Stereochemical Role of Lone Pairs in Main-group Elements. Part 2.[1] Structure and Bonding in Trichloro(tetramethylthiourea)antimony(III) studied by Means of *X*-Ray Crystallography and Antimony-121 Mössbauer Spectroscopy

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The crystal structure of the title compound has been determined from *X*-ray diffractometer data by Patterson and Fourier methods. Crystals are monoclinic, space group *Cc*, with $Z = 4$ in a unit cell of dimensions $a = 10.180(2)$, $b = 15.306(2)$, $c = 7.699(1)$ Å, and $\beta = 105.48(1)°$. The structure was refined to *R* 0.019 for 1 426 observed reflections. The antimony(III) atoms are in distorted trigonal-bipyramidal sites surrounded by three chlorine atoms at 2.428(2), 2.527(3), and 2.687(2) Å and by a tetramethylthiourea sulphur atom at 2.505(2) Å. The stereochemistry and distortion at the antimony(III) site is consistent with the lone pair occupying an equatorial position. The ^{121}Sb Mössbauer parameters are reported and compared with literature values for related complexes. The increased negative shifts on going from $SbCl_3$ to the complexes, together with the signs and magnitudes of the quadrupole interactions, are interpreted within a covalent framework in terms of the use of antimony 5*s* and 5*p* valence orbitals and the desire of these systems to lower their total energies by distortions which maximise the populations of the lower-energy 5*s* orbital.

WITH few exceptions, a dominant feature of complexes of *p*-block elements in lower valence states is the role played by their lone pairs in producing irregular co-ordinations. In the case of 1 : 1 complexes of antimony(III) halides, AX_3YE (A = central atom; X = halide; Y = ligand; and E = lone pair), few crystal structures where Y is a neutral donor molecule are available. The structure of the aniline adduct with antimony(III) chloride shows that the lone pair occupies an equatorial position of a pseudo-trigonal bipyramid with the ligand co-ordinating from an axial position.[2] This indicates that aniline is a comparatively weak donor towards antimony(III) since it is well known that the poorer donor in an X, Y ligand combination is relegated to the axial position.

Since it is established that the sulphur atom of thiourea is a strong donor towards tin(II) [3] and tellurium(IV),[4,5] we anticipated that this ligand should be a good enough donor to bond to antimony from an equatorial position thereby referring a halogen to an axial site.

We report here the crystal structure of trichloro(tetramethylthiourea)antimony(III) and its 121-antimony Mössbauer spectrum.

EXPERIMENTAL

Preparation.—The complex was prepared by dissolving antimony(III) chloride (0.56 g) in hydrochloric acid (15 cm^3) and adding the solution dropwise to a boiling solution of tetramethylthiourea (1 g) in hydrochloric acid (10 cm^3). The complex crystallised rapidly on cooling and crystals suitable for diffraction work were obtained by dissolving the complex in hydrochloric acid (50 cm^3, 2 mol dm^{-3}) and allowing the solution to cool from 90 to 25 °C over several hours.

Crystal Data.—$C_5H_{12}Cl_3N_2SSb$, $M = 360.1$, Monoclinic, $a = 10.180(2)$, $b = 15.306(2)$, $c = 7.699(1)$ Å, $\beta = 105.48(1)°$, $U = 1\,156.21$ Å^3, $D_m = 2.0$ g cm^{-3} (flotation), $Z = 4$, $D_c = 2.07$ g cm^{-3}, $F(000) = 648$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å μ(Mo-K_α) = 30.3 cm^{-1}. Absent spectra are consistent with space groups *C*2/*c* and *Cc*. The density of the complex implies a unit-cell occupancy of four and one molecule in the asymmetric unit if the space group is *Cc*, whereas in the alternative, *C*2/*c*, the molecule is required to be centro- or two-fold-symmetric.

Intensity Data Collection and Structure Refinement.—A crystal with approximate dimensions 0.3 × 0.3 × 0.18 mm was mounted in a general orientation and intensity data collected at room temperature in the θ—2θ scan mode on a Nonius CAD4 automatic four-circle diffractometer out to θ = 30° using monochromatised Mo-K_α radiation. The crystal was stable under data collection. Of the 1 514 reflections measured, 1 426 were classified as observed, *i.e.* $I_{net} > 2.58\sigma(I)$. Data were corrected for Lorentz, polarisation, and absorption effects. Scattering factors for light atoms were taken from International Tables [6] and for antimony from Cromer and Mann; [7] solution refinement was carried out using the '*X*-RAY '76' system of programs.[8] The structure was solved by the heavy-atom method and successfully refined in space group *Cc* to an *R* factor of 0.019 with anisotropic temperature factors for all atoms. The atomic positions are given in Table 1, and Table 2 contains the interatomic distances and valence angles. Structure factors and thermal parameters have

TABLE 1

Final positional parameters (×10^5 for Sb and ×10^4 for other atoms) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Sb	25 000	6 029(2)	25 000
Cl(1)	527(2)	266(1)	4 129(3)
Cl(2)	4 187(2)	1 142(1)	858(3)
Cl(3)	3 804(2)	1 268(1)	5 290(2)
S	996(2)	1 920(1)	1 735(2)
C(1)	1 808(6)	2 176(4)	709(8)
C(2)	2 140(9)	4 310(5)	693.3(11)
C(3)	2 389(11)	3 528(6)	3 568(12)
C(4)	2 989(9)	3 043(6)	−1 622(10)
C(5)	1 123(9)	1 935(5)	−2 209(10)
N(1)	2 198(7)	3 459(4)	1 582(9)
N(2)	1 922(6)	2 595(4)	−968(7)

TABLE 2

Bond distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Antimony co-ordination			
Sb–Cl(1)	2.687(2)	Sb–Cl(2)	2.527(3)
Sb–Cl(3)	2.428(2)	Sb–S	2.505(2)
Cl(1)–Sb–Cl(2)	171.38(6)	Cl(1)–Sb–Cl(3)	88.15(6)
Cl(1)–Sb–S	77.18(6)	Cl(2)–Sb–Cl(3)	91.23(7)
S–Sb–Cl(3)	91.48(6)	S–Sb–Cl(2)	94.24(7)
(*b*) Tetramethylthiourea			
C(1)–S	1.772(7)	C(1)–N(1)	1.327(9)
C(1)–N(2)	1.340(9)	N(1)–C(2)	1.465(9)
N(1)–C(3)	1.490(10)	N(2)–C(4)	1.480(10)
N(2)–C(5)	1.476(9)	S–C(1)–N(1)	118.4(5)
S–C(1)–N(2)	120.3(5)	C(1)–N(1)–C(2)	123.8(6)
C(1)–N(1)–C(3)	121.2(7)	C(1)–N(2)–C(4)	121.5(6)
C(1)–N(2)–C(5)	123.0(6)	C(2)–N(1)–C(3)	113.2(7)
C(4)–N(2)–C(5)	115.1(7)		

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The experimental details concerning the ^{121}Sb Mössbauer measurements and data reductions have already been described.[9]

RESULTS AND DISCUSSION

The crystal structure, part of which is shown in Figure 1, consists of $SbCl_3$(tmtu) (tmtu = tetramethylthiourea) molecules linked by intermolecular Sb–Cl contacts (3.123 Å) to form sheets of parallel chains which in turn are linked by van der Waals contacts. The immediate antimony environment (Figure 2) has C_1 point symmetry and the co-ordination polyhedron is best described as a pseudo-trigonal bipyramid with the fifth position (the equatorial one in the idealised polyhedron) evidently being occupied by a stereochemically active lone pair. This arrangement is fully consistent with the distorted polyhedron predicted by the Valence Shell Electron Pair Repulsion (VSEPR) model[10] for discrete AX_3YE species.

The Sb–S distance [2.505(2) Å] may be compared with the slightly shorter Sb–S equatorial bonds [2.444(4)—2.458(5) Å] recently reported[11] for the pseudo-trigonal bipyramidal $SbClS_4E$ and $SbCl_2S_2E$ fragments in $Sb^{III}_4S_5Cl_2$, thereby indicating that the tmtu molecule is bonded relatively strongly to antimony. This is consistent with both the internal evidence as presented by the C–S bond length (see below) and the equatorial position preferred by the ligand. The equatorial Sb–Cl bond length [2.428(2) Å] is somewhat longer than those in antimony(III) chloride itself [2 × 2.368(1) and 2.340(2) Å], the structure of which has been recently redetermined.[12] The axial Sb–Cl distances are as usual the most elongated, one being even longer than the other by as much as 0.259 Å. This latter chlorine atom is further co-ordinated to a neighbouring antimony *via* a longer range interaction [3.123(2) Å]. Interactions of this type are described as secondary bonds by Alcock,[13] and defined as those interatomic distances, often regarded as non-bonding, which are longer than normal bonds but shorter than van der Waals distances.

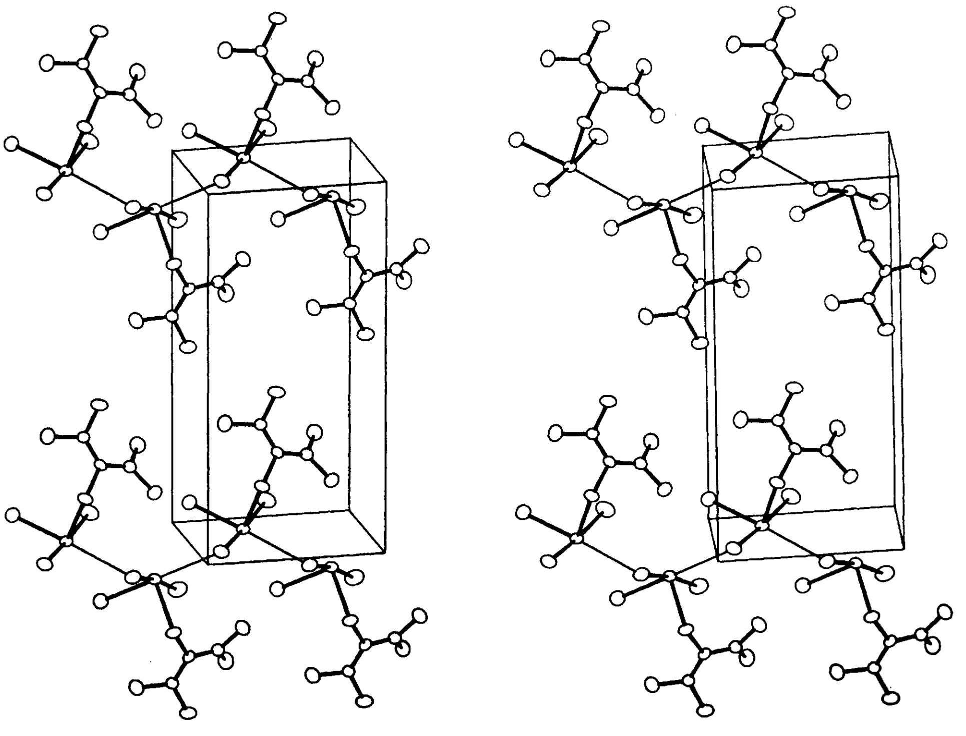

FIGURE 1 Stereoscopic drawing of part of one sheet of $SbCl_3$(tmtu) molecules

Discussion on the bonding in trichloro(tetramethylthiourea)antimony(III) is aided by comparing its struc-

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

tural and Mössbauer parameters with those reported[2,14] for the structurally related compounds, pyridinium tetrachloroantimonate(III) and trichloro(aniline)antimony(III). The ^{121}Sb Mössbauer spectrum of $SbCl_3$(tmtu) taken at 4.2 K was least-squares fitted to the following parameters: chemical shifts, $\delta = -15.9$ mm s^{-1} (relative to $Ba^{121}SnO_3$ source; InSb $= -8.5$ mm s^{-1}); quadrupole coupling constant, $eQV_{zz} = 12.3$ mm s^{-1}; half-width, $\Gamma = 2.8$ mm s^{-1}; asymmetry parameter, $\eta = 0.3$. Estimated errors are 0.1 mm s^{-1} in δ and 0.5 mm s^{-1} in eQV_{zz}. The chemical shift provides a measure for the total *s*-electron density experienced by the probe nucleus. For ^{121}Sb the change in nuclear radius $\delta R/R$ is negative, which means that an increase in *s*-electron density is mirrored by a proportional decrease (more negative) in chemical shift. Factors influencing chemical shifts include the 5*s* character of the antimony lone pair, delocalisation of antimony 5*s*-electron density into bonding levels, and the use of 5*p* orbitals which, because of their shielding properties, modify the total *s*-electron density at the nucleus. For antimony(III) compounds, it is the *s*-electron character of the lone pair which dominates the chemical shift.[15] The chemical shift for $SbCl_3$(tmtu) (-15.86 mm s^{-1}) is more negative than that for $SbCl_3$ itself (-13.74 mm s^{-1}; relative to $BaSnO_3$),[16] thereby indicating an increase in the total *s*-electron density at the antimony nucleus for the adduct. The same conclusion applies to $[C_5H_5NH][SbCl_4]$ and $SbCl_3(C_6H_5NH_2)$ (Table 3).

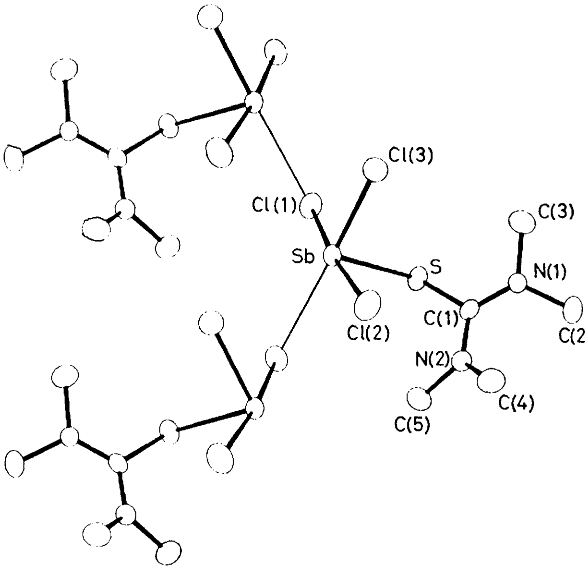

FIGURE 2 Three $SbCl_3$(tmtu) molecules showing the immediate Sb environment

Although the simplest interpretation would be to attribute the increases in negative shifts to increases in ionic characters and closer approaches to the *ionic* 5s^2 configuration, the true picture is undoubtedly more involved. There has been much discussion concerning the nature of the bonding in compounds of main-group elements. This applies especially to the question of whether or not *d* orbitals are significant to σ-bond formation.[1,17-20] In the case of tin(II) chemistry, 1 : 1 complexes between tin(II) acceptors and various unidentate donors are well known. This is consistent with the available 5*p* orbital in tin-acceptor compounds.[21] However, for adducts of antimony(III) and tellurium(IV) and 1 : 2 complexes with tin(II), simple descriptions in terms of hybridisation language place considerable weight on the importance of *d*-orbital participation because the co-ordination number then exceeds four (including lone pairs) and sp^3 hybridisation becomes inadequate. This model requires the use of *d* orbitals in order to accommodate the excess of electrons. Thus, in order to form a complex with a donor molecule, antimony(III) and tellurium(IV) would have to make use of their 5*d* orbitals in sp^3d and sp^3d^2 hybrids respectively. For tin compounds at least, this has been considered unlikely in view of the energy separation between the tin 5*p* and 5*d* orbitals.[21]

TABLE 3

^{121}Sb Mössbauer parameters for some antimony(III) chloride complexes at 4.2 K. Chemical shifts are relative to InSb[a]

Complex	δ/mm s^{-1}	eQV_{zz}/mm s^{-1}	Γ/mm s^{-1}	Ref.
$[NEt_4][SbCl_4]$	-7.47	$+10.6$	3.3	15
	-8.17	$+8.9$	2.6	*b*
$[C_5H_5NH][SbCl_4]$	-7.98	$+9.1$	2.2	15
	-8.10	$+11.3$	3.6	*b*
$SbCl_3(C_6H_5NH_2)$	-6.3	$+12.0$	3.0	*a*
$SbCl_3(C_6H_5OC_2H_5)$	-6.1	$+13.2$	2.9	*a*
$SbCl_3(COPh_2)$	-5.8	$+14.0$	2.8	*a*
$SbCl_3(C_6H_5COCH_3)$	-6.5	$+14.6$	2.8	*a*

[a] L. H. Bowen, K. A. Taylor, H. K. Chin, and G. G. Long, *J. Inorg. Nucl. Chem.*, 1974, **36**, 101. [b] J. G. Ballard, T. Birchall, J. B. Milne, and W. D. Moffett, *Can. J. Chem.*, 1974, **52**, 2376.

In addition to these considerations, the assumption that the physical foundation of the VSEPR model is the Pauli Exclusion Principle, which forces electron pairs to occupy different regions of space, has been questioned.[22] On the basis of extended Hückel theory, Hall[23,24] suggests that the only important Pauli repulsions in covalent molecules are those between bond pairs, and that lone pair stereochemical activity results, not primarily from Pauli forces, but from the systems desire to lower its total energy through maximum population of the lower-energy valence *s* orbital. This end is achieved through appropriate distortions.

An explanation for the increased *s*-electron densities and the signs and magnitudes of the quadrupole interactions is therefore sought in terms of an essentially covalent framework where the bonding is described by using a qualitative molecular-orbital model without recourse to significant 5*d* involvement, although it should be remembered that small contributions from higher orbitals are contained within the total wavefunctions. For $SbCl_4^-$ (point group C_{2v}) the 5*s* and 5*p* valence orbitals on antimony transform irreducibly as $A_1(s)$, $B_1(p_x)$, $B_2(p_y)$, and $A_1(p_z)$. Following a similar description of the electronic structures of the antimony(III) halides [20] the electronic structure is represented by four lowest-energy ($1a_1$, $1b_1$, $1b_2$, $2a_1$) bonding levels, which possess major ligand character, and a higher-energy level largely associated with the antimony lone pair. The latter can be identified with the $3a_1$ (antibonding) level, as the crystallographic environment of the antimony atom is consistent with the lone pair being directed along the symmetry axis. Since the antimony 5s and $5p_z$ orbitals have the same symmetry they can mix, so that the $3a_1$ level represents a large degree of the overall 5s contribution to the lone pair. The lone pair is now explicitly described in terms of contributions from a number of a_1 symmetry molecular orbitals and its stereochemical activity is mainly attributable to the balance attained between bonding and antibonding a_1 orbitals. The long axial bonds are identified with the a_1 levels and, consistent with their close to 90° equatorial bond angles, the equatorial Sb-Cl bonds are predominately associated with the $1b_1$ and $1b_2$ levels. A similar description applies to the aniline and tetramethylthiourea adducts but with the distinction that, as these complexes are asymmetric (C_1 point group) with all atomic orbitals transforming irreducibly as A, the bonding and antibonding levels are no longer symmetry restricted as to s or p character.

For fifth-row elements, the large sizes of the lower-valent central atoms reduce the importance of Pauli repulsions between bonds. A number of crystal structures on tin(II) and antimony(III) complexes (*e.g.* refs. 1, 25, 26 and see above) with this stereochemistry show that the equatorial angles are close to 90° for non-chelating and non-second-row donors. The chemical shifts and bond angles are considered to reflect the desire of these systems to maximise 5s occupation; hence the s-electron densities are a consequence of the high degrees of p character in the equatorial bonds and concomitant large s-orbital admixtures in the lone pair as the systems move, within the constraints imposed by the crystal lattices, towards maximum population of the lower-energy valence s orbital.

The quadrupole coupling constant, eQV_{zz}, contains information on the relative distributions of antimony $5p$ electron densities over the bonds and lone pair. In covalent compounds such as these the major contributions to quadrupole interactions at the antimony nuclei arise out of subtle imbalances in $5p$ orbital occupations caused by deviations of the *electronic* environments from cubic symmetry. The C_{2v} and C_1 point groups imply deviations from cylindrical symmetry (*i.e.* p_x and p_y orbital degeneracies are lifted) and there is accordingly no constraint on the asymmetry parameter (η) to be zero, and the principal axis of the electric field gradient (e.f.g.) tensor is therefore not uniquely defined by symmetry. The e.f.g. axes, signs and magnitudes of the quadrupole interactions depend on the orderings and relative energies of the molecular orbitals associated with antimony.

The signs of the quadrupole coupling constants for $SbCl_3$(tmtu) and the complexes listed in Table 3 are positive. The sign of the principal component, V_{zz}, of the e.f.g. tensor is therefore negative since Q for ^{121}Sb is negative. The principal electric field axis is identified with the direction of the lowest degree of $5p$ orbital delocalisation into the molecular orbitals.[9] Accordingly, the negative V_{zz} stems from higher admixtures of $5p_x$ and $5p_y$ electron density into the $1b_1$ and $1b_2$ levels than is the case for $5p_z$ admixtures into a_1 levels. The direction of the principal axis is identified as lying either along (C_{2v}) or near (C_1) the remaining equatorial direction expected for the lone pair; in the asymmetric cases the lone pair is not solely restricted as to s or p_z character. Interestingly, cases are known where V_{zz} is positive,[15] which means that the a_1 levels with highest p_z admixtures now lie below $1b_1$ and $1b_2$ with the principal axis lying in the vicinity of the 'axial' ligands. For the present compounds, the magnitudes of eQV_{zz} indicate significant energy differences between the relevant a_1 and lower lying $1b_1$ and $1b_2$ levels as would be expected for relatively strong $5p_x$ and $5p_y$ contributions to equatorial bonding.

The Tetramethylthiourea Ligand.—Tetramethylthiourea has recently been studied in the gas phase by electron diffraction.[27] The bond lengths (Å) are: S-C [1.673(3)], C-N [1.388(5)], N-Me [1.461(3)]. *X*-Ray [28,29] and neutron [30] diffraction show that thiourea itself is planar to within 0.01 Å, excluding those hydrogen atoms engaged in hydrogen bonding. This would be expected of a system with delocalised π molecular orbitals involving the nitrogen atoms. However, in the case of tmtu both the present work and that of Fernholt *et al.*[27] reveal a pyramidal configuration at the nitrogen atoms with pyramid heights of 0.11 Å (electron diffraction) and 0.10, 0.05 Å (this work). Similar observations are reported by Åse and Roti.[31]

Bond distances and angles for tmtu in $SbCl_3$(tmtu) are within the previously observed range for tmtu adducts.[4,5,31] The lengthening of the S-C bond on complexation is a measure of metal-thiourea bond strength.[32] In $SbCl_3$(tmtu) the S-C bond length [1.772(7) Å] is considerably longer than that in the uncomplexed molecule but similar to the value observed for strongly bound thiourea in sulphatobis(thiourea)tin(II),[32] thereby indicating that the Sb-S bond is relatively strong. The Sb-S-C bond angle is within the range (106—116°) usually found [33] for metal-sulphur-carbon angles in transition-metal-thiourea complexes thought to contain σ bonds formed by sulphur atoms donating electrons from non-bonding sp^2 lobes.

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