APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2002; **16**: 155–159

Syntheses and structures of $Me_3Sb^+CH_2COO^-\cdot H_2O$, the monohydrate of the antimony analogue of betaine, and related compounds

Gàbor Balàzs, Lucia Balàzs, Hans J. Breunig* and Enno Lork

Institut für Anorganische und Physikalische Chemie, Fachbereich 2 der Universität Bremen, D-28334 Bremen, Germany

Received 18 June 2001; Accepted 19 October 2001

The syntheses of the antimony analogue of betaine, $Me_3Sb^+CH_2COO^-$ (1), of the precursor $[Me_3SbCH_2COOH][Br]$ (2) and of $[Me_3SbCH_2COOCH_2CH_3][Br]$ (3) are reported. A new method for the synthesis of solvent-free Me_3Sb is described. The structures of $1\cdot H_2O$ and 3 were determined by single crystal X-ray diffractometry. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: antimony; betaine; X-ray structure

Analogues of betaine, $Me_3N^+CH_2COO^-$, with the heavier pnicogens as central atoms play important roles in the biological and environmental chemistry of the respective elements.[1–4] A representative example is arsenobetaine, $Me_3As^+CH_2COO^-$, which can be found in fish used as sea food or in other biological samples and takes part in processes leading to detoxification and transport of arsenic in environmental systems.[3,4] The preparation of arsenobetaine is achieved by hydrolysis of $[Me_3As^+CH_2COOCH_2CH_3][Br]$ in a column filled with Dowex 2 in the OH form.[4]

Here we report the syntheses of the antimony analogue of betaine, $Me_3Sb^+CH_2COO^-$ (**1**), of the precursors trimethylantimony (Me_3Sb), $[Me_3SbCH_2COOH][Br]$ (**2**) and $[Me_3SbCH_2COOCH_2CH_3][Br]$ (**3**). Crystallographic characterization of **1** revealed a surprising structure of the monohydrate (**1**$\cdot H_2O$), where chains of hydrogen-bonded water molecules are guests in channels between stacks of the antimony component. **1** has not yet been detected in biological or environmental samples. However, antimony is present in different environments[5] and bioalkylation leading to Me_3Sb was recently reported.[6–10] Extended structures of water molecules in organic host crystals are a focus of current research.[11] The crystal structure of **3** is also reported.

RESULTS AND DISCUSSION

The synthesis of **1** is achieved in an overall yield of 90% by the reaction of pure Me_3Sb with excess bromoacetic acid in toluene with formation of the precursor compound **2** and subsequent elimination of HBr with Ag_2O in water. Me_3Sb[12] was prepared by heating Me_2SbBr at 160–180 °C and distillation from the resulting $MeSbBr_2$. An attempted synthesis of **1** by hydrolysis of **3** with Dowex 2 in the OH form or with KOH in water failed because of the formation of $Me_3Sb(OH)_2$ instead of antimony betaine. The stibonium compound **3** is easily accessible by reaction of bromo ethylacetate with Me_3Sb.

The synthetic pathways are summarized in Scheme 1.

Crystals of the monohydrate of antimony betaine (**1**) were obtained from methanol at 7 °C. **1**$\cdot H_2O$ crystallizes in the $P4_3$ space group with four molecules in the unit cell. The molecular structure, including the positions of the hydrogen atoms of water, was determined by X-ray crystallography. The structure consists of parallel helical stacks of $Me_3Sb^+CH_2COO^-$ and water, where the molecules are connected through Sb···O interactions and hydrogen bonds. The molecular structure and the neighbourhood of the $Me_3Sb^+CH_2COO^-$ molecule are shown in Fig. 1.

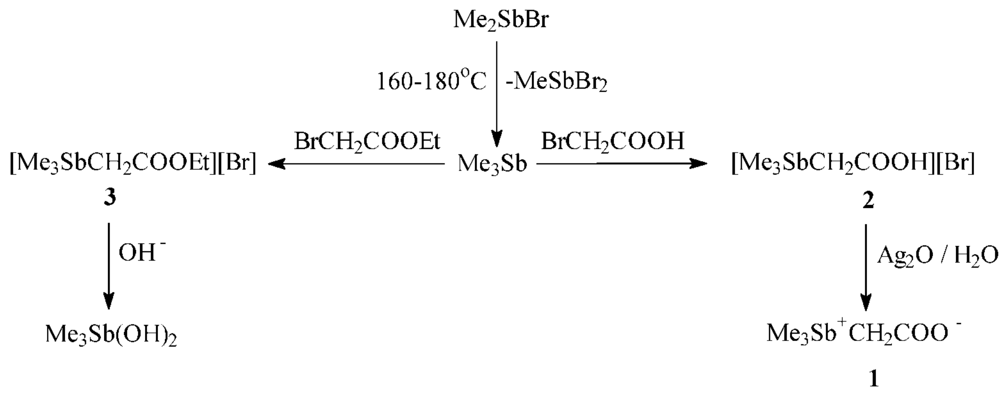
The antimony atom is situated in a distorted tetrahedral environment of the CH_3 and CH_2 carbon atoms. Two carboxylic oxygen atoms, one from the same molecule and the other from a neighbouring molecule, occupy capping positions. The Sb—C bonds range between 2.097(7) and 2.109(5) Å. These values compare well with the same distances in other stibonium compounds, cf. $[Me_4Sb]I_3$ [Sb—C, 2.092(7)–2.099(7) Å].[13] The Sb···O contact dis-

---

*Correspondence to: H. J. Breunig, Institut für Anorganische und Physikalische Chemie, Fachbereich 2 der Universität Bremen, D-28334 Bremen, Germany.

Contract/grant sponsor: University of Bremen.

DOI:10.1002/aoc.255



Scheme 1

tances—Sb(1)···O(2), 2.985(1); Sb(1)···O(2′) 2.992(3) Å—lie between the values expected for van der Waals interactions [$\sum(r_{vdW})$ Sb···O, 3.70 Å] and covalent bonds [$\sum(r_{cov})$ Sb—O, 2.07 Å]. One of the Sb···O contacts is intramolecular, and the other intermolecular. The former leads to an almost planar four-membered heterocycle with an Sb(1)—C(4)—C(5)—O(2) torsion angle of −3.1(6)°. The latter connects the $Me_3Sb^+CH_2COO^-$ units to tube-like stacks built of helical chains of molecules. Two of the methyl groups of each molecule of **1** are directed into the centre of the stacks. One of the oxygen atoms and one of the methyl groups are in an external positions. Channels between the parallel stacks of **1** contain the water molecules, which are also associated with stacks of helical chains with four molecules in the repeating unit. A view along the helical axes showing the 4/4 coordination of the stacks of **1** and H_2O is depicted in Fig. 2. Figure 3 shows a view perpendicular to these axes.

The water molecules are three-coordinated. They participate in a system of hydrogen bonds, which exist not only along the water helix but also between water molecules and carboxylic groups. The distances [O(1)···H(2), 1.96(9) Å, O(1)···O(3), 2.725(6) Å] correspond to hydrogen bonds of medium strength. The O(1)—H(1)···O(3) angle is 146.45(9)°. The O···O distance between water molecules is 2.840(6) Å, a

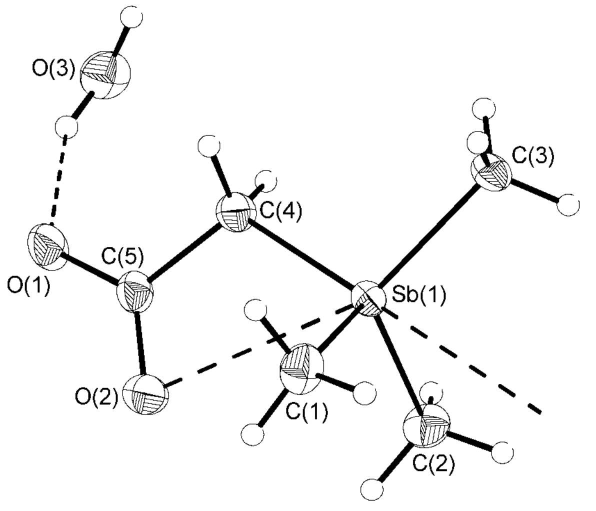


Figure 1. Molecular structure of $\mathbf{1}\cdot H_2O$. Thermal ellipsoids are drawn with 50% probability, except hydrogen atoms. Selected distances (Å) and angles (°): Sb(1)—C(1) 2.096(7), Sb(1)—C(3) 2.100(4), Sb(1)—C(2) 2.104(5), Sb(1)—C(4) 2.108(5), C(4)—C(5) 1.528(6), C(5)—O(2) 1.250(6), C(5)—O(1) 1.263(6), Sb(1)···O(2′) 2.99(1), Sb(1)···O(2) 2.993(3), O(1)···O(3) 2.722(6), O(3)—H(1) 0.75(6), O(3)—H(2) 1.01(10), O(1)···H(2) 1.81(11); C(1)—Sb(1)—C(3) 110.5(2), C(1)—Sb(1)—C(2) 112.1(2), C(5)—C(4)—Sb(1) 111.2(3), O(2)—C(5)—O(1) 126.6(4).

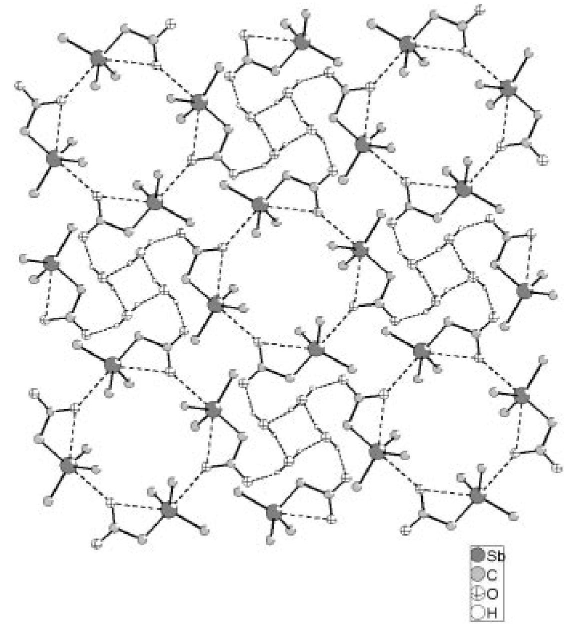


Figure 2. View of the crystal structure of $\mathbf{1}\cdot H_2O$ along the *c* axis, showing the tube-like helical stack of **1** in the centre surrounded by four water helices.

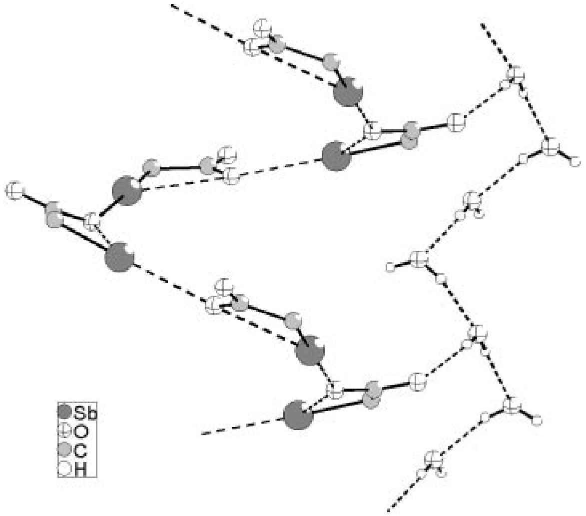


Figure 3. View of a section of the crystal structure of **1**·H_2O, showing the helical arrangements of **1** (left) and H_2O (right). The molecules of **1** surrounding the water helix have been partially omitted for clarity.

value that is similar to the O$\cdots$O distance of 2.85 Å in liquid water.[14]

The crystal structure of the analogous arsenobetaine monohydrate[4] is similar to the structure of **1**·H_2O with respect to the $Me_3E^+CH_2COO^-$ (E = As, Sb) units, but the arrangement of these units and the packing of the water molecules in the crystal is different. Crystals of arsenobetaine hydrate consist of dimers with bridging water molecules that differ considerably from the helical polymers in the crystal structure of **1**·H_2O.

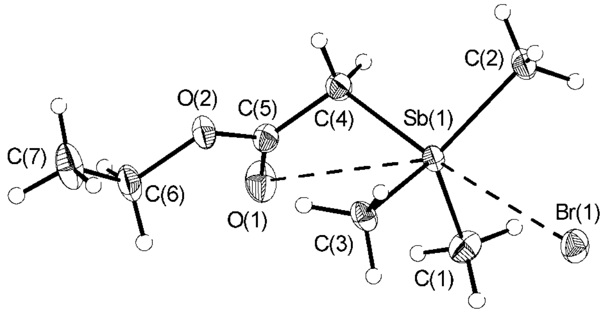


Figure 4. ORTEP representation of the structure of $[Me_3SbCH_2COOC_2H_5][Br]$ (**3**). Thermal ellipsoids are represented with 30% probability, except hydrogen atoms. Selected bond lengths (Å) and angles (°): Sb(1)—C(1) 2.095(6), Sb(1)—C(2) 2.099(5), Sb(1)—C(3) 2.108(5), Sb(1)—C(4) 2.157(5), O(1)—C(5) 1.209(7), O(2)—C(5) 1.334(7), C(4)—C(5) 1.475(7); C(1)—Sb(1)—C(2) 112.5(3), C(1)—Sb(1)—C(3) 109.9(2), C(2)—Sb(1)—C(3) 127.9(2), C(1)—Sb(1)—C(4) 101.3(2), C(2)—Sb(1)—C(4) 97.8(2), C(3)—Sb(1)—C(4) 102.3(2), C(5)—O(2)—C(6) 116.1(5), C(5)—C(4)—Sb(1) 112.1(3), O(1)—C(5)—O(2) 122.7(5), O(1)—C(5)—C(4) 125.5(5).

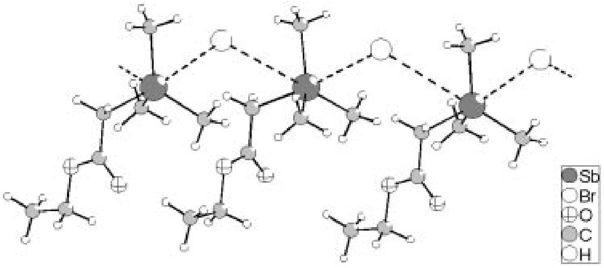


Figure 5. Chain structure of $[Me_3SbCH_2COOC_2H_5][Br]$ (**3**). Contact distances (Å) and angles (°): Sb$\cdots$Br 3.132(1) 3.755(1); Br$\cdots$Sb$\cdots$Br 96.74(1), Sb$\cdots$Br$\cdots$Sb 126.95(1).

The stibonium compounds $[Me_3SbCH_2COOH][Br]$ (**2**) and $[Me_3SbCH_2COOCH_2CH_3][Br]$ (**3**) are colourless solids; They have a low solubility in chloroform or acetone but have good solubility in methanol and water. **2** is a weak acid (p*K* 3.4) that decomposes within weeks with the formation of acetic acid when exposed to atmosphere. **3** is stable in the air in the solid state but decomposes slowly in solution.

Crystals of **3** suitable for X-ray crystallography were obtained from acetone at −28 °C after 2 weeks. **3** crystallizes in the monoclinic spacegroup *P*2(1)/*c* with four molecules in the unit cell. The structure contains stibonium ions in a distorted tetrahedral environment with two Br^- ions and one oxygen atom of the internal carboxylic group in capping positions. The molecular structure of **3** is depicted in Fig. 4.

The Sb−C bonds range between 2.095(6) and 2.157(5) Å, comparable with the Sb−C bonds in **1** [2.097(7)–2.109(5) Å]. The intramolecular Sb$\cdots$O contact distance in **3** [3.664(5) Å] is much longer than in **1**. The $CH_2COOCH_2CH_3$ group is almost planar (mean deviation 0.0087 Å). The bromide ions are in bridging positions involved in two different interactions with neighbouring cations [Sb$\cdots$Br, 3.132(9), 3.755(13) Å; Sb$\cdots$Br$\cdots$Sb, 126.96(0) °] to form zigzag chains. The structure of the chains is shown in Fig. 5.

1, 2 and **3** were also characterized by IR, ^1H, ^{13}C NMR spectroscopy, showing the expected signals, and by mass spectrometry (MS) using the fast atom bombardment (FAB) technique. In the FAB positive mass spectra of **1** and **2** the signals at highest mass correspond to molecular ions of the dimer with loss of a proton. The protonated monomeric form $[Me_3SbCH_2COOH]^+$ appears as a base peak. Other fragments result from the loss of the carboxyl group and the successive loss of methyl groups. In the FAB negative mass spectra of **2** and **3** were the fragments resulting from the attachment of an additional bromide ion observed as the base peaks. In the FAB positive spectra of **3** the most intensive signals result from the cation $[Me_3SbCH_2COOCH_2CH_3]^+$.

Table 1. Crystallographic data and measurements for **1**·H_2O and **3**

Compound	**1**·H_2O	**3**
Empirical formula	$C_5H_{13}O_3Sb$	$C_7H_{16}BrO_2Sb$
Formula weight	242.90	267.09
Temperature (K)	173(2)	173(2)
Crystal system	Tetragonal	Monoclinic
Space group	$P4_3$	$P2(1)/c$
a (Å)	10.865(2)	10.025(2)
b (Å)	10.865(2)	11.307(2)
c (Å)	7.084(2)	10.3280(10)
α (°)	90	90
β (°)	90	102.890(10)
γ (°)	90	90
Volume (nm^3)	0.8363(3)	1.1412(3)
Z	4	4
Diffractometer	Siemens P4	Siemens P4
Crystal size (mm^{-3})	0.80 × 0.30 × 0.20	0.8 × 0.6 × 0.5
$F(000)$	472	640
θ range (°)	2.65 to 27.50	2.71 to 27.50
Index range	$-14 \leq h \leq 1, -14 \leq k \leq 1, -9 \leq 1 \leq 1$	$-1 \leq h \leq 13, -1 \leq k \leq 14, -13 \leq 1 \leq 13$
Absorption coeff. (mm^{-1})	3.245	5.880
Reflections collected	1588	2921
Independent reflections	1185 ($R_{int} = 0.0160$)	2226 ($R_{int} = 0.0463$)
Completeness to $\theta = 27.50°$ (%)	99.9	85.0
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1185/2/95	2226/0/107
Absorption correction	Difabs	Psiscans
Max. and min. transmission	0.5631 and 0.1811	
Absolute structure parameter	0.02(5)	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0206, wR_2 = 0.0499$	$R_1 = 0.0382, wR_2 = 0.1065$
R indices (all data)	$R_1 = 0.0223, wR_2 = 0.0507$	$R_1 = 0.0382, wR_2 = 0.1065$
Min. and max. ($e^- Å^{-3}$)	0.369 and −0.373	1.073 and −0.840

EXPERIMENTAL

The syntheses of **2** and **3** were carried out in an argon atmosphere using dried solvents distilled under argon. The NMR spectra were recorded on a Bruker DPX 200 instrument. For the MS a Finnigan MAT 8222 instrument was used, and for IR spectr an FT-IR SPEKTRUM 1000 instrument was used.

Me_3Sb

41.1 g (126 mmol) Me_3SbBr_2 was heated in a metal bath at 180–200 °C and 80–1.5 × 10^{-1} mbar. Me_2SbBr distilled off as a yellowish viscous oil. Yield 27.7 g (95%). The collected Me_2SbBr was heated at 160–180 °C and atmospheric pressure, when Me_3Sb distilled off as a colourless liquid. Yield 14.4 g (72%).

$Me_3Sb^+CH_2COO^-$ (1)

3.1 g (13 mmol) Ag_2O was added to a solution of 8.5 g (28 mmol) $[Me_3SbCH_2COOH][Br]$ (**2**) in 40 ml water and the mixture was stirred for 3 h. After filtration the solvent was pumped off and a white precipitate of **1**·H_2O was formed. Yield 5.9 g (90%). Single crystals were obtained from methanol at +7 °C (m.p. 93–95 °C). ^1H NMR (D_2O): 1.64 (s, 9H, $(C\underline{H}_3)_3Sb$), 3.21 (s, $Sb-C\underline{H}_2$). ^{13}C NMR (D_2O): 0.77 (s, $(\underline{C}H_3)_3Sb$), 29.03 (s, $Sb-\underline{C}H_2$), 175.5 (s, $\underline{C}OO$). MS (FAB positive, glycerine) *m/z* (%): 451 (16) $[(Me_3SbCH_2COO)_2H^+]$, 225 (54) $[M^+ + H]$, 166 (6) $[Me_3Sb^+]$, 151 (5) $[Me_2Sb^+]$, 136 (2) $[MeSb^+]$; (FAB negative, glycerine): 209 (8) $[M^+ - Me]$. IR (KBr): 3401 $[H_2O]$, 1584 $[COO^-]$, 861 $[Sb-C]$, 572 $[Sb-O]$. Anal. Found: C, 24.78; H, 4.88. Calc. for $C_5H_{13}O_3Sb$: C, 24.72; H, 5.39%.

$[Me_3SbCH_2COOH][Br]$ (2)

8.3 g (60 mmol) $BrCH_2COOH$ was added to a solution of 5.0 g (30 mmol) Me_3Sb in 40 ml toluene and the mixture was stirred for 24 h, and **2** was formed as a white precipitate. The product was washed with toluene. Yield 8.4 g (92%), m.p. 75–

76 °C. ^{1}H NMR (D_2O): 1.74 (s, 9 H ($C\underline{H}_3)_3Sb$), 3.19 (s, 2H, $Sb-C\underline{H}_2$). ^{13}C NMR (D_2O): 2.37 (s, ($\underline{C}H_3)_3Sb$), 25.16 (s, $Sb-\underline{C}H_2$), 173.46 (s, $\underline{C}OO$). MS (FAB positive, glycerine) *m/z* (%): 451 (22) [$(Me_3SbCH_2COO)_2H^+$], 225 (100) [$M^+ + H$], 166 (5) [Me_3Sb^+], 151 (5) [Me_2Sb^+], 136 (3) [$MeSb^+$]; (FAB negative, glycerine), 305 (28) [$M^- - H$], 81 (42) [Br^-]. IR (KBr): 3421 [H_2O], 2924 [$CO\underline{OH}$], 1702 [COO^-], 865 [$Sb-C$], 574 [$Sb-O$]. Anal. Found: C, 19.64; H, 4.02. Calc. for $C_5H_{12}BrO_2Sb$: C, 19.64; H, 3.96%.

[$Me_3SbCH_2COOCH_2CH_3$][Br] (3)

6.6 ml (10.0 g, 60 mmol) $BrCH_2COOCH_2CH_3$ was added to a solution of 5.0 g (30 mmol) Me_3Sb in 50 ml benzene. The mixture was stirred for 12 h and **3** was formed as a white precipitate. The product was washed with benzene and recrystallized from acetone. Yield 6.1 g, 61%, m.p. 59–60 °C. ^{1}H NMR ($CDCl_3$): 1.25 (t, 3H, $OCH_2C\underline{H}_3$, $^3J_{H-H} = 7.16$ Hz), 2.14 (s, 9H, $(C\underline{H}_3)_3Sb$), 2.6 (s, 2H, $Sb-C\underline{H}_2$), 4.13 (q, 2H, $OC\underline{H}_2CH_3$, $^3J_{H-H} = 7.14$ Hz). MS (FAB positive, glycerine) *m/z* (%): 253 (100) [$Me_3SbCH_2COOCH_2CH_3^+$], 166 (4) [Me_3Sb^+], 151 (3) [Me_2Sb^+], 136 (2) [$MeSb^+$]; (FAB negative, glycerine): 415 (52) [$M^- + Br$], 261 (17) [$Me_3SbCH_2^- + Br$], 79 (100) [Br^-]. Anal. Found: C, 24.85; H, 4.79. Calc. for $C_7H_{16}BrO_2Sb$: C, 25.18; H, 4.83%.

The reaction of 5.0 g (15 mmol) **3** with Dowex 2 × 8 (OH form) was carried out as described in Ref. 4. After work up 2.5 g $Me_3Sb(OH)_2$ (83%) was obtained. The ^{1}H NMR and MS data were found as reported.[15]

Acknowledgements

We thank the University of Bremen, Germany, for financial support.

REFERENCES

1. Pichereau V, Cosquer A, Gaumont A-C and Bernard T. *Bioorg. Med. Chem. Lett.* 1997; **7**: 2893.
2. Edmonds JS, Francesconi KA, Cannon JR, Raston CL, Skelton BW and White AH. *Tetrahedron Lett.* 1977; **18**: 1543.
3. Kühnelt D, Lintschinger J and Gössler W. *Appl. Organomet. Chem.* 2000; **14**: 411.
4. Cannon JR, Edmonds JS, Francesconi KA, Raston CL, Saunders JB, Skelton BW and White AH. *Aust. J. Chem.* 1981; **34**: 787.
5. Krachler M, Burow M and Emons H. *Analyst* 1999; **124**: 777.
6. Dodd M, Pergantis SA, Cullen WR, Li H, Eigendorf GK and Reimer KJ. *Analyst* 1996; **121**: 223.
7. Andrews P, Cullen WR and Polishchuk E. *Appl. Organomet. Chem.* 1999; **13**: 659.
8. Andrews P, Cullen WR and Polishchuk E. *Chemosphere* 2000; **41**: 1717.
9. Andrews P, Cullen WR, Polishchuk E and Reimer KJ. *Appl. Organomet. Chem.* 2001; **15**: 473.
10. Andrews P, Cullen WR, Feldmann J, Koch I and Polishchuk E. *Appl. Organomet. Chem.* 1999; **13**: 681.
11. Custelcean R, Afloroaiei C, Vlassa M and Polverejan M. *Angew. Chem.* 2000; **112**: 3224; *Angew. Chem. Int. Ed. Engl.* 2000; **39**: 3094.
12. Wieber M. Gmelin Handbook of Inorganic Chemistry, Sb Organoantimony Compounds, part 1. Springer-Verlag: Berlin, 1981; 10–18.
13. Breunig HJ, Denker M, Ebert KH and Lork E. *Z. Anorg. Allg. Chem.* 1997; **623**: 1151.
14. Narten AH, Thiessen WE and Blum L. *Science* 1982; **217**: 1033.
15. Lang G, Klinkhammer KW, Recker C and Schmidt A. *Z. Anorg. Allg. Chem.* 1998; **624**: 689.