Syntheses and Structures of $[n\mathrm{Bu}_4\mathrm{N}][n\mathrm{Bu}_2\mathrm{SbCl}_4]$ and $[\mathrm{Et}_3\mathrm{SbMe}]_2[(\mathrm{MeSbCl}_3)_2]$

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$[n\mathrm{Bu}_4\mathrm{N}][n\mathrm{Bu}_2\mathrm{SbCl}_4]$ (**1**) is synthesized by reaction of $n\mathrm{Bu}_4\mathrm{NCl}$ and $n\mathrm{Bu}_2\mathrm{SbCl}_3$. $[\mathrm{Et}_3\mathrm{SbMe}]_2$-$[(\mathrm{MeSbCl}_3)_2]$ (**2**) is formed from $[\mathrm{Et}_3\mathrm{SbMe}]\mathrm{I}$ and $\mathrm{Me}_2\mathrm{SbCl}_3$. The structures of **1** and **2** were determined by single-crystal X-ray diffractommetry.

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

Introduction

Organoantimony halides of the types $\mathrm{R}_2\mathrm{SbX}_3$ and RSbX_2 are strong Lewis acids. They readily accept additional halide ions with formation of the corresponding hypercoordinate antimonates $[\mathrm{R}_2\mathrm{SbX}_4]^-$ and $[\mathrm{RSbX}_3]^-$. Crystal structure determinations revealed the octahedral *trans* structure of $[\mathrm{R}_2\mathrm{SbX}_4]^-$ (R = Me, Ph; X = F, Cl, Br) [1 – 3] and the dimeric nature of $[(\mathrm{RSbX}_3)_2]^{2-}$, R = Ph, X = Cl [4, 5], I [6, 7]; R = $\mathrm{Me}_3\mathrm{SiCH}_2$, 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 $[n\mathrm{Bu}_4\mathrm{N}][n\mathrm{Bu}_2\mathrm{SbCl}_4]$ (**1**) and $[\mathrm{Et}_3\mathrm{SbMe}]_2$ $[(\mathrm{MeSbCl}_3)_2]$ (**2**).

Results and Discussion

$[n\mathrm{Bu}_4\mathrm{N}][n\mathrm{Bu}_2\mathrm{SbCl}_4]$ (**1**) is formed by the reaction of $n\mathrm{Bu}_4\mathrm{NCl}$ with $n\mathrm{Bu}_2\mathrm{SbCl}_3$ in methanol at ambient temperature. $n\mathrm{Bu}_2\mathrm{SbCl}_3$ is prepared by reaction of $(n\mathrm{Bu}_2\mathrm{Sb})_2$ with $\mathrm{SO}_2\mathrm{Cl}_2$. **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 $\mathrm{M}[\mathrm{Me}_2\mathrm{SbCl}_4]$ salts (M = $\mathrm{Ph}_4\mathrm{P}$, Sb–C 2.098(6), 2.110(8), Sb–Cl 2.4675(10) Å; M = $\mathrm{Ph}_4\mathrm{Sb}$, Sb–C 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 SbCl_4 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 ^{1}H NMR spectrum of **1** in CDCl_3 contains multiplet signals for the methylene groups and triplet signals for the methyl groups of the *n*-butyl substitutents on antimony and nitrogen. The ^{13}C 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 $[n\mathrm{BuSbCl}_3]^-$ and $[(n\mathrm{Bu}_4\mathrm{N})_2\mathrm{Cl}]^+$.

$[\mathrm{Et}_3\mathrm{SbMe}]_2[\mathrm{Me}_2\mathrm{Sb}_2\mathrm{Cl}_6]$ (**2**) was obtained serendipitously from the reaction of $[\mathrm{Et}_3\mathrm{SbMe}]\mathrm{I}$ and $\mathrm{Me}_2\mathrm{SbCl}_3$. The reaction pathways have not been elucidated, and thorough investigations are necessary to

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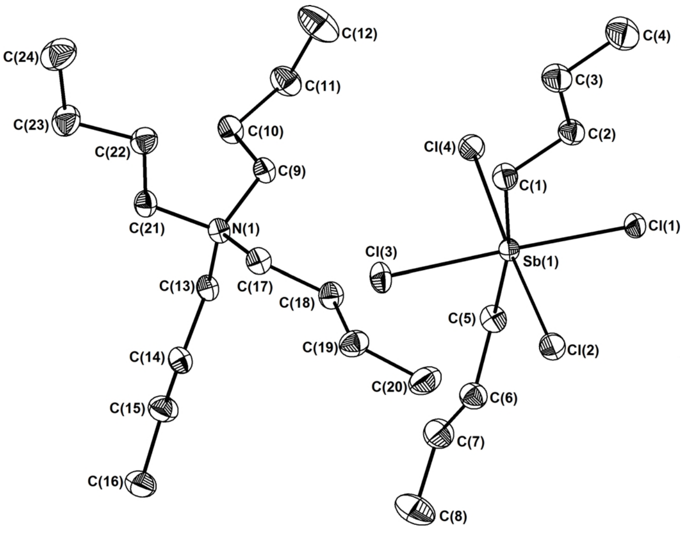

Fig. 1. Displacement ellipsoid representation (30 %) of the molecular structure of **1** in the crystal with hydrogen atoms omitted for clarity. Selected distances (Å) and angles (deg): C(1)–Sb(1) 2.139(2), C(5)–Sb(1) 2.143(2), Cl(1)–Sb(1) 2.4609(14), Cl(2)–Sb(1) 2.4577(6), Cl(3)–Sb(1) 2.5017(15), Cl(4)–Sb(1) 2.5108(7); C(1)–Sb(1)–C(5) 169.89(8), Cl(1)–Sb(1)–Cl(3) 177.915(19), Cl(2)–Sb(1)–Cl(4) 176.732(19).

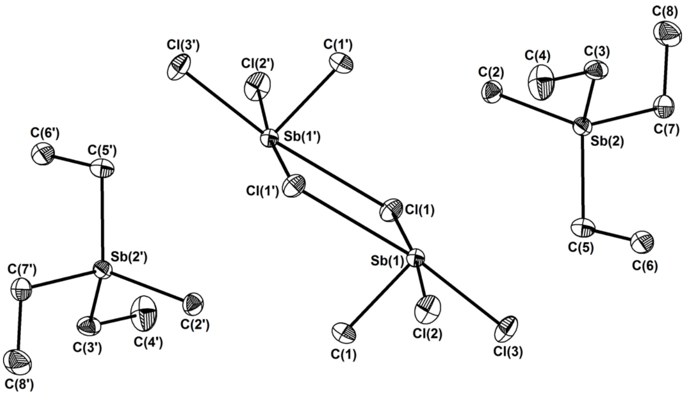

Fig. 2. Displacement ellipsoid representation (30 %) of **2** with hydrogen atoms omitted for clarity. Selected distances (Å) and angles (deg): C(1)–Sb(1) 2.129(5), Cl(1)–Sb(1) 2.9013(14), Cl(1′)–Sb(1) 2.9258(14), Cl(2)–Sb(1) 2.4789(15), Cl(3)–Sb(1) 2.4703(13), C(2)–Sb(2) 2.104(4), C(3)–Sb(2) 2.121(4), C(5)–Sb(2) 2.104(4), C(7)–Sb(2) 2.112(4); C(1)–Sb(1)–Cl(1) 83.84(16), Cl(1)–Sb(1)–Cl(2) 173.44(5), Cl(1′)–Sb(1)–Cl(3) 170.37(5).

solve this chemical puzzle. For the preparation of the onium salts with [R$_2$SbCl$_4$]$^-$ or [(RSbCl$_3$)$_2$]$^{2-}$ anions it is preferable to avoid iodide and to react onium chlorides with R$_2$SbCl$_3$ or RSbCl$_2$. **2** is an air-stable crystalline 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 Et$_3$SbMe cations and centrosymmetric Me$_2$Sb$_2$Cl$_6$ 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 structural features are not unusual. Similar arrangements were also observed for the closely related compound, *i. e.* [(Me$_3$SiCH$_2$SbCl$_3$)$_2$]$^{2-}$ (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 [D$_6$]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 $[\mathrm{MeSbCl}_3]^-$ are observed.

Conclusion

$[n\mathrm{Bu}_4\mathrm{N}][n\mathrm{Bu}_2\mathrm{SbCl}_4]$ (**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 $[\mathrm{Et}_3\mathrm{SbMe}]\mathrm{I}$ and $\mathrm{Me}_2\mathrm{SbCl}_3$ is interesting with respect to the redox chemistry of organoantimony(V) compounds, but for the synthesis of salts with the $[(\mathrm{MeSbCl}_3)_2]^{2-}$ ion a synthesis starting from MeSbCl_2 is to be preferred. The organoantimony compounds **1** and **2** are stable and easy to handle, and therefore useful for synthetic or analytical purposes in organometallic chemistry.

Experimental Section

$(n\mathrm{Bu}_2\mathrm{Sb})_2$ [11], $[\mathrm{Et}_3\mathrm{SbMe}]\mathrm{I}$ [12] and $\mathrm{Me}_2\mathrm{SbCl}_3$ [13] were prepared according to previously described methods. ^{1}H and ^{13}C NMR spectra were recorded in CDCl_3 or $[\mathrm{D}_6]$DMSO with Bruker DPX 200 or Bruker Avance 400 instruments. Mass spectra were recorded on a Bruker Esquire LC instrument. The C and H elemental analyses were performed by Mikroanalytisches Laboratorium Beller-Matthies in Göttingen, Germany.

Synthesis of $[n\mathrm{Bu}_4\mathrm{N}][n\mathrm{Bu}_2\mathrm{SbCl}_4]$ *(**1**)*

A solution of 7.6 g (57 mmol) $\mathrm{SO}_2\mathrm{Cl}_2$ in 75 mL $\mathrm{CH}_2\mathrm{Cl}_2$ was added dropwise at −70 °C to 8.9 g (18.9 mmol) $(n\mathrm{Bu}_2\mathrm{Sb})_2$ in 25 mL $\mathrm{CH}_2\mathrm{Cl}_2$. An orange-yellow precipitate formed which became colorless in the further course of the reaction. Subsequently the temperature was raised to r. t., and evolution of SO_2 gas occurred. Stirring for 15 h and removal of the solvent gave 9.5 g (73 %) $n\mathrm{Bu}_2\mathrm{SbCl}_3$. A solution of 1.0 g (3 mmol) $n\mathrm{Bu}_2\mathrm{SbCl}_3$ in 25 mL methanol was added dropwise to a solution of 0.9 g (3 mmol) $n\mathrm{Bu}_4\mathrm{NCl}$ in 25 mL methanol. **1** was formed as a colorless solid. The suspension was stirred for 1 h, and the solvent was removed at reduced pressure. Crystallization from acetonitrile at −3 °C gave 0.77 g (41 %) of colorless crystals of **1**. M. p. = 125 °C. – ^{1}H NMR (400 MHz, CDCl_3): δ = 0.90 (t, J = 7.4 Hz, 6H, $\mathrm{C}H_3\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{Sb}$), 1.00 (t, J = 7.3 Hz, 8H, $\mathrm{C}H_3\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{N}$), 1.33 (m, 4H, $\mathrm{CH}_3\mathrm{C}H_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{Sb}$), 1.43 (m, 8H, $\mathrm{CH}_3\mathrm{C}H_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{N}$), 1.64 (m, 8H, $\mathrm{CH}_3\mathrm{CH}_2\mathrm{C}H_2\mathrm{CH}_2\mathrm{N}$), 2.06 (m, 4H, $\mathrm{CH}_3\mathrm{CH}_2\mathrm{C}H_2\mathrm{CH}_2\mathrm{Sb}$), 3.24 (m, 8H, $\mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}_2\mathrm{C}H_2\mathrm{N}$), 3.32 (m, 4H, $\mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}_2\mathrm{C}H_2\mathrm{Sb}$). – ^{13}C NMR (101 MHz, CDCl_3): δ = 13.79 ($C\mathrm{H}_3\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{N}$), 13.96 ($C\mathrm{H}_3\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{Sb}$), 19.85 ($\mathrm{CH}_3C\mathrm{H}_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{N}$), 23.95 ($\mathrm{CH}_3C\mathrm{H}_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{Sb}$), 24.11 ($\mathrm{CH}_3\mathrm{CH}_2C\mathrm{H}_2\mathrm{CH}_2\mathrm{N}$), 29.33 ($\mathrm{CH}_3\mathrm{CH}_2C\mathrm{H}_2\mathrm{CH}_2\mathrm{Sb}$), 59.01 ($\mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}_2C\mathrm{H}_2\mathrm{N}$), 75.88 ($\mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}_2C\mathrm{H}_2\mathrm{Sb}$). – MS ((+)-ESI): *m/z* (%) = 242 (100) $[\mathrm{Bu}_4\mathrm{N}]^+$, 520 (15); MS ((–)-ESI): *m/z* (%) = 285 (100) $[\mathrm{BuSbCl}_3]^-$, 377 (84) $[\mathrm{Bu}_2\mathrm{SbCl}_4]^-$. – $\mathrm{C}_{24}\mathrm{H}_{54}\mathrm{Cl}_4\mathrm{NSb}$ (620.3): calcd. C 46.47, H 8.78; found C 46.57, H 8.18.

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

A solution of $\mathrm{Et}_3\mathrm{MeSbI}$ (2.7 g, 7.7 mmol) in 50 mL methanol was added dropwise to $\mathrm{Me}_2\mathrm{SbCl}_3$ (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 was dissolved in $\mathrm{CH}_3\mathrm{CN}$. 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. – ^{1}H NMR (400 MHz, $[\mathrm{D}_6]$DMSO): δ = 1.29 (t, J = 7.9 Hz, 9H, $\mathrm{CH}_2\mathrm{C}H_3$), 1.38 (s, 3H, $\mathrm{SbC}H_3$), 1.54 (s, 3H, $\mathrm{Cl}_3\mathrm{SbC}H_3$), 2.18 (q, J = 7.9 Hz, 6H, $\mathrm{C}H_2\mathrm{CH}_3$). – ^{13}C NMR (101 MHz, $[\mathrm{D}_6]$DMSO): δ = −4.25 ($\mathrm{Sb}C\mathrm{H}_3$), 9.37 ($\mathrm{CH}_2C\mathrm{H}_3$), 12.27 ($C\mathrm{H}_2\mathrm{CH}_3$), 34.03 ($\mathrm{Cl}_3\mathrm{Sb}C\mathrm{H}_3$). – $\mathrm{C}_{16}\mathrm{H}_{42}\mathrm{Cl}_6\mathrm{Sb}_4$ (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 KelF 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**: $\mathrm{C}_{24}\mathrm{H}_{54}\mathrm{Cl}_4\mathrm{NSb}$, M_r = 620.23, crystal size 0.3 × 0.4 × 0.4 mm^3, monoclinic, $C2/c$, Z = 8, a = 28.401(6), b = 13.305(3), c = 22.142(4) Å, β = 129.52(3) deg, V = 6455(2) Å^3, D_calcd = 1.28 g cm^{-3}, $\mu(\mathrm{Mo}K_\alpha)$ = 1.2 cm^{-1}, $F(000)$ = 2592 e, *hkl* ranges −6/11, ± 10, ± 13, 44790 measured refl., 6316 unique refl., R_int = 0.0778, 277 refined param., $R(F)$ (all reflections) = 0.0312, $wR(F^2)$ (all reflections) = 0.0511, GoF (F^2) = 1.047, $\Delta\rho_\mathrm{fin}$ (max / min) = 0.52 / −0.28 e Å^{-3}, weighting scheme details: $w = 1/[\sigma^2(F_\mathrm{o}^2)+(0.0089P)^2+4.0804P]$ where $P = (F_\mathrm{o}^2+2F_\mathrm{c}^2)/3$. Crystal and refinement data for **2**: $\mathrm{C}_{24}\mathrm{H}_{54}\mathrm{Cl}_4\mathrm{NSb}$, M_r = 467.12, crystal size 0.70 × 0.60 × 0.40 mm^3, triclinic, $P\bar{1}$, Z = 2, a = 9.0140(18), b = 9.3450(19), c = 10.673(2) Å, α = 65.81(3), β = 87.82(3), γ = 74.15(3) deg, V = 786.1(3) Å^3, D_calcd = 1.97 g cm^{-3}, $\mu(\mathrm{Mo}K_\alpha)$ = 3.9 cm^{-1}, $F(000)$ = 444 e, *hkl* ranges ± 35, ± 16, ± 27, 4182 measured refl., 3458 unique refl., R_int = 0.0158, 123 refined param., $R(F)$ (all reflections) = 0.0301, $wR(F^2)$ (all reflections) = 0.0777, GoF (F^2) = 1.179, $\Delta\rho_\mathrm{fin}$ (max / min) = 0.81 / −0.92 e Å^{-3}, weighting scheme details: $w = 1/[\sigma^2(F_\mathrm{o}^2)+(0.0276P)^2+2.1718P]$ where $P = (F_\mathrm{o}^2+2F_\mathrm{c}^2)/3$.

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.

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