Syntheses and Structures of [nBu₄N][nBu₂SbCl₄] and [Et₃SbMe]₂[(MeSbCl₃)₂]

Hans Joachim Breunig a, Tim Koehne a, Enno Lork a, Ovidiu Moldovan a, Jörn Poveleit a, and Ciprian Ionut Rățăb

a Institut für Anorganische und Physikalische Chemie, Fachbereich 2 der Universität Bremen, Postfach 330 440, 28334 Bremen, Germany
b Facultate de Chimie și Inginerie Chimică, Universitatea Babeș-Bolyai, 11 Arany Janos, 400028 Cluj-Napoca, Romania

Reprint requests to Prof. Dr. H. J. Breunig. Fax: 0049-421-218-62809.
E-mail: hbreunig@uni-bremen.de

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[97x755]nBu₄N][nBu₂SbCl₄] (1) is synthesized by reaction of nBu₄NCl and nBu₂SbCl₃. [Et₃SbMe]₂[(MeSbCl₃)₂] (2) is formed from [Et₃SbMe]I and Me₂SbCl₃. The structures of 1 and 2 were determined by single-crystal X-ray diffraclometry.

Key words: Antimony, Nitrogen, Chlorine, X-Ray Crystallography

Introduction

Organoantimony halides of the types R₂SbX₃ and RSbX₂ are strong Lewis acids. They readily accept additional halide ions with formation of the corresponding hypercoordinate antimonates [R₂SbX₄]⁻ and [RSbX₃]⁻. Crystal structure determinations revealed the octahedral trans structure of [R₂SbX₄]⁻ (R = Me, Ph; X = F, Cl, Br) [1 – 3] and the dimeric nature of [(RSbX₃)₂]²⁻. R = Ph, X = Cl [4, 5], I [6, 7]; R = Me₃SiCH₂, X = Cl [8]; R = Me, X = Br [9]. In an extension of our previous work in this field we report on the syntheses and structures of [nBu₄N][nBu₂SbCl₄] (1) and [Et₃SbMe]₂[(MeSbCl₃)₂] (2).

Results and Discussion

[nBu₄N][nBu₂SbCl₄] (1) is formed by the reaction of nBu₄NCl with nBu₂SbCl₃ in methanol at ambient temperature. nBu₂SbCl₃ is prepared by reaction of (nBu₂Sb)₂ with SO₂Cl₂. 1 is an air-stable solid melting at 125 °C. Single crystals of 1 are obtained from acetonitrile. The structure of 1 consists of tetrahedral tetra-n-butylammonium cations and octahedral dibutyltetrachloroantimonate(V) anions with the alkylgroups in trans-positions to each other. A pair of ions is depicted in Fig. 1. The Sb–C and the Sb–Cl bond lengths of the anion of 1 [Sb(1)–C(1) 2.139(2), Sb(1)–C(5) 2.143(2), Sb(1)–Cl 2.4577(6)–2.5108(7) Å] are similar to the corresponding values found in the structures of the M[Me₂SbCl₄] salts (M = Ph₄P, Sb–Cl 2.098(6), 2.110(8), Sb–Cl 2.4675(10) Å; M = Ph₃Sb, Sb–Cl 2.099(12), 2.148(9), Sb–Cl 2.4950(15) Å [3]); however, it is remarkable that the deviations from the ideal trans octahedral symmetry are larger in the anion of 1 than in the analogous methyl compound which contains centrosymmetric SbCl₄ units. In the crystal there is a 4:4 anion cation coordination. Between the chlorine atoms of the anion and hydrogen atoms of the methylene groups bonded to the nitrogen atom there are intermolecular C–H···Cl interactions.

The ¹H NMR spectrum of 1 in CDCl₃ contains multiplet signals for the methylene groups and triplet signals for the methyl groups of the n-butyl substituents on antimony and nitrogen. The ¹³C NMR spectrum shows the expected eight signals for the two different n-butyl groups. Characteristic mass spectra were obtained by the electron spray ionization (ESI) technique. The molecular ions both of the cation and the anion of 1 appear in the positive or negative modes of the measurements, respectively. Additional signals that are visible in the mass spectra correspond to the ions [nBuSbCl₃]⁻ and [(nBu₄N)₂Cl]⁺.

[Et₃SbMe]₂[Me₂Sb₂Cl₆] (2) was obtained serendipitously from the reaction of [Et₃SbMe]I and Me₂SbCl₃. The reaction pathways have not been elucidated, and thorough investigations are necessary to
solve this chemical puzzle. For the preparation of
the onium salts with \([R_2SbCl_4]^{-}\) or \([(RSbCl_3)_2]^2-\) anions
it is preferable to avoid iodide and to react onium chlo-
rides with \(R_2SbCl_3\) or \(RSbCl_2\). \(2\) is an air-stable crys-
talline solid melting at 138 – 140 °C. The structure of
\(2\) was also determined by single-crystal X-ray diffraction.
Two cations and one dianion of \(2\) are depicted in
Fig. 2.

The structure of \(2\) is composed of tetrahedral
Et₃SbMe cations and centrosymmetric Me₂Sb₂Cl₆
dianions where the antimony and chlorine atoms
lie in a plane and the methyl groups point in
opposite directions, perpendicular to this plane.
The C–Sb bond length in the anion (C(1)–Sb(1)
2.129(5) Å) is similar to the corresponding value
in the anion of \(1\) (2.139(2) Å). In the Cl–Sb–Cl
bridges the Sb–Cl distances [Cl(1)–Sb(1) 2.9013(14),
Cl(1′)–Sb(1) 2.9258(14)] are significantly longer than
those of the terminal Sb–Cl bonds [Cl(2)–Sb(1)
2.4789(15), Cl(3)–Sb(1) 2.4703(13)]. These struc-
tural features are not unusual. Similar arrangements
were also observed for the closely related com-
 pound, i.e. \([(Me_3SiCH_2SbCl_3)_2]^2-\) (Sb–C 2.141(4),
Sb–Cl (bridging) 2.809(1), 2.977(1), Sb–Cl (terminal)
2.467(1), 2.521(1) Å) [8], and for \([(MeSbBr_3)_2]^2-\)
[9], \([(PhSbCl_3)_2]^2-\) [4] or \([(pTolSbCl_3)_2]^2-\) [10]. The
crystal structure of \(2\) is also consolidated by the
presence of hydrogen bonds between the hydrogen
atoms of a methylene group and a terminal chlorine
atom.

The \(^1\)H NMR spectrum of a solution of \(2\) in
[D₆]DMSO shows the expected signals, a quartet and
a triplet for the ethyl groups and two singlet signals
for the methyl groups. It cannot be excluded that
the anion in solution is in fact the mononuclear adduct
\([DMSO(MeSbCl_3)]^{-}\).
ESI positive mass spectra of 2 show signals of the intact cation. In the negative mode no signals assignable to the dimeric anion, but very weak signals of \([\text{MeSbCl}_3]^-\) are observed.

**Conclusion**

\([\text{Et}_3\text{SbMe}]_2[\text{(MeSbCl}_3)_2]\) (1) is the first member of the large family of diorgano(tetrahalo)antimonates with \(n\)-butyl groups both in the anion and in the cation. The formation of 2 by reaction between \([\text{Et}_3\text{SbMe}]\) and \(\text{Me}_2\text{SbCl}_3\) is interesting with respect to the redox chemistry of organoantimony(V) compounds, but for

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\text{J} (t, \text{CH}_3\text{C}_n \text{(101 MHz, CDCl}_3) = 1.64 \text{ (m, 8H, CH}_3\text{CH}_2\text{C}_n), 3.32 \text{ (m, 4H, CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Sb}). – \text{ }^{13}\text{C NMR (101 MHz, CDCl}_3) = 13.79 \text{ (CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}), 7.98 \text{ (CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}), 19.85 \text{ (CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}), 23.95 \text{ (CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}), 29.33 \text{ (CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}, 59.01 \text{ (CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}), 75.88 \text{ (CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}). – MS ((+-)ESI): m/z = 242 \text{ (100) [Bu}_4\text{N}]^+, 520 \text{ (15); MS } (-)-ESI): m/z = 285 \text{ (100) [Bu}_2\text{SbCl}_3]^-\). – \text{C}_2\text{H}_4\text{SbCl}_4\text{NSb (620.3): calcd} C 46.47, H 8.78; found C 46.57, H 8.18.

**Synthesis of \([\text{Et}_3\text{SbMe}]_2[\text{(MeSbCl}_3)_2]\) (2)**

A solution of \(\text{Et}_3\text{SbMe}\) (2.7 g, 7.7 mmol) in 50 mL methanol was added dropwise to \(\text{Me}_2\text{SbCl}_3\) (2.0 g, 7.7 mmol) in 50 mL of methanol, and the mixture was stirred for 3 h. The solution turned yellow, and a light-yellow precipitate formed. The solvent was removed, and the remaining solid dissolved in \(\text{CH}_3\text{CN}\). Slow evaporation of the solvent in the open atmosphere gave colorless crystals and a solid yellow product, which were both identified as 2. Yield: 2.24 g. M. p. 138 – 140 °C. – \text{H NMR (400 MHz, [D}_6\text{DMSO)}: \(\delta = 0.90 \text{ (t, J = 7.9 Hz, CH}_3\text{CH}_2\text{CH}_2\text{N), 1.38 \text{ (s, 3H, SbCl}_3\text{), 1.54 \text{ (s, 3H, Cl}_3\text{SbCl}_3\text{), 2.18 \text{ (q, J = 7.9 Hz, CH}_3\text{CH}_2\text{CH}_2\text{N), – }^{13}\text{C NMR (101 MHz, [D}_6\text{DMSO)}: \(\delta = -4.25 \text{ (SbCl}_3\text{), 9.37 \text{ (CH}_3\text{CH}_2\text{CH}_2\text{N), 12.27 \text{ (CH}_3\text{CH}_2\text{CH}_2\text{N), 34.03 \text{ (Cl}_3\text{SbCl}_4\text{). – C}_{16}\text{H}_{42}\text{Cl}_4\text{Sb} (934.3): calcd} C 20.57; H 4.53; found C 20.46, H 4.61.

**X-Ray structure determinations**

Crystals of 1 and 2 were mounted on a glass fiber using KClF oil and placed under a cold nitrogen stream on a Siemens P4 and on a Stoe IPDS diffractometer, respectively. Crystal and refinement data for 1: \(\text{C}_{24}\text{H}_{54}\text{Cl}_4\text{NSb, M}_r = 620.23\), crystal size 0.3 \(\times\) 0.4 \(\times\) 0.04 mm\(^3\), monoclinic, \(\text{C}2/c\); \(Z = 8, \alpha = 28.401(6), \beta = 13.305(3), \gamma = 22.142(4) \), \(\beta = 129.52(3) \) deg, \(V = 6455.2 \) \(\text{Å}^3\), \(D_{\text{calc}} = 1.28 \text{ g cm}^{-3}\), \(\mu_{\text{MoK}a} = 1.2 \text{ cm}^{-1}\), \(F(000) = 2592 \), hkl ranges \(-6/11, \pm 10, \pm 13, 44790 \) measured refl., 6316 unique refl., \(R_{\text{int}} = 0.0778, 277 \) refined param., \(R(F) \) (all reflections) = 0.0312, \(wR(F^2) \) (all reflections) = 0.0511, \(GoF(F^2) = 1.047, \Delta \rho_{\text{min}} \) (max/min) = 0.52/ – 0.28 e \(\text{Å}^{-3}\), weighting scheme details: \(w = 1/[(\sigma^2(F_0^2)+0.0089P^2)^{+}]^{0.04084P}\) where \(P = (F_0^2+2F_c^2)/3\). Crystal and refinement data for 2: \(\text{C}_{24}\text{H}_{54}\text{Cl}_4\text{NSb, M}_r = 657.12\), crystal size 0.70 \(\times\) 0.60 \(\times\) 0.40 mm\(^3\), triclinic, \(\text{P}1\), \(Z = 2, \alpha = 90.0418(10), \beta = 9.3450(19), \gamma = 10.673(2) \), \(\alpha = 65.81(3), \beta = 87.82(3), \gamma = 74.15(3) \) deg, \(V = 786.13 \) \(\text{Å}^3\), \(D_{\text{calc}} = 1.97 \text{ g cm}^{-3}\), \(\mu_{\text{MoK}a} = 3.9 \text{ cm}^{-1}\), \(F(000) = 444 \), hkl ranges \(\pm 35, \pm 16, \pm 27, 4182 \) measured refl., 3458 unique refl., \(R_{\text{int}} = 0.0158, 123 \) refined param., \(R(F) \) (all reflections) = 0.0301, \(wR(F^2) \) (all reflections) = 0.0777, \(GoF(F^2) = 1.179, \Delta \rho_{\text{min}} \) (max/min) = 0.81/ – 0.92 e \(\text{Å}^{-3}\), weighting scheme details: \(w = 1/[(\sigma^2(F_0^2)+0.0276P^2)^{+}]^{2.1718P}\) where \(P = (F_0^2+2F_c^2)/3\).

All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included...
in riding positions with isotropic displacement parameters set at 1.2 times those of the carbon atoms directly attached for methylene groups, and 1.5 for hydrogen atoms of the methyl groups.

CCDC 777531 and 777532 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.