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Crystal structure of $[Me_3Sb–SbMe_2]_2[(MeSbBr_3)_2]$, a trimethylstibine adduct of the dimethylstibenium ion or a stibinostibonium salt?

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Scrambling reactions of dimethylantimony bromide in absence of solvent give the ionic complex $[Me_3Sb–SbMe_2]_2$-$[(MeSbBr_3)_2]$, with cations consisting of pyramidal Me_3Sb bound to bent Me_2Sb units through short (282 pm) Sb–Sb bonds and dimeric anions adopting the geometry of edge sharing tetragonal pyramids where methyl groups are in apical *trans* positions.

In contrast to the rich chemistry of phosphenium cations[1] very little is known of stibenium cations, R_2Sb^+ or of Lewis acid base adducts of the type $[B\rightarrow SbR_2]^+$. The diphenylstibenium cation, Ph_2Sb^+ was reported as a product of the electrochemical oxidation of $Ph_2Sb–SbPh_2$ in tetrahydrofuran (thf).[2] Pioneering work in the field of adducts was done by Summers and Sisler and others,[3–6] who studied reactions of trialkyls of phosphorus, arsenic or antimony with organohalo-phosphines, -arsines, or -stibines and reported the formation of ‘arsinophosphonium salts’ and related compounds of the type $[R_3EER_2]X$ (E = P, As, Sb; X = Cl, Br, I). These ionic species were characterized by measurement of their conductance in nitromethane. Recently an X-ray crystal structure analysis of an adduct was carried out on the ionic complex $[Me_2Sb–SbMe_2–SbMe_2][Me_2SbBr_2]$ obtained by reaction of Me_2SbBr with $Me_2Sb–SbMe_2$.[7] The chemical properties of the cation of this complex correspond to an adduct of tetramethyldistibine coordinated on the dimethylstibenium ion, Me_2Sb^+, the latter being formed together with $Me_2SbBr_2^-$ by transfer of Br^- from one Me_2SbBr molecule to another. However neither the distibine nor the dimethylstibenium unit could be distinguished in the crystal structure. The geometrical data of the cation correspond instead to the stibonium ion, $[R_2R'_2Sb]^+$ (R = Me, R′ = Me_2Sb).[7]

We have now investigated reactions with transfer of bromide between Me_2SbBr and $MeSbBr_2$ in presence of Me_3Sb as donor and report here the formation and the X-ray crystal structure determination of a novel ionic complex $[Me_3Sb–SbMe_2]_2$-$[(MeSbBr_3)_2]$ **1**. The cation of **1** is a trimethylstibine adduct of the dimethylstibenium ion and with view on isolobal relations between Me_2Sb^+ and CH_2 or Me_3Sb and Me_3P it can be considered as an analogue of phosphorus ylides. The alternative description as stibonium ion $[R_3R'Sb]^+$ (R = Me, R′ = Me_2Sb) is useful to underline the close relation with $[R_2R'_2Sb]^+$[7] and $[R_4Sb]^+$[8] in a family of stibonium ions, where now only the members $[RR'_3Sb]^+$ and $[R'_4Sb]^+$ are still unknown. Also the relation between **1** and tetramethyldistibine is intriguing. In fact, **1** might also be envisaged as a quaternization product of $Me_2SbSbMe_2$, which is not accessible by other methods. In contrast to tetraalkyldiphosphines which are easily quaternized by reactions with methylating agents such as methyl iodide, the analogous reactions of diarsines or distibines lead to fission of the (weaker) As–As or Sb–Sb bonds.[14] The anion of **1** is a dimer of methyltribromoantimonate(III). It is a novel example of a known type of ‘ate’ complexes of antimony(III). Several related aryl compounds[9–12] and one alkyl derivative[13] have been reported.

Crystals of **1** were grown in 80% yield in an attempt to crystallize dimethylantimony bromide by cooling the melt to −28 °C for several weeks. The formation of **1** can be explained by stepwise reactions according to eqn. (1) and (2). First the irreversible formation of the components Me_3Sb and $MeSbBr_2$ according to eqn. (1) may occur, which is a known reaction.[14] The following possible steps are summarized in eqn. (2). They include the transfer of bromide from Me_2SbBr to $MeSbBr_2$ and the coordination of Me_3Sb on the cation. The dimethylantimony bromide used as starting material should be of very high purity. It is best prepared by the reaction of tetramethyldistibine with bromine.[14]

$$2\,Me_2SbBr \longrightarrow Me_3Sb + MeSbBr_2 \qquad (1)$$

$$2\,Me_2SbBr + 2\,Me_3Sb + 2\,MeSbBr_2 \rightleftharpoons \underset{\mathbf{1}}{[Me_3Sb\text{-}SbMe_2]_2[MeSbBr_3]_2} \qquad (2)$$

In contrast to other organometallic compounds with Sb–Sb bonds such as the yellow or red distibines or cyclostibines, crystals of **1** are colourless. They are slightly soluble in nonpolar organic solvents. ^1H NMR spectra in C_6D_6 show however that on dissolution the components Me_2SbBr, Me_3Sb and $MeSbBr_2$ are formed in the reverse of reaction (2). Later Me_3SbBr_2 and reduced methylantimony species are formed irreversibly.[15]

The crystal structure of **1** was determined by single crystal X-ray structure analysis. The structure of the cation is shown in Fig. 1. Fig. 2 shows the arrangement and the interactions between the ions. The cation consists of a pyramidal trimethylantimony unit bonded to a bent dimethylantimony unit through an antimony–antimony bond. The Sb–Sb bond length of **1** [282.05(12) pm] lies in the normal range of Sb–Sb single bond lengths as found in $Me_2Sb–SbMe_2$ [283.8(1)],[16] $(PhSb)_6$ [283.6–283.9(1)],[17] $[Me_2Sb–SbMe_2–SbMe_2][Me_2SbBr_2]$ [282.03(4)],[7] $Me_3Sb–Sb(Me)I_2$ [285.9(1)][18] and $Me_3Sb–SbI_3\cdot thf$ [284.3(1) pm].[19] The C–Sb bond lengths to the onium centre of **1** [Sb(2)–C 210.6(11)–212.1(11)] are shorter than in the Me_2Sb group [Sb(1)–C 214.9(10), 216.5(12)] but longer than in $[Me_4Sb]I$ [Sb–C 204.3(2), 207.0(1) pm].[20] The C–Sb–C bond angles in the Me_3Sb unit in **1** are wide [103.1(5)–104.4(5)°] compared to uncoordinated Me_3Sb (94, 98°)[21] or the angles in solid $Me_2Sb–SbMe_2$ [C–Sb–C

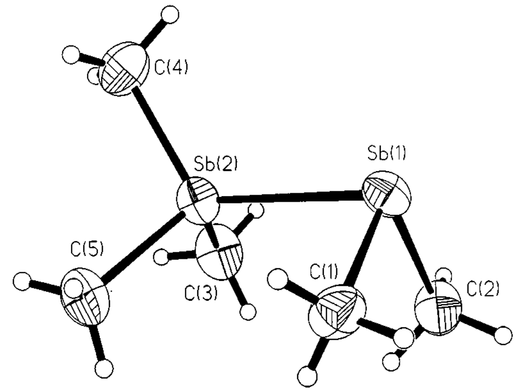

Fig. 1 The molecular structure of the cation $[Me_3Sb–SbMe_2]^+$ of **1**. Distances (pm) and angles (°): Sb(1)–Sb(2) 282.05(12), Sb(1)–C 214.9(10), 216.5(12), Sb(2)–C 210.6(11)–211.1(12); C(1)–Sb(1)–Sb(2) 91.0(4), C(2)–Sb(1)–Sb(2) 91.3(3), C(1)–Sb(1)–C(2) 94.3(5), C–Sb(2)–C 103.7(6), 103.1(5), 104.4(5), C(2)–Sb(1)–Sb(2)–C(3) 23.09(1), C(1)–Sb(1)–Sb(2)–C(5) 0.82(1).

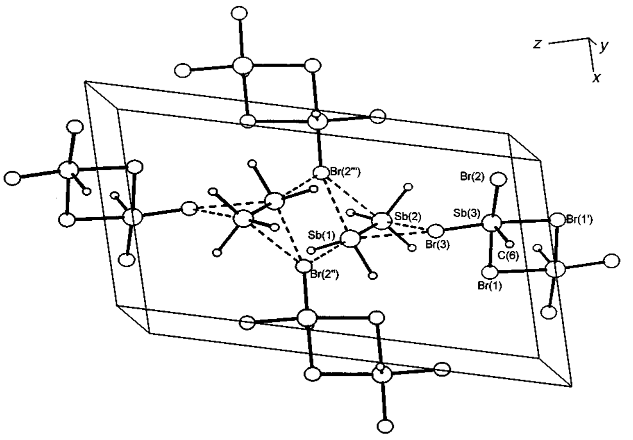

Fig. 2 Crystal structure of **1** with intermolecular interactions. Distances (pm) and angle (°): Sb(3)–C(6) 212.1(11), Sb(3)–Br(3) 263.24(16), Sb(3)–Br(2) 273.04(13), Sb(3)–Br(1) 289.17(13), Sb(3)–Br(1′) 302.72(16); Sb(1)···Br(2″) 354.3(21), Sb(1)···Br(2‴) 373.2(9), Sb(1)···Br(3) 383.0(23), Sb(2)···Br(2‴) 384.2(28), Sb(2)···Br(3) 391.2(4); Sb(2)–Sb(1)···Br(2″) 170.92(1).

88.6(5)–100.7(5)°, C–Sb–Sb [94.3(4)–94.4(4)°][16] but they lie in the range of C–Sb–C angles of the other complexes of Me_3Sb, *cf.* $Me_3Sb \rightarrow SbI_2Me$ [C–Sb–C, 101.3(3)–106.1(4)],[18] $Me_3Sb–SbI_3 \cdot thf$ [102.9(5)–105.6(5)].[19] The widening of the angles on complexation may indicate a transition from the p^3 configuration of the free Me_3Sb to the sp^3 hybridisation in the adducts. The bond angles around the antimony atom of the Me_2Sb unit lie between 91.0(4) and 94.3(5)° corresponding to the p^3 configuration. In terms of the VSEPR model the angles at Sb(1) would reflect the stereochemical activity of the lone pair at antimony.

The loss of colour going from $Me_2Sb–SbMe_2$ (yellow melt and solution, red crystals) to $Me_3Sb–SbMe_2^+$ may result from the different orbitals forming the antimony–antimony bonds of the respective species.

The almost rectangular angles of $Me_2Sb–SbMe_2$ suggest that the Sb–Sb bond is formed by overlap of two 5p orbitals. In contrast, in the case of **1** the overlap of a sp^3 orbital at the four-coordinate antimony atom and a p-orbital at the three-coordinate Sb should be more effective resulting in the stabilization of the HOMO, a Sb–Sb σ-orbital and an increase in energy of the LUMO, a Sb–Sb σ*-orbital. HOMO–LUMO transitions lie in the visible region in the case of $Me_2SbSbMe_2$ but shift to the UV region of the spectra for **1**. The structure of the anions is composed of two tetragonal pyramids around the antimony atoms sharing an edge of the square base. The methyl groups are in apical positions, *trans* to each other. This type of structure is usual for organo halogeno antimonates.[9–13] It is also of interest to consider the interactions between the cation and the anion of **1**. There are three interionic Sb···Br contacts with distances shorter than the sum of van der Waals radii of Sb and Br (410 pm). The closest intermolecular contact [354.3(21) pm] exists between Sb(1) of the dimethylantimony unit and Br(2‴), one of the terminal bromine atoms of the anion. The Sb–Sb···Br angle is close to linearity. It is easy to assume that a prolongation of the dative Sb–Sb bond and a shortening of the Sb(1)···Br(2‴), contact leads to Me_2SbBr, the starting material.

Br(2‴) and Br(3) are in bridging positions above the Sb–Sb bond with contact distances of 373.2(9), 384.2(28) pm and 383.0(23); 391.2(4) pm, respectively. It is very likely that this interaction not only stabilizes the cation but also controls the unusual ecliptic conformation of the cation.

Notes and references

† *Crystal data* for $C_{12}H_{36}Br_6Sb_6$ **1**: M = 1390.35, monoclinic, a = 1189.4(2), b = 771.1(2), c = 1906.7(5) pm, β = 107.06(2), V = 1671.8(7) Å^3, T = 173(2) K, space group $P2_1/n$, Z = 2, μ(Mo-K) = 11.949 mm^{-1}, 4409 reflections measured, 3408 unique (R_{int} = 0.0354) which were used in all calculations. The final $wR(F^2)$ was 0.1391. The crystal was attached with Kel-F-oil to a glass fiber and cooled under a nitrogen stream to 173 K. After L_p and absorption correction (ψ-scans) the structure was solved by direct methods. CCDC 182/1398. See http://www.rsc.org/suppdata/cc/1999/1971/ for crystallographic files in .cif format.

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