Antimony(III) Acetate and Thioacetate: Spectra and Crystal Structures

By **Michael Hall** and **D. Bryan Sowerby**,* Department of Chemistry, University of Nottingham, Nottingham NG7 2RD

Antimony(III) tris(monothioacetate) has been prepared from thioacetic acid and antimony(III) oxide as a water-stable compound, in contrast to the extreme instability to water of the analogous triacetate. *X*-Ray structure determinations, however, show similar molecular structures for the two compounds. Crystals of antimony triacetate are monoclinic, space group $P2_1$, $Z = 2$, with $a = 7.463(5)$, $b = 9.346(5)$, $c = 7.740(5)$ Å, and $\beta = 116.20(5)°$, whereas those of antimony tris(monothioacetate) are monoclinic, space group $P2_1/c$, $Z = 4$, with $a = 8.884(5)$, $b = 16.819(5)$, $c = 8.964(5)$ Å, and $\beta = 117.26(5)°$. Primary bonding in the former is to three oxygen atoms (mean Sb–O, 2.06 Å) but to three sulphur atoms (mean Sb–S, 2.47 Å) in the latter. Vibrational spectra suggest the presence of secondary bonding in both compounds, which has been confirmed by the observation of three weak intramolecular interactions (Sb–O, 2.596—2.775 Å in the acetate and 2.745—2.918 Å in the thioacetate). One of the ligands, in addition to behaving as a chelate, bridges between molecules (Sb–O, 2.600 and 3.043 Å for the acetate and thioacetate respectively) leading to polymeric chains in the solid. The overall coordination polyhedron, which includes the stereochemically active lone pair, is best described in terms of a distorted dodecahedron.

RECENT *X*-ray crystallographic investigations are providing an increasing number of instances where atom separations are longer than those usually accepted as being representative of a single bond but which are well within the sum of the appropriate van der Waals' radii. This is often referred to as secondary bonding [1] and occurs in many carboxylate compounds. We have recently shown that secondary bonding is important in the structures of $[SbPh_3(O_2CMe)_2]$,[2] $[SbPh_4(O_2CMe)]$,[3] and $[SbPh_2(O_2CMe)]$,[4] but in contrast, the formate [5] $[SbPh_4(O_2CH)]$ shows little extra bonding. To extend this work it seemed appropriate to consider the structures of antimony(III) triacetate [6] and the previously unknown antimony(III) tris(monothioacetate), and to compare these with the antimony(III) tris(trifluoroacetate) structure.[7]

DISCUSSION

Antimony triacetate, which is readily prepared by refluxing a mixture of antimony(III) oxide and acetic anhydride,[6,8] can be recrystallised as extremely hygroscopic white crystals from a mixture of acetic anhydride and acetic acid.

Although i.r. data have been interpreted as indicating basically unidentate acetate groups in the solid state, the small (285 cm^{-1}) separation between the two C–O stretches,[9] the complexity of these bands, and the simplification of the spectrum in a chloroform solution all point to the presence of secondary bonds.

Antimony tris(monothioacetate), reported here for the first time, results when thioacetic acid and antimony(III) oxide are heated to 50 °C in hexane as shown in the equation. (The As and Bi analogues can be prepared

$$Sb_2O_3 + 6CH_3COSH \longrightarrow 2Sb(SOCCH_3)_3 + 3H_2O$$

similarly.[10]) A low-temperature reaction is necessary or the solutions become increasingly orange, finally depositing the orange-red antimony(III) sulphide. The compound dissolves in a range of organic solvents, but surprisingly it appears to be completely unaffected by moisture. When freshly prepared it is white, but on standing it develops an orange colouration presumably due to surface decomposition to Sb_2S_3.

Vibrational and Mass Spectra.—Infrared and Raman data for solid samples of the monothioacetate are summarized in Table 1 and indicate conclusively that the major bonding is between antimony and the sulphur atoms of the thioacetate group, in agreement with the 'soft' character of antimony(III). The region around 1 640 cm^{-1} contains at least two C=O stretching modes indicative of secondary bonding. The strong complex bands at *ca.* 380 and 260 cm^{-1} have been assigned respectively to the stretching and deformation of the SbS_3 unit in accordance with assignments given previously for SbS_4 [3,11] and thioantimonites of the type $Sb(SR)_3$ (R = aryl group).[12]

TABLE 1

Vibrational data for solid $[Sb(SOCMe)_3]$

Infrared	Raman	Assignment
	1 652m	$\nu(CO)$
1 640s	1 642m	
1 627s	1 632w	
1 410w	1 420w	$\delta_a(CH_3)$
1 353m		$\delta_s(CH_3)$
1 147s		$\rho(CH_3)$
1 112s		
960m	958w	$\nu(C–C)$
640s	648m	$\nu(C–S)$
	644 (sh)	
512m	512w	$\delta(C–C)$
	494w	
385m	384m	$\nu_a(SbS_3)$
	374m	$\nu_s(SbS_3)$
265vs	262vs	$\delta(SbS_3)$
	256 (sh)	
	130m	
	50s	

Mass spectrometric data for antimony-containing species, expressed as a percentage of the ion current generated by species with $m/e \geqslant 42$, are listed for the acetate and thioacetate in Table 2. The data clearly point to the greater stability of the thioacetate and the presence of *S*- rather than *O*-bonding. Although both molecules give only weak parent-ion signals, there is high intensity for the ion resulting from the loss of one ligand group in the thioacetate spectrum while the analogous species from the acetate is still of very low intensity. In a similar way, ions arising by the partial or complete loss of the second and third ligands are of higher intensity for the thioacetate but the differences with the acetate here are less marked. Of the species not included in Table 2, there is high intensity for the CH_3CO^+ ion from the thioacetate which is 30 times stronger than the alternative CH_3CS^+ fragment ion. For the acetate, major current-carrying species are CH_3COOH^+, $C_2H_5O^+$, CO^+, and H_2O^+.

TABLE 2

Mass spectra of [Sb(XOCMe)$_3$], showing intensities of antimony containing ions as % ion current carried by species with *m*/*e* > 42

Ion	X = O	X = S
$Sb(XOCMe)_3$	Trace	0.1
$SbX(XOCMe)_2$		0.3
$Sb(XOCMe)_2$	0.7	41.0
$Sb(XOCMe)X_2H$		0.3
$Sb(XOCMe)XH$	0.3	1.6
$Sb(XOCMe)X$	0.2	0.4
SbX_3H_2/SbX_3H		0.3
$Sb(XOCMe)CH_3$		0.1
$Sb(XOCMe)$	0.1	0.4
SbX_2H_2	0.1	1.5
SbX_2H		0.2
SbX_2	0.1	0.4
$SbXH$	0.1	
SbX	0.1	6.6
Sb	0.1	0.4

These experimental data give little direct information on the extent of secondary bonding, which if substantial would lead to systems based on seven or more electron pairs.

Crystal Structure of [Sb(O_2CMe)$_3$].—*Crystal data.* $C_6H_9O_6Sb$, $M = 298.9$, Monoclinic, $a = 7.463(5)$, $b = 9.346(5)$, $c = 7.740(5)$ Å, $\beta = 116.20(5)°$, $U = 484.4$ Å^3, $Z = 2$, $D_c = 2.05$ g cm^{-3}, $F(000) = 288$, space group $P2_1$, from systematic absences and subsequent refinement, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 28.8 cm^{-1}, crystal dimensions *ca.* 0.6 × 0.5 × 0.5 mm, $\mu R = 0.72$.

The unit-cell parameters, initially obtained from oscillation and Weissenberg photographs, were refined by a least-squares procedure on the positions of 23 strong reflections on a Hilger and Watts four-circle diffractometer. Intensity data were then collected using an ω—2θ scan for 1 523 reflections in the range $0 \leqslant \theta \leqslant 30°$ using Mo-K_α radiation. The intensities of the 1 347 reflections for which $I > 3\sigma(I)$ were corrected for Lorentz and polarization effects but no absorption correction was necessary. Data reduction and subsequent crystallographic calculations used the CRYSTALS programs;[13] atomic scattering factors were taken from reference 14.

The position of the antimony atom was obtained from a three-dimensional Patterson synthesis and after two cycles of refinement with the *y* co-ordinate fixed, a difference-Fourier synthesis phased by this atom gave a set of peaks which were incompatible with space group symmetry $P2_1/m$ in which the antimony atom would necessarily lie on the special position $x, \frac{1}{4}, z$. In $P2_1$ symmetry, the Fourier output could be interpreted in terms of three oxygen atoms bonded to antimony and the expected set of mirror-image peaks. A set of three chemically consistent oxygen atoms were chosen for further refinement in the space group $P2_1$. After three cycles of full-matrix refinement, a second difference-Fourier synthesis revealed the presence of the remaining non-hydrogen atoms. Convergence at *R* 8.6% occurred after four cycles with isotropic thermal parameters and at *R* 6.2% after four cycles with anisotropic thermal parameters. Application of a four-coefficient Chebyshev weighting scheme followed by four cycles of refinement gave final convergence at *R* 5.2%. A final difference-Fourier synthesis showed high residual electron density (*ca.* 2 e Å^{-3}) in the vicinity of the antimony atom, probably a function of the data, and it was not possible to locate the methyl group hydrogen atoms.

Crystal Structure of [Sb(SOCMe)$_3$].—*Crystal data.* $C_6H_9O_3S_3Sb$, $M = 347.1$, Monoclinic, $a = 8.884(5)$, $b = 16.819(5)$, $c = 8.964(5)$ Å, $\beta = 117.26(5)°$, $U = 1\,190.7$ Å^3, $Z = 4$, $D_c = 1.94$ g cm^{-3}, $F(000) = 672$, space group $P2_1/c$ from systematic absences, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 28.2 cm^{-1}, crystal dimensions *ca.* 0.5 × 0.3 × 0.25 mm, $\mu R = 0.42$.

Oscillation and Weissenberg photographs clearly showed that this compound was not isomorphous with the triacetate. Data were collected for 1 841 reflections in the range $0 \leqslant \theta \leqslant 25°$ for which $I > 3\sigma(I)$ and were corrected for Lorentz and polarization effects but again an absorption correction was not necessary. A possible position for the antimony atom was obtained from a three-dimensional Patterson synthesis and a difference-Fourier synthesis phased on the refined antimony position revealed three sulphur atoms bonded to the heavy atom. After three cycles of refinement, a second difference Fourier gave positions for all the remaining non-hydrogen atoms. The refinement converged at *R* 8.3% after four cycles with isotropic thermal parameters and at *R* 3.8% after four cycles with anisotropic

TABLE 3

Fractional co-ordinates (× 10^4), with estimated standard deviations in parentheses, for [Sb(O_2CMe)$_3$]

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Sb(1)	277.5(6)	0	920.8(5)
O(1)	−708(10)	−1 684(10)	1 908(11)
C(1)	−2 623(15)	−1 525(13)	1 164(16)
C(4)	−3 718(17)	−2 660(14)	1 734(19)
O(4)	−3 431(11)	−512(10)	99(13)
O(2)	2 916(10)	−560(8)	3 232(10)
C(2)	4 099(17)	542(16)	3 590(16)
C(5)	6 099(19)	407(21)	5 303(24)
O(5)	3 499(15)	1 620(11)	2 545(14)
O(3)	−291(10)	1 206(8)	2 905(9)
C(3)	−1 043(12)	2 436(11)	2 123(11)
C(6)	−1 615(20)	3 446(17)	3 252(20)
O(6)	−1 226(13)	2 762(8)	492(11)

thermal parameters. Again, the final difference Fourier gave no evidence for the hydrogen-atom positions. Residual electron density >0.2 e $Å^{-3}$ was in the vicinity of either the heavy atoms or the carbon atoms of the methyl groups.

Final atomic co-ordinates for the acetate and thioacetate are collected in Tables 3 and 4 respectively.

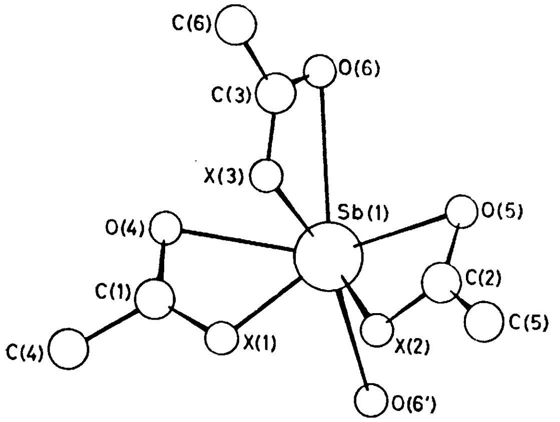

FIGURE 1 View of the molecule and numbering of the atoms; X = O for $[Sb(O_2CMe)_3]$ and X = S for $[Sb(SOCMe)_3]$

Observed and calculated structure factors and anisotropic thermal parameters for both compounds are listed in Supplementary Publication No. SUP 22769 (33 pp.).* The numbering of the atoms is shown in Figure 1.

Discussion of the Structures.—The bond distance and angle data, summarized in Tables 5 and 6 respectively, show that for both compounds the bonding is primarily of the AB_3E type. In the acetate the three Sb–O distances have a mean value of 2.06 Å and the differences are probably not significant. The Sb–S bonds are more closely similar with a mean distance of 2.469 Å. The Sb–O distance is comparable to that in $[Sb(O_2CCF_3)_3]$ (2.043 Å),[7] but substantially shorter than that in $[SbPh_2(O_2CMe)]$ (2.137 Å),[4] reflecting probably the reduced Lewis acidity in the latter compound as a result of the lower electronegativity of the phenyl groups. For comparison Sb–S distances of 2.487, 2.626, and 2.631 Å were found for antimony(III) diethyldithiocarbamate,[15] and 2.43 Å in antimony(III) hydrogenbis(thioglycolate).[16]

TABLE 4

Fractional co-ordinates (× 10^4) with estimated standard deviations in parentheses, for $[Sb(SOCMe)_3]$

Atom	*x/a*	*y/b*	*z/c*
Sb(1)	2 669.1(5)	1 782.3(2)	567.4(4)
S(1)	4 632(2)	1 193(1)	−394(2)
C(1)	6 250(8)	1 202(4)	1 674(8)
C(4)	7 980(9)	913(5)	1 978(11)
O(4)	5 967(6)	1 410(3)	2 818(5)
S(2)	488(2)	1 449(1)	−2 289(2)
C(2)	−1 093(9)	1 785(3)	−1 784(8)
C(5)	−2 897(10)	1 736(4)	−3 119(9)
O(5)	−699(6)	2 035(3)	−374(6)
S(3)	2 238(2)	531.5(8)	1 745(2)
C(3)	2 621(7)	976(3)	3 661(7)
C(6)	2 607(10)	410(5)	4 958(8)
O(6)	2 875(8)	1 672(3)	3 905(6)

TABLE 5

Bond distances (Å) with estimated standard deviations in parentheses for $[Sb(XOCMe)_3]$, X = O and X = S

	X = O	X = S
Sb(1)–X(1)	2.025(9)	2.479(2)
Sb(1)–X(2)	2.059(7)	2.466(2)
Sb(1)–X(3)	2.094(6)	2.461(1)
Sb(1)–O(4)	2.596(9)	2.763(5)
Sb(1)–O(5)	2.643(10)	2.745(5)
Sb(1)–O(6)	2.775(8)	2.918(5)
Sb(1)–O(6') *	2.600(8)	3.043(4)
C(1)–X(2)	1.29(1)	1.750(7)
C(2)–X(2)	1.30(1)	1.754(7)
C(3)–X(3)	1.30(1)	1.757(5)
C(1)–O(4)	1.23(1)	1.213(8)
C(2)–O(5)	1.24(2)	1.222(8)
C(3)–O(6)	1.25(1)	1.193(7)
C(1)–C(4)	1.52(2)	1.513(10)
C(2)–C(5)	1.50(1)	1.500(10)
C(3)–C(6)	1.47(2)	1.508(9)

* This atom is related to O(6) by the transformation $x, y, z \longrightarrow \bar{x}, y - \frac{1}{2}, \bar{z}$ for X = O and $x, y, z \longrightarrow x, \frac{1}{2} - y, z - \frac{1}{2}$ for for X = S.

The angles between these primary bonds, with mean values of 83.9 and 90.4° respectively for the acetate and

TABLE 6

Bond angles (°) with estimated standard deviations in parentheses for $[Sb(XOCMe)_3]$, X = O and X = S

X(1)–Sb(1)–X(2)	80.9(3)	83.79(5)
X(1)–Sb(1)–X(3)	85.2(3)	94.59(6)
X(2)–Sb(1)–X(3)	85.7(3)	92.79(5)
X(1)–Sb(1)–O(4)	54.8(3)	58.9(1)
X(2)–Sb(1)–O(5)	54.0(3)	59.2(1)
X(3)–Sb(1)–O(6)	52.0(2)	57.0(1)
X(1)–Sb(1)–O(5)	132.2(3)	142.8(1)
X(1)–Sb(1)–O(6)	125.0(3)	127.4(1)
X(1)–Sb(1)–O(6') *	75.2(3)	87.8(1)
X(2)–Sb(1)–O(4)	132.3(3)	140.6(1)
X(2)–Sb(1)–O(6)	121.4(3)	134.5(1)
X(2)–Sb(1)–O(6')	80.1(3)	83.1(1)
X(3)–Sb(1)–O(4)	74.9(3)	79.3(1)
X(3)–Sb(1)–O(5)	77.2(3)	84.4(1)
X(3)–Sb(1)–O(6')	157.4(2)	175.0(1)
O(4)–Sb(1)–O(5)	150.4(3)	154.4(2)
O(4)–Sb(1)–O(6)	79.1(3)	71.9(2)
O(4)–Sb(1)–O(6')	102.0(3)	105.6(2)
O(5)–Sb(1)–O(6)	76.1(3)	82.7(2)
O(5)–Sb(1)–O(6')	107.6(3)	91.1(2)
O(6)–Sb(1)–O(6')	150.3(1)	124.5(1)
Sb(1)–X(1)–C(1)	104.9(7)	89.7(2)
Sb(1)–X(2)–C(2)	106.4(7)	90.0(2)
Sb(1)–X(3)–C(3)	108.6(6)	93.3(3)
Sb(1)–O(4)–C(1)	79.8(6)	90.5(4)
Sb(1)–O(5)–C(2)	80.6(7)	91.2(4)
Sb(1)–O(6)–C(3)	78.1(6)	87.5(4)
Sb(1)–O(6')–C(3')	134.0(8)	151.5(4)
Sb(1)–O(6')–Sb(1')	128.9(3)	117.3(2)
X(1)–C(1)–O(4)	120(1)	120.7(5)
X(1)–C(1)–C(4)	115(1)	117.5(5)
O(4)–C(1)–C(4)	125(1)	121.8(6)
X(2)–C(2)–O(5)	119(1)	119.6(5)
X(2)–C(2)–C(5)	116(1)	117.7(5)
O(5)–C(2)–C(5)	125(1)	122.7(7)
X(3)–C(3)–O(6)	121(1)	122.1(5)
X(3)–C(3)–C(6)	118(1)	114.7(5)
O(6)–C(3)–C(6)	121(1)	123.1(6)

* See footnote to Table 5.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

thioacetate, point to a basically pyramidal structure, pseudo-tetrahedral if the stereochemically active lone pair is included in the primary co-ordination polyhedron.

The presence of secondary bonding in both compounds is not surprising but it is a little unusual that in both compounds two of the ligands act as unsymmetrical chelates while the third is effectively tridentate (bridging-chelating). The latter links the molecules into polymeric chains parallel to the *b* axis in the acetate and to the *c* axis in the thioacetate (see Figures 2 and 3). All the secondary bonding involves donation of electron density from oxygen atoms to antimony with distances ranging between 2.60 and 3.04 Å. The antimony and oxygen van der Waals' radii sum to 3.6 Å and the distances above are equivalent to partial bond orders [17] from 0.12 to 0.02, if the single Sb–O distance is taken as 2.05 Å.

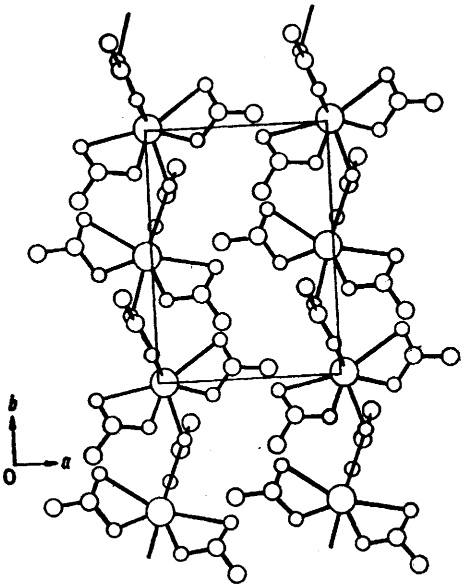

FIGURE 2 Projection of the unit-cell contents down *c* for $[Sb(O_2CMe)_3]$

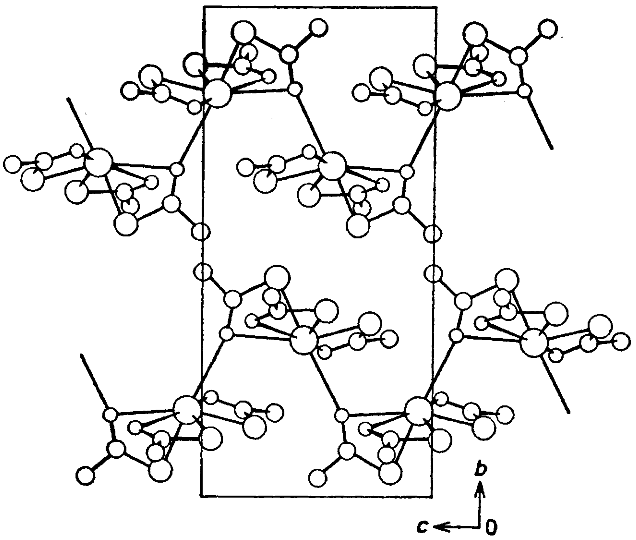

FIGURE 3 Projection of the unit-cell contents down *a* for $[Sb(SOCMe)_3]$

The pattern of secondary bonding in the two compounds is very similar but the following differences should be noted. (a) Intramolecular interactions in the thioacetate (mean, 2.81 Å) are much weaker than those in the acetate (mean, 2.67 Å), a consequence probably of the decreased Lewis acidity of the antimony when attached primarily to the less electronegative sulphur atoms.

(b) The intermolecular bonding is weaker in the thioacetate as shown by the increase in the Sb(1)–O(6′) bond length from 2.60 Å in the acetate to 3.04 Å in the thioacetate. Paralleling this increase is the decrease in melting point from 123 °C for the acetate to 61 °C for the thioacetate. Antimony(III) trifluoroacetate, which melts at *ca.* 115 °C, has a structure in which the primary Sb–O bonding (2.04 Å) is supplemented by three intramolecular contacts at 2.87 Å and three intermolecular ones at 3.04 Å.[7]

(c) The bridging character of the tridentate ligand is more pronounced in the acetate [Sb(1)–O(6′) 2.60 Å, Sb(1)–O(6) 2.775 Å] while for the thioacetate the chelating tendency is the more pronounced [Sb(1)–O(6) 2.918 Å, Sb(1)–O(6′) 3.043 Å].

In general, the carbon–oxygen distances of the ' non-bonded ' oxygen atoms parallel the extent of secondary bonding and there is less π character in those from the acetate (mean C–O, 1.24 Å) compared with the corresponding thioacetate groups (mean C–O, 1.21 Å).

The molecular flexibility necessary for supporting the chelate structures occurs at the Sb–X–C angles which average 106.6° for the acetate and 91.0° for the thioacetate. The lower angle at the sulphur atom partially compensates for the increased Sb–S and C–S bond distances and enables the ' non-bonded ' oxygen to approach the antimony more closely and so maximise the secondary bonding. Although there is no imposed crystallographic symmetry in either molecule, there is an approximate mirror plane which includes the tridentate ligand, the central antimony atom and the bridging oxygen atom [O(6′)] (see Table 7).

TABLE 7

Molecular planes

Atoms in plane	Deviations (Å) from the best plane
Sb(1) O(3) O(6) O(6′)	Sb(1) 0.04, O(3) −0.01, O(6) −0.01, O(6′) −0.02, O(1) −1.19, O(2) 1.46 O(4) −2.48, O(5) 2.58
Sb(1) S(3) O(6) O(6′)	Sb(1) 0.08, S(3) −0.04, O(6) 0.00, O(6′) −0.03, S(1) −1.91, S(2) 1.38, O(4) −2.67, O(5) 2.66

Before considering the overall co-ordination polyhedron, it is interesting to note the relationship between the secondary bonds and the basic pseudo-tetrahedral $\colon SbX_3$ unit. As shown in Figure 4, interaction with the oxygen atoms of the two bidentate groups takes place above the lone pair–X(1)–X(3) and lone pair–X(2)–X(3) triangular faces of the tetrahedron, while the third intramolecular interaction occurs along the lone pair–X(3) edge. The polyhedron is completed by the intermolecular bond which places the O(6′) atom above the lone pair–X(1)–X(2) face. The antimony atom in both compounds is thus in effective eight-fold co-ordination and the resulting geometry is best described as a distorted dodecahedron. In this respect, there is a similarity between the structures described here and those previously determined for antimony(III) and bismuth(III) diethyldithiocarbamates.[15]

Although the acetate and thioacetate crystallize in different space groups, the overall structures are very similar. Rather surprisingly, the corresponding trifluoroacetate has crystallographically imposed three-fold symmetry (space group, $P4_332$) and when the secondary bonding is considered the antimony is in effective ten-fold co-ordination.[7] The nine oxygen atoms occupy the corners of a distorted tricapped-trigonal prism with the lone pair being accommodated above one of the triangular faces. It is clear that because of its weakness, secondary bonding will be modified by minor changes in both electronic and steric factors associated with the ligands and changes such as those found for the trifluoroacetate on one hand and the acetate and thioacetate on the other are to be expected.

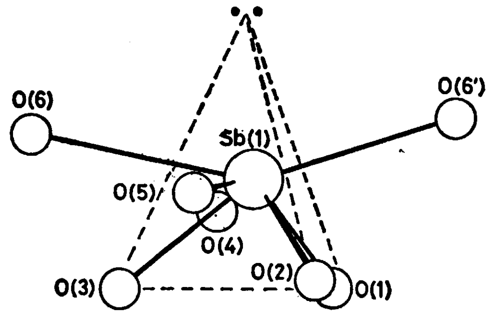

FIGURE 4 The secondary bonding in $[Sb(XOCMe)_3]$ in relation to the $:SbX_3$ pseudo-tetrahedral unit

EXPERIMENTAL

Antimony Triacetate.—The compound was prepared by the method of Nerdel and Kleinwächter [8] and was stored under acetic anhydride until required.

Antimony Tris(monothioacetate).—Antimony(III) oxide (3.0 g, 0.01 mol) was suspended in n-hexane (100 cm^3) and an excess of thioacetic acid (5 g) in n-hexane (20 cm^3) was added. The mixture was heated to 50 °C and the clear solution decanted from any remaining solid. On cooling an oil separated which on recrystallization from hot n-hexane gave white crystals. Yield: 1.8 g, 49%. M.p. 61—62 °C (Found: C, 20.8; H, 2.9. Calc. for $C_6H_9O_3S_3Sb$: C, 21.0; H, 2.7%).

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