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Synthesis and structures of stiba choline bromide, $[Me_3SbCH_2CH_2OH]Br$ and $(Me_3SbCH_2COO)_8(NaBr)_7(MeOH)_9(H_2O)$, a supramolecular derivative of stiba betaine

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The antimony analogue of choline bromide, $[Me_3SbCH_2CH_2OH]Br$ (1), is formed by the reaction of Me_3Sb with $BrCH_2CH_2OH$. Crystals of $(Me_3SbCH_2COO)_8(NaBr)_7(MeOH)_9(H_2O)$ (2) are obtained from $[Me_3SbCH_2COOH]Br$ and Na_2CO_3 in methanol. Crystals of 1 contain stibonium cations with intramolecular coordination of the ethanolic group. The structure of 2 features supramolecular units where the carboxylic groups of stiba betaine molecules are in bridging positions between sodium ions. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: antimony; betaine; choline; X-ray structure

INTRODUCTION

Although, with respect to biomethylation, antimony belongs to the less-studied elements, methyl antimony compounds have been reported in natural environments, their formation through biomethylation has been confirmed, and it was shown that the behaviour of antimony strongly parallels that of arsenic.[1–6] Biomethylation products of arsenic including, arseno choline and arseno betaine, are well known.[7,8] In order to develop research into the biomethylation of antimony, Sb analogues of these species are required as standards and the full characterization of biorelevant methyl antimony compounds appears to be useful.

Very little is known of the structures of the first methyl antimony species reported in aquatic environments, i.e. methylstibonic acid and dimethylstibinic acid.[1] Only $[Me(OH)_3SbO_2Sb(OH)_3Me]^{2-}$, a derivative of methylstibonic acid, has been characterized by X-ray crystallography.[9] Antimony analogues of the biomethylation products of arsenic with known crystal structures are derivatives of Me_3Sb,[10] $Me_3Sb(OH)_2$,[11–14] Me_4Sb^+,[15] $(Me_2Sb)_2O$,[16] $(Me_2Sb)_2S$[16] and stiba betaine, $Me_3Sb^+ CH_2COO^-$.[17] In extension to this work we report here the synthesis and characterization of two new stibonium salts, stiba choline bromide $[Me_3SbCH_2CH_2OH]Br$ (**1**) and $(Me_3SbCH_2COO)_8(NaBr)_7(MeOH)_9(H_2O)$ (**2**), a complex derivative of stiba betaine, formed as a serendipitous product of the reaction of $[Me_3SbCH_2COOH]Br$ with sodium carbonate in methanol.

RESULTS AND DISCUSSION

Stiba choline bromide $[Me_3SbCH_2CH_2OH]Br$ (**1**) is obtained in a quaternization reaction of trimethylstibine with 2-bromoethanol in absence of solvent [eq. (1)]. It is a colourless, air-sensitive compound that is very soluble in water or methanol.

$$Me_3Sb + BrCH_2CH_2OH \longrightarrow \underset{\mathbf{1}}{[Me_3SbCH_2CH_2OH]Br} \quad (1)$$

Crystals of **1** belong to the monoclinic space group $P2_1/n$ with four molecular units, comprising stiba choline cations and bromide anions, in the unit cell. The structure of a molecular unit is depicted in Fig. 1. Crystallographic data are summarized in Table 1.

The antimony atom is situated in a distorted tetrahedral environment of one CH_2 and three CH_3 groups with C–Sb–C bond angles ranging between 105.5(2) and 113.4(2)°. The Sb–C bond lengths lie between 2.095(5) and 2.117(5) Å.

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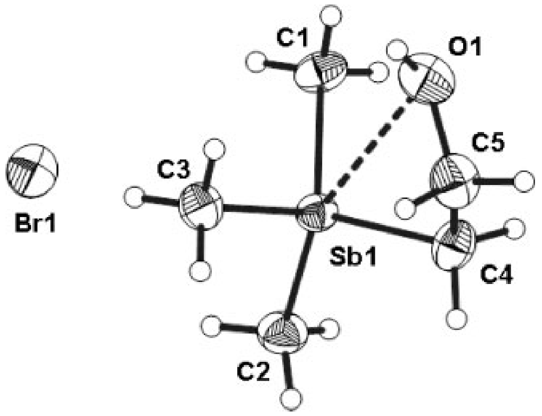

Figure 1. ORTEP[18] representation of the structure of [$Me_3SbCH_2CH_2OH$]Br (**1**). Thermal ellipsoids are represented at 50% probability level. Sb1–C1 2.105(4), Sb1–C2 2.105(4), Sb1–C3 2.095(5), Sb1–C4 2.117(5), C5–O1 1.430(6), C4–C5 1.505(7).

The oxygen atom of the pendant ethanolic group and the bromide counter ion are in capping positions above tetrahedral faces of the cation with contact distances [Sb···O 2.973(8); Sb–Br 4.083(1) Å], which are shorter than the sum of the van der Waals radii of the respective elements [Σ(r.v.d.W. Sb, O 3.70 Å; Sb, Br 4.1 Å]. Crystal structures of the As or P analogues of **1** are unknown. Related compounds with known structures include salts containing the cations [$Me_3NCH_2CH_2OH$]$^+$, [$Ph_3PCH_2CH_2OH$]$^+$ or [$Me_3AsCH_2CH_2OC(O)Me$]$^+$.[19–21]

^1H NMR spectra of solutions of **1** in D_2O show singlet signals for the methyl and triplets for the methylene groups. The spectra reveal that the intramolecular O–Sb coordination is not preserved in solution and free rotation around the bonds of the ethanolic group can be assumed. Mass spectra of **1** were obtained using the FAB technique. In the FAB positive mass spectrum of **1**, the base peak corresponds to the [$Me_3SbCH_2CH_2OH$]$^+$ ion. In the negative spectra of **1** the signals at highest mass correspond to [($Me_3SbCH_2CH_2OH$)Br_2]$^-$ and the base peak to Br^-.

The stiba betaine derivative, $(Me_3SbCH_2COO)_8(NaBr)_7(MeOH)_9(H_2O)$ (**2**), is obtained by reaction of [Me_3SbCH_2COOH]Br with Na_2CO_3 in methanol. In the first step the stiba betaine is formed according to eq. (2). Association of the reaction products Me_3Sb^+ CH_2COO^- and NaBr and the solvent molecules leads to the unusual supramolecular product **2**. The formation of the pure monohydrate of stiba betaine was achieved by reaction of [Me_3SbCH_2COOH]Br with Ag_2O.[17]

$$2\,[Me_3SbCH_2COOH]Br + Na_2CO_3 \longrightarrow 2\,Me_3Sb^+CH_2COO^- + 2\,NaBr + CO_2 + H_2O \quad (2)$$

Table 1. Crystal data and structure refinement for [$Me_3SbCH_2CH_2OH$]Br (**1**) and $(Me_3SbCH_2COO)_8(NaBr)_7(MeOH)_9(H_2O)$ (**2**)

Compound	1	2
Empirical formula	$C_5H_{14}BrOSb$	$C_{49}H_{126}Br_7Na_7O_{26}Sb_8$
Formula weight	291.82	2825.80
Crystal size (mm^3)	0.20 × 0.30 × 0.50	0.40 × 0.50 × 0.60
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	7.338(1)	13.280(1)
b (Å)	10.882(2)	13.526(1)
c (Å)	12.369(2)	15.246(1)
α (°)	90	113.60(1)
β (°)	106.84(3)	97.83(1)
γ (°)	90	98.11(1)
Volume (Å)	945.3(3)	2427.7(3)
Z	4	1
Absorption coefficient (mm^{-1})	7.074	5.160
$F(000)$	552	1348
θ range for data collections (°)	2.5–26.1	2.6–27.5
Reflections collected	12839	12163
Independent reflections	1839 [$R_{int} = 0.074$]	10609 [$R_{int} = 0.020$]
Data with $I > 2\sigma(I)$	1488	8565
Goodness-of-fit on F^2	0.982	1.053
Data/restraints/parameters	1839/0/80	10609/3/479
Final R indices [$I > 2\sigma(I)$] (R_1, wR_2)	0.026, 0.060	0.038, 0.082
R indices (all data) (R_1, wR_2)	0.039, 0.066	0.054, 0.088
CCDC deposition number	253528	253527

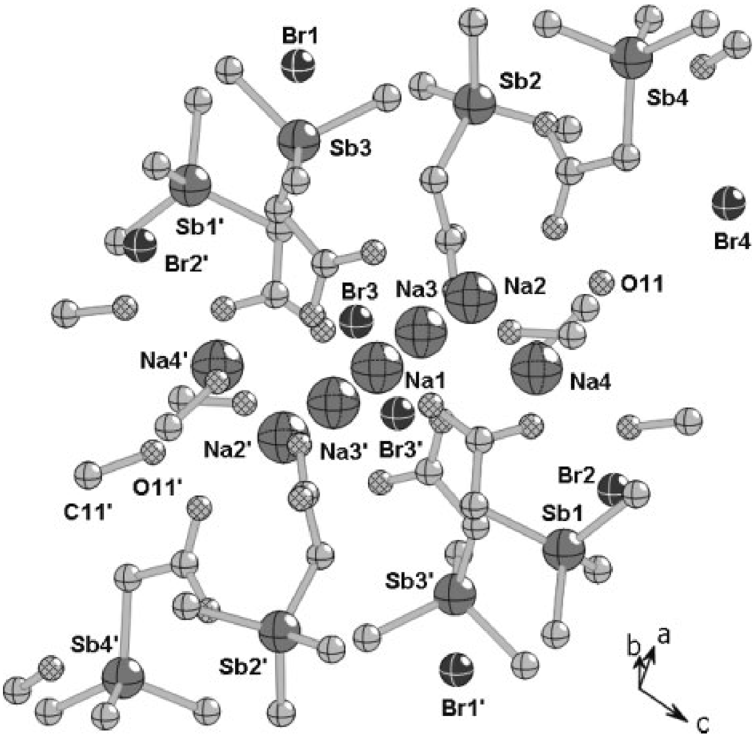

Figure 2. Structure of $(Me_3SbCH_2COO)_8(NaBr)_7(MeOH)_9(H_2O)$ (**2**). Br4, O11 and C11 are in bridging positions. Hydrogen atoms have been omitted.

Crystals of **2** suitable for X-ray diffraction were obtained directly from the solution at 7 °C. They belong to the triclinic space group $P\bar{1}$. The crystal structure is composed of centrosymmetric supramolecular $(Me_3SbCH_2COO)_8(NaBr)_7(MeOH)_9(H_2O)$ units (see the Experimental section), which are aligned in chains through bridging bromides, water and methanol molecules. An overall view on one of the supramolecular units is shown in Fig. 2.

The unit can be described as an ellipsoid consisting of a central sodium oxygen core and stiba betaine molecules directed to the periphery. The methanol molecules and two of the bromide atoms fill the gaps in the central part of the structure; the remaining bromide atoms are in the periphery. A view of the central core showing the linkage of the sodium atoms is given in Fig. 3.

The Na1 atom occupies the central position in an octahedral coordination sphere of six carboxylic oxygen atoms derived from three different stiba betaine molecules. Pairs of oxygen atoms form bridges between Na1 and each of the remaining six sodium atoms, which adopt an anti-prismatic arrangement. Views of the different sodium environments are presented in Fig. 4.

Na1, Na2 and Na4 are six-coordinate, occupying the centres of more or less distorted octahedra, but Na3 is five-coordinate. The molecular structures of the stiba betaine molecules are inconspicuous, comprising tetrahedral stibonium centres and planar carboxyl groups, which act as monodentate or bidentate ligands to sodium centres; the intramolecular Sb···O separations are included in the caption to Fig. 4.

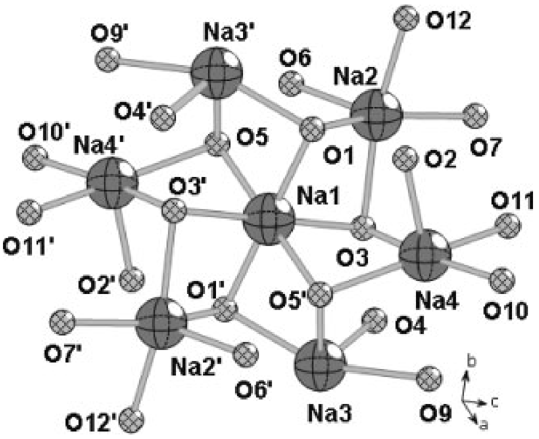

Figure 3. The arrangement of sodium and oxygen atoms in the centre of the structure of **2**.

The bonding in the supramolecular units of **2** probably results from a combination of coordinative and electrostatic interactions between shells. Four concentric shells with alternating polarity can be distinguished. The central sodium ion is positively charged. It is surrounded by a layer of six oxygen atoms, a shell composed of six sodium ions, a second oxygen layer and a final shell consisting of stibonium units.

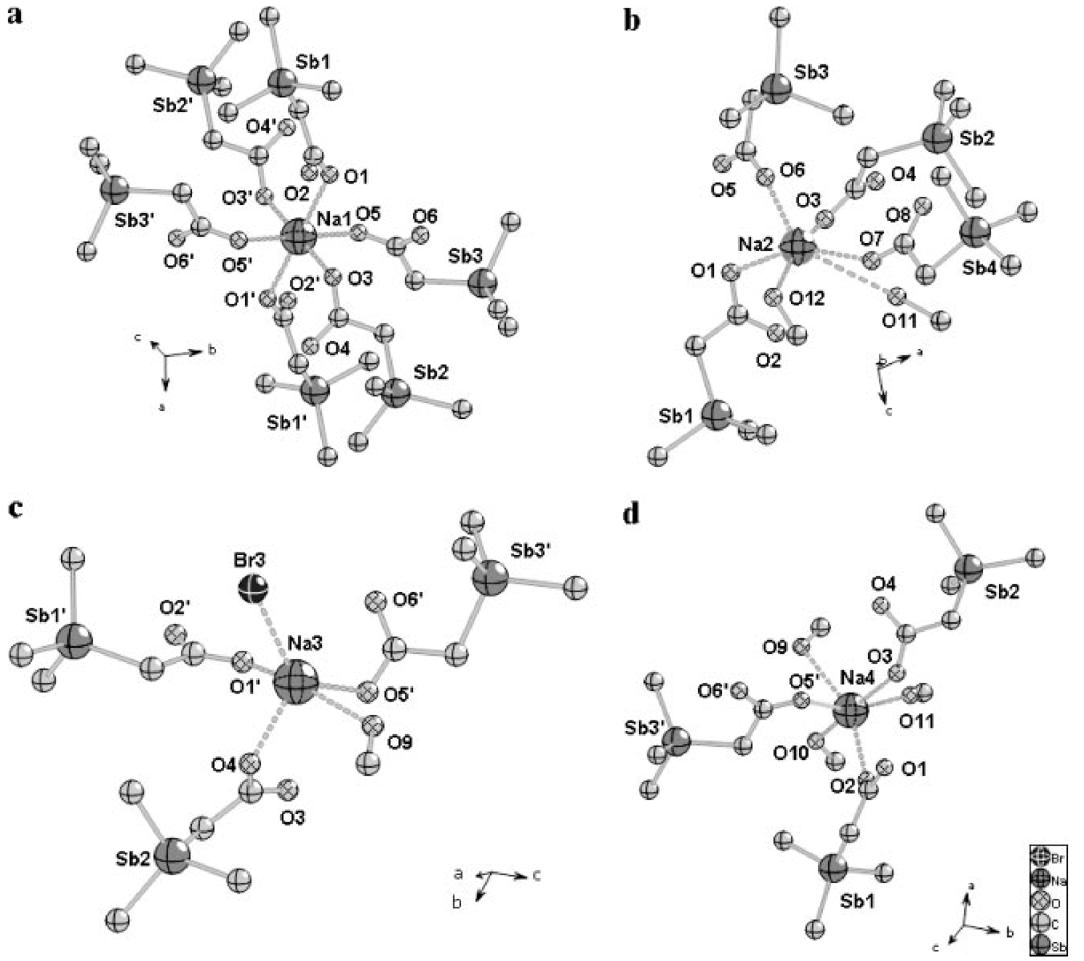

Figure 4. Coordination of the sodium centres in the structure of **2**. Selected distances (Å): (a) Sb1· · ·O2 2.936(4), Na1−O1 2.335(3), Na1−O3 2.322(3), Na1−O5 2.381(3); (b) Sb2· · ·O4 3.008(4), Na2−O1 2.439(4), Na2−O3 2.392(4), Na2−O6 2.358(4), Na2−O7 2.313(4), Na2−O11 3.619(5), Na2−O12 2.298(6); (c) Sb3· · ·O6 2.896(4), Na3−O1′ 2.376(4), Na3−O4 2.335(4), Na3−O5′ 2.414(4), Na3−O9 2.509(5); (d) Sb4· · ·O8 2.744(4), Na4−O2 2.357(4), Na4−O3 2.463(4), Na4−O5′ 2.422(4), Na4−O9 2.605(5), Na4−O10 2.368(5), Na4−O11 2.348(5). Hydrogen atoms have been omitted.

The supramolecular structure of **2** is unique and is the first complex of stiba betaine with a known structure. Complexes of related ligands are the metal derivatives of $Me_3N^+ CH_2COO^-$ or $Ph_3P(CH_2)_3CO_2^-$.[22,23]

EXPERIMENTAL

The synthesis of **1** and **2** was 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 mass spectrometry a Finnigan MAT 8222 instrument was used and for the IR spectra a FT–IR SPEKTRUM 1000. Data were collected at 173(2) K on STOE IPDS (**1**) and Siemens P4 (**2**) diffractometers using MoKα radiation and corrected for absorption effects using DIFABS.[24] Structure solutions and refinements (full-matrix least-squares on F^2, anisotropic displacement parameters and H atoms in calculated positions) were carried out using the software package Bruker SHELXTL.[25] For the refinement of **2**, the O−H and N−H bond lengths were restrained to 0.9 Å and 1.42 Å. The maximum residual electron density peak (1.04 e Å^{-3}) was located near the atom Br2. Br4 is included as half weight so as to maintain the $P\overline{1}$ space group. Where Br4 is present in the structure, a molecule of H_2O is coordinated to the atom Na4. Where Br4 is not present, the place of the water molecule is occupied by a CH_3OH molecule. Water and methanol molecules share the same oxygen atom, O11. Crystallographic data are given in Table 1.

*[Me$_3$SbCH$_2$CH$_2$OH]Br (**1**)*

A 1.12 g (0.88 mmol) aliquot of $BrCH_2CH_2OH$ was added to 1.5 g (0.9 mmol) neat Me_3Sb and the mixture was stirred for 24 h. **1** was formed as an air-sensitive oil which crystallized slowly. ^1H NMR (D_2O): 1.91 (s, 9H, $(C\underline{H}_3)_3Sb$), 3.52 (t, 2H, Sb−$C\underline{H}_2$), 3.88 (t, 2H, $C\underline{H}_2$). MS (FAB positive, NBA) m/z

(%): 211 (100) [Me_3Sb^+ CH_2CH_2OH], 166 (6) [Me_3Sb^+], 151 (5) [Me_2Sb^+], 136 (2) [$MeSb^+$]; (FAB negative, NBA) 79 (100) [Br^-]. Anal. calc. for $C_5H_{14}OBrSb$: C, 20.58%, H, 4.84%. Found: C, 19.68%, H, 4.55%.

$(Me_3SbCH_2COO)_8(NaBr)_7(MeOH)_9(H_2O)$ (**2**)

A 69.5 mg (0.65 mmol) aliquot of Na_2CO_3 was added to a solution of 400 mg (1.31 mmol) [Me_3SbCH_2COOH]Br in 10 ml MeOH, and the mixture was stirred for 2 h. Removal of the solvent gave **2** as a colourless oil which crystallized in 3 h at +7 °C (melting point 80–82 °C). ^1H NMR (D_2O, TMS), 1.69 [s, 9H, $(C\underline{H}_3)_3$-Sb, $^1J_{C-H} = 140.10$ Hz], 3.29 (s, Sb-$C\underline{H}_2$), 3.36 (s, $C\underline{H}_3OH$). ^{13}C NMR: (D_2O), 2.06 [s, $(\underline{C}H_3)_3$-Sb], 35.40 (s, Sb-$C\underline{H}_2$), 48.58 (s, $\underline{C}H_3OH$) 170.35 (s, $\underline{C}OO$). MS (70 eV, 25 °C): FAB positive 273 [$Me_3SbCH_2COONa_2{}^+$], 247 [$Me_3SbCH_2COONa^+$], 225 [$Me_3SbCH_2COOH^+$], 166 [Me_3Sb^+], 151 [Me_2Sb^+], 136 [$MeSb^+$], FAB negative: 79 [Br]. IR (KBr): 3921, 2966, 3012 [MeOH], 1590, 1614 [COO^-], 861 [Sb-C], 570 [Sb-O].

Acknowledgements

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