NHEt,[4] 1,3-dimethylimidazole-2-thione,[17] and tetramethylthiourea[18] where the lone pair occupies the vacant co-ordination site shows that for the latter complexes the Sb–S distances are much shorter, being on average 2.66, 2.51, and 2.51 Å respectively. Since the nature of the sulphur atom is similar to that in compound (**1**), *i.e.* C=S, one might have expected the Sb–S bonds to be similar in strength (and length). The longer Sb–S bonds observed in (**1**) are thus attributed to stereochemical activity of the lone pair causing lone pair–bond pair repulsions. This is presently supported by Mössbauer spectroscopic evidence. Thus in this system antimony is in a pseudo-seven-co-ordinate environment with the lone pair taking up a position somewhere near the centre of the triangular face formed by the three sulphurs. This gives a trigonal C_{3v} distortion as shown below. Indeed the observed bond angles are



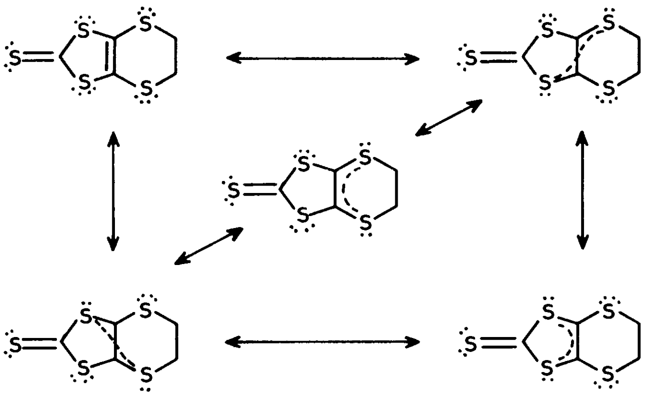
consistent with this kind of distortion. Angles Cl(1)–Sb(1)–Cl(2), Cl(1)–Sb(1)–Cl(3), and Cl(2)–Sb(1)–Cl(3) are much less distorted from octahedral being 91.8, 93.6, and 92.5° respectively. It seems most likely that the lone pair is distorted from a central position in the triangular face to a position closer to $S(1^I)$, a factor which is contributory to (*a*) the $Sb(1)–S(1^I)$ bond being the longest of the three Sb–S bonds, and (*b*) the observed variation in S–Sb–S angles, angles including $S(1^I)$ *e.g.* $S(21)–Sb(1)–S(1^I)$ 111.1° and $S(1)–Sb(1)–S(1^I)$ 107.4° being much larger than S(1)–Sb(1)–S(21) which is only 85.7°.

Pseudo-eight-co-ordination around antimony has been observed in its complex with *N,N*-diethyldithiocarbamate,[19] also pseudo-seven-co-ordination in some antimony(V) acetate complexes.[20]

It is noteworthy that the terminal C=S bridges two separate Sb centres in compound (**1**). A comparison of this complex with other C=S donor complexes (*e.g.* those in refs. 1, 4, 17, and 18) shows that monodentate co-ordination is preferred for C=S where this carbon atom is also bonded to a nitrogen atom. The lack of bridging properties of these sulphurs may be attributed to the delocalisation of the π electrons in C=S across to the more electronegative nitrogen. This effect is obviously not pronounced in the case of transition-metal complexes with thiourea-type ligands.[21]



In L^1 the C=S group lies in an electron-rich environment with limiting structures, *e.g.* as shown below. Presentation of the ligand in this form may explain the surprising lack of participation of the sulphur atoms in either ring in any form of co-ordination to the metal atoms as found in complexes of $SbCl_3$ with cyclic thioethers such as $S_2C_4H_8$ (1,4-dithiane),[5] $S_3C_3H_6$ (1,3,5-trithiane),[15] and $S_2C_5H_{10}$ (1,4-dithiacycloheptane).[16] In these ligands the ring sulphurs are not contributing to a π-delocalised circuit within the molecule. In the present ligand all possible donor electrons on the ring sulphurs are more spread out through the entire ligand.



The dimensions of the ligand have been determined accurately only in the crystal structure of the free ligand (Figure 2, Table 5). The dimensions in the antimony complex (**1**) are much less accurately determined due to the poor quality of the crystal and we can draw no conclusions about whether the dimensions of the ligand are changed on complexation. In the free ligand the S(1)–C(2) distance at 1.633(8) Å is a pure double bond. Of the other distances, S(5)–C(6) and C(7)–S(8) to the methylene carbon atoms are 1.800(9) and 1.816(10) Å respectively, indicative of single bonds. The remaining six S–C bonds are comparable in the range 1.701(9)—1.750(8) Å, indicative of a delocalisation of the double bonds. The C(4)–C(9) bond length of 1.341(12) Å corresponds to that of a C–C double bond. Least-square planes calculations show that the ligand is relatively planar. Indeed with the one exception of C(7) the atoms are coplanar within 0.03 Å, C(7) is 0.83 Å from this plane showing that the six-membered ring has the envelope conformation.

Table 5. Molecular dimensions in L^1 (distances in Å, angles in °)

S(1)–C(2)	1.633(8)	S(8)–C(9)	1.741(8)
S(3)–C(2)	1.741(8)	S(10)–C(2)	1.701(9)
S(3)–C(4)	1.734(7)	S(10)–C(9)	1.745(8)
S(5)–C(4)	1.750(8)	C(4)–C(9)	1.341(12)
S(5)–C(6)	1.800(9)	C(6)–C(7)	1.510(13)
S(8)–C(7)	1.816(10)		
C(2)–S(3)–C(4)	97.5(4)	S(3)–C(4)–C(9)	116.0(5)
C(4)–S(5)–C(6)	102.9(4)	S(5)–C(4)–C(9)	128.6(6)
C(7)–S(8)–C(9)	98.4(4)	S(5)–C(6)–C(7)	114.7(6)
C(2)–S(10)–C(9)	98.1(4)	S(8)–C(7)–C(6)	111.9(6)
S(1)–C(2)–S(3)	122.4(5)	S(8)–C(9)–S(10)	116.3(5)
S(1)–C(2)–S(10)	125.1(5)	S(8)–C(9)–C(4)	127.8(6)
S(3)–C(2)–S(10)	112.5(5)	S(10)–C(9)–C(4)	115.8(6)
S(3)–C(4)–S(5)	115.3(4)		

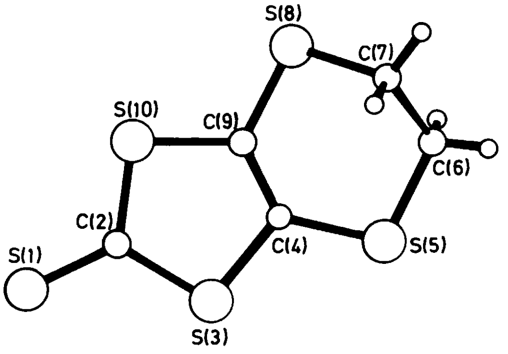


Figure 2. The crystal structure of L^1

The ^{121}Sb Mössbauer parameters for $SbCl_3(L^1)_{1.5}$ are typical of 'inorganic' antimony(III) compounds with stereochemically active lone pairs (see Table 6). The large positive quadrupole coupling constants (e^2qQ) of such compounds arise from appreciable 5*p* character of the lone pair (*eQ* is negative). Variations from compound to compound represent the combined effect of rehybridisation of the lone pair and of contributions from the ligands; the former effect usually dominates. Similarly, the isomer shift (i.s.) reflects principally the 5*s* character of the lone pair, and becomes more negative as the *s* character increases (δR^2 is negative, R = antimony atomic radius). An increase in the covalency of the antimony–ligand bonds reduces the *s* character of the lone pair and increases its *p* character, and both Mössbauer parameters increase. An increase in the co-ordination number usually has the reverse effect, as the antimony–ligand bonds become longer and less covalent; this is well illustrated by the data for SbX_3, SbX_4^-, and SbX_5^{2-} (X = Cl or Br).

The present compound has an i.s. very similar to that for $SbCl_3$ while e^2qQ is slightly less. The formal increase in co-ordination number from three to six thus has little effect on the Mössbauer parameters, which is consistent with the observed length of the Sb–S bonds. The three shortest bonds, Sb–Cl, are mutually perpendicular and should therefore make no contribution to the electric field gradient, *eq*. The Sb–S bonds define angles rather different from 90° but their length suggests that

Table 6. ^{121}Sb Mössbauer parameters for antimony(III) compounds with stereochemically active lone pairs

Compound	I.s. (In/Sb)/ mm s^{-1}	e^2qQh^{-1}/mm s^{-1}	Ref.
$SbCl_3(L^1)_{1.5}$	$-5.6(1)$	$+10.9(4)$	
$SbCl_3$	-5.24	$+12.2$	*a*
	-5.9	$+13.9$	*b*
	-5.9	$+13.2$	*c*
$SbCl_3[SC(NMe_2)_2]$	-6.4	$+12.3$	18
$SbCl_3[SC(NHEt)_2]$	-9.0	$+9.8$	*d*
$SbCl_3[SC(NHC_6H_{11})_2]$	-8.3	$+9.1$	*d*
$SbCl(L^3)$	-5.17	$+14.6$	*e*
$SbCl(L^4)$	-4.99	$+17.0$	*e*
$A[SbCl_4]$[f]	-7.16 to -8.17	$+8.0$ to $+11.3$	*b*, *g*
$[NH_4]_2[SbCl_5]$	-6.52	$+11.2$	*h*
$SbCl_3$·phen	-6.88	$+9.2$	*i*
$SbBr_3$	-5.9	$+11.6$	*j*
$A[SbBr_4]$[k]	-7.6 to -8.2	$+6.9$ to 8.1	*j*
$A_2[SbBr_5]$[l]	-8.2 to -9.3	0.0 to $+9.7$	*j*
$SbBr_3$·phen	-7.45	$+5.7$	*i*
$Sb(SC_6H_4R\text{-}2)_3$[m]	-3.7 to -4.3	$+11.8$ to $+13.9$	*n*
$Sb(S_2CNEt_2)_3$	-6.9	$+7.5$	19
$Sb(S_2CNBu^n{}_2)_3$	-6.8	$+7.8$	19

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any contribution to *eq* is likely to be small. The substantial value of e^2qQ therefore indicates that the lone pair has appreciable 5*p* character. It should therefore be stereochemically active and presumably occupies a position opposite the three Sb–Cl bonds, on the same side of the antimony atoms as the three ligand-sulphur atoms. This is consistent with the length of the Sb–S bonds, their distortion from bond angles of 90°, and the weakness of the interaction. The closest analogy with previously studied systems is for $Sb(S_2CNR_2)_3$ (R = Et or Bu).[19] In these compounds the bidentate ligands are unsymmetrically bonded, with three short and three long Sb-S bonds. There are also two contacts with neighbouring ligands, and a distinct 'gap' for the lone pair. The greater covalency of Sb–S than Sb–Cl bonds results in greater *s* character and lower *p* character for the lone pair, and this is reflected in the more negative i.s. and smaller e^2qQ values for the dithiocarbamates.

Acknowledgements

We are grateful to Mrs. L. S. Moore for recording the Mössbauer spectrum and Mr. A. W. Johans for his assistance with the crystallographic investigations.

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Received 13*th August* 1986; *Paper* 6/1652