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Syntheses, structures and intermolecular interactions of tetraorganoammonium, -phosphonium and -stibonium dimethyl- and diphenyltetrahaloantimonates

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ABSTRACT

The syntheses and spectroscopic (NMR, MS) investigations of the antimonates $[Ph_4P]^+[Me_2SbCl_4]^-$ (**1**), $[Me_4Sb]^+[Me_2SbCl_4]^-$ (**2**), $[Et_4N]^+[Ph_2SbCl_4]^-$ (**3**), $[Bu_4N]^+[Ph_2SbCl_4]^-$ (**4**), $[Me_4Sb]^+[Ph_2SbCl_4]^-$ (**5**), $[Et_3MeSb]^+[Ph_2SbCl_4]^-$ (**6**), $[Et_4N]^+[Ph_2SbF_4]^-$ (**7**) and $[Et_4N]^+[Ph_2SbBr_4]^-$ (**8**) are reported. Halogen scrambling reactions of Et_4NBr or Ph_4EBr (E = P, Sb) with R_2SbCl_3 (R = Me, Ph) produce mixtures of compounds from which crystals of $[Et_4N]^+[Ph_2SbBr_{1.24}Cl_{2.76}]^-$ (**9**), $[Et_4N]^+[Ph_2SbBr_{2.92}Cl_{1.08}]^-$ (**10**) or $[Ph_4Sb]^+[Me_2SbCl_4]^-$ (**11**) were isolated. The crystal and molecular structures of **1** and **3**–**11** are reported.

1. Introduction

Salts consisting of the pyridinium ion, $(C_5H_5NH)^+$, as cation and diaryltetrachloro antimonate anions, $[R_2SbCl_4]^-$, have been known since 1920 [1,2]. They were prepared by reactions of pyridine hydrochloride with diarylantimony(V) trichlorides and were widely used as intermediates for the synthesis and purification of stibinic acids $R_2Sb(O)OH$ [3,4]. Later also dialkyl- and diaryltetrachloroantimonates with cations like aryldiazonium, tetraalkylammonium or tetraphenylarsonium ions were synthesized by combining the corresponding onium chloride with a diorganoantimony(V) trichloride [2]. Salts with the mixed-halide $[Ph_2SbBr_nCl_{4-n}]^-$ anion were obtained by addition of Et_4NBr or other onium bromides to Ph_2SbCl_3 [2,5–7]. The only known diorganotetrabromoantimonate, $[Ph_4As]^+[Ph_2SbBr_4]^-$ was prepared from $Ph_2SbCl_3{\cdot}H_2O$ or $Ph_2Sb(O)OH$, HBr and $[Ph_4As]X$ (X = Cl or Br) [7]. Diorganotetraiodoantimonates are unknown, but diorganotetrafluoroantimonates were described frequently [2]. The fluoro derivatives $M[Ph_2SbF_4]$ (M = H, Na, K) were obtained by reactions of C_6H_6 with SbF_5 and water, NaOH or KOH. $[Ph_4As]^+[Ph_2SbF_4]^-$ was formed from $Ph_2SbCl_3{\cdot}H_2O$, Ph_4AsCl and HF [7]. Structural studies of diorganotetrahaloantimonates were carried out using Mössbauer, infrared and Raman spectroscopies and the resulting data were interpreted in terms of the presence of $[trans\text{-}R_2SbX_4]^-$ species (R = Me, Ph; X = F, Cl, Br) [5–7]. Crystallographic studies for $[HBipy]^+[Ph_2SbCl_4]^-$ [8] and $[HPy]^+[Ph_2SbCl_4]^-$ [9] were reported.

Compounds with lower melting points, chemically related to onium diorganotetrahaloantimonates, were used as environmentally friendly ionic solvents for various organic reactions [10]. Also onium diorganotetrahaloantimonates are candidates for applications as ionic liquids because the introduction of longer alkyl substituents both on the cations and the anions may decrease the lattice energy and result in the formation of low melting salts. Another possible application for the permethylated salt $[Me_4Sb]^+[Me_2SbCl_4]^-$ (**2**) is the use as standard for the analyses of methylantimony compounds formed by biomethylation of antimony in the environment [11].

Searching for diorganoantimony(V) reagents that can be used for the syntheses of organoantimony polyoxometalates [12] in aqueous conditions we became interested in the chemistry of diorganoantimony(V) trihalides and onium diorganotetrahaloantimonates. Our previous related studies had focused on diphenylantimony tribromide and onium organoantimonates(III) [13–15].

We report here the syntheses and spectroscopic (NMR, MS) investigation of the several tetrahaloantimonates as well as the crystal and molecular structures of $[Ph_4P]^+[Me_2SbCl_4]^-$ (**1**), $[Et_4N]^+[Ph_2SbCl_4]^-$ (**3**), $[Bu_4N]^+[Ph_2SbCl_4]^-$ (**4**), $[Me_4Sb]^+[Ph_2SbCl_4]^-$ (**5**), $[Et_3MeSb]^+[Ph_2SbCl_4]^-$ (**6**), $[Et_4N]^+[Ph_2SbF_4]^-$ (**7**), $[Et_4N]^+[Ph_2SbBr_4]^-$ (**8**), $[Et_4N]^+[Ph_2SbBr_{1.24}Cl_{2.76}]^-$ (**9**), $[Et_4N]^+[Ph_2SbBr_{2.92}Cl_{1.08}]^-$ (**10**) and $[Ph_4Sb]^+[Me_2SbCl_4]^-$ (**11**).

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2. Results and discussion

2.1. Preparation and spectroscopic characterization

The syntheses of the salts **1**–**7** were performed by reactions of dimethyl- or diphenylantimonytrichloride with R'_4NCl (R′ = Et, Bu), Ph_4PCl, Me_4SbI or Et_3MeSbI in methanol or a mixture of methanol and hydrochloric acid. The reactions between R'_4ECl and R_2SbCl_3 are straight forward with the transfer of the chloride ion from the ammonium or phosphonium compound to the Lewis acidic diorganoantimony trichloride (Scheme 1):

The reactions between stibonium iodides and R_2SbCl_3 combine redox processes with formation of iodine or triiodide, as suggested by the brown color of the reaction mixture, and chloride transfer, as indicated by single-crystal X-ray diffraction studies. The iodine can further react with the stibonium iodide with formation of a triiodide (Scheme 2).

By contrast, the reactions between onium bromides and R_2SbCl_3 lead to mixtures of chloro/bromo derivatives due to scrambling of halogens. The ES MS (negative) data are consistent with this behavior, several anions being observed, e.g. $[Ph_2SbBr_2Cl_2^-]$, $[Ph_2SbBrCl_3^-]$ and $[Ph_2SbCl_4^-]$ for the crude product isolated from the reaction of Et_4NBr with $Ph_2SbCl_3{\cdot}H_2O$. From such mixtures of compounds crystals of $[Et_4N]^+[Ph_2SbBr_{1.24}Cl_{2.76}]^-$ (**9**), $[Et_4N]^+[Ph_2SbBr_{2.92}Cl_{1.08}]^-$ (**10**) or $[Ph_4Sb]^+[Me_2SbCl_4]^-$ (**11**) were isolated. Attempts to complete the exchange of halogen by reacting the crude $[Et_4N]^+[Ph_2SbBr_nCl_{4-n}]^-$ (n = 0–4) with NaBr have failed. Pure $[Et_4N]^+[Ph_2SbBr_4]^-$ (**8**) was obtained by reacting Et_4NBr with Ph_2SbBr_3. However, the full exchange of halogen was achieved when $[Et_4N]^+[Ph_2SbCl_4]^-$ (**3**) was reacted with NaF and the tetrafluoroantimonate $[Et_4N]^+[Ph_2SbF_4]^-$ (**7**) was obtained.

The pure tetrahaloantimonates **1**–**8** were isolated as air stable, colorless crystalline solids. Mass spectra obtained with the electrospray ionization technique (ESI) show the cation and the anion for these compounds. Consistent with their ionic nature, the majority of the compounds were soluble in DMSO. However, $[Bu_4N]^+[Ph_2SbCl_4]^-$ (**4**) was found to be also soluble in $CHCl_3$, a behavior suggesting that increase in the length of the alkyl groups on nitrogen might increase considerably the solubility of such ionic compounds in organic solvents.

The ^1H and ^{13}C NMR spectra of compounds **1**–**8** show the expected resonances both for the cations and anions. The presence of one set of signals suggests the equivalence, in solution, of the organic groups attached to antimony in the $[R_2SbCl_4]^-$ anions.

$$R'_4ECl + R_2SbCl_3 \longrightarrow [R'_4E]^+[R_2SbCl_4]^-$$

1 R = Me; R' = Ph; E = P
3 R = Ph; R' = Et; E = N
4 R = Ph; R' = Bu; E = N

Scheme 1.

2.2. Crystal and molecular structures

Single crystals suitable for X-ray diffraction studies were obtained from acetonitrile solutions by slow evaporation, at room temperature, in an open atmosphere, for compounds **1** and **3**–**11**. As representative examples the structures of **1, 4, 5, 7** and **8**, showing both the cation and the anion, are depicted in Figs. 1–3. In the mixed-halogen compounds, i.e. **9** and **10**, there was disorder involving the bromine or chlorine atoms. The best solution was obtained with Br/Cl occupancy of 0.31/0.69 for **9** and 0.73/0.27 for **10**, respectively (see also Supplementary material). Disorder phenomena were also observed for the $[Et_4N]^+$ cation in the corresponding salts, i.e. **3** and **7**–**10**.

All the salts are composed of tetrahedral onium cations and octahedral anions. In all cases, regardless the nature of the halogen, the methyl or phenyl groups in the $[R_2SbX_4]^-$ anions are placed in *trans* positions. This is consistent with the previous reports on related salts based on Raman, IR and Mössbauer data and also with the results of our NMR investigations in solution.

The major difference in the anions containing phenyl groups is concerned to the relative orientation of the two aromatic rings. In all compounds the phenyl rings are basically bisecting the X–Sb–X angles of the square planar SbX_4 plane. For compound **5** (Fig. 1) the phenyl rings are coplanar, while in compounds **4** and **7** (Fig. 2) they are slightly deviated from coplanarity (dihedral angles of 8.3° and 11.3°, respectively). Compound **6** contains three independent anions in the unit cell: two of them, i.e. anions **6b** and **6c**, contain coplanar phenyl rings, while in anion **6a** a slight deviation from coplanarity (dihedral angle of 7.2°) was observed. By contrast, for compounds **3**, **8** (Fig. 3), **9** and **10**, which contain the $[Et_4N]^+$ counter-cation, the phenyl rings are orthogonal.

The Sb–F bond lengths in **7** [1.957(2), 1.960(3) Å] are slightly shorter than in the monomeric Me_3SbF_2 [1.993(4), 2.004(4) Å] [16]. In the tetrachloroantimonates described here the Sb–Cl bond distances are in the range 2.456(1)–2.503(3) Å, being of intermediate length between terminal and bridging antimony–halogen bonds in the dimers $(Ph_2SbCl_3)_2$ [2.346(4), 2.388(4) Å vs. 2.620(4), 2.839(4) Å] [17] or $(Me_2SbCl_3)_2$ [2.353(2), 2.356(2) Å vs. 2.798(2), 2.801(2) Å] [18] and of same magnitude as found for the equatorial Sb–Cl bonds in *trans* to each other in the monomer $Ph_2SbCl_3{\cdot}H_2O$ [2.462(2) Å] [19]. The Sb–Br bonds in **8** [2.646(1) Å] are larger than the Sb–Br bonds in the adduct $Ph_2SbBr_3{\cdot}MeCN$ [2.519(2), 2.605(1) Å] [19] or the terminal Sb–Br bonds [2.478(3), 2.557(3) Å] in the polymeric association found in the crystal of Ph_2SbBr_3 [20], but compare well with the shorter bridging antimony–bromine bond distance [2.673(3) Å] in the latter compound.

The values of the Sb–C bond lengths in the $[R_2SbX_4]^-$ anions (see also Supplementary material) are comparable with the values found in the related starting materials, i.e. $(Me_2SbCl_3)_2$ [2.1316(2), 2.1349(2) Å] [18], $(Ph_2SbCl_3)_2$ [2.125(9) Å] [17], $Ph_2SbCl_3{\cdot}H_2O$ [2.1218(8) Å] [19] or Ph_2SbBr_3 [2.149(12) Å] [20]. The same considerations apply for the lengths of the Sb–C bonds in the cations $[Me_4Sb]^+$ in **5** [2.097(3), 2.098(3) Å], $[Et_3MeSb]^+$ in **6** [range 2.065(19)–2.150(19) Å] or $[Ph_4Sb]^+$ in **11** [2.104(5) Å], which

$$2\ R'_3MeSbI + 3\ R_2SbCl_3 \longrightarrow 2\ [R'_3MeSb]^+[R_2SbCl_4]^- + R_2SbCl + I_2$$

2 R = Me; R' = Me
5 R = Ph; R' = Me
6 R = Ph; R' = Et

$$R'_3MeSbI + I_2 \longrightarrow [R'_3MeSb]^+[I_3]^-$$

Scheme 2.

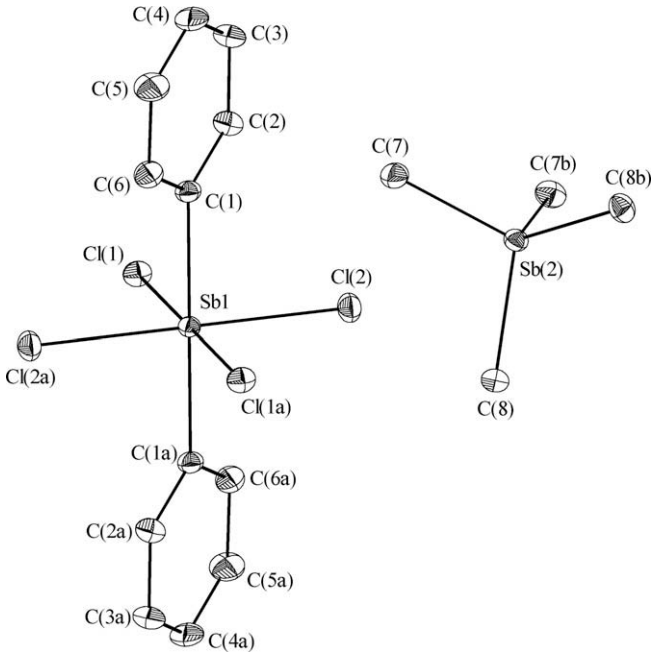

Fig. 1. ORTEP representation at 30% probability and atom numbering scheme for **5** [symmetry equivalent position $(0.5 - x, 1.5 - y, 2 - z)$ is given by "a" for the anion, and $(1 - x, y, 1.5 - z)$ by "b" for the cation; hydrogen atoms are omitted for clarity]. Selected distances (Å) and angles (°): Sb(1)–C(1) 2.136(3), Sb(1)–Cl(1) 2.4720(7), Sb(1)–Cl(2) 2.4710(7); C(1)–Sb(1)–C(1a) 180.00(6), C(1)–Sb(1)–Cl(1) 90.50(7), C(1)–Sb(1)–Cl(2) 89.91(7), C(1)–Sb(1)–Cl(1a) 89.50(7), C(1)–Sb(1)–Cl(2a) 90.09(7), C(1a)–Sb(1)–Cl(1) 89.50(7), C(1a)–Sb(1)–Cl(2) 90.09(7), C(1a)–Sb(1)–Cl(1a) 90.50(7), C(1a)–Sb(1)–Cl(2a) 89.91(7), Cl(1)–Sb(1)–Cl(1a) 180.00(3), Cl(2)–Sb(1)–Cl(2a) 180.0, Cl(1)–Sb(1)–Cl(2) 90.20(2), Cl(1)–Sb(1)–Cl(2a) 89.80(2), Cl(1a)–Sb(1)–Cl(2a) 90.20(2), Cl(1a)–Sb(1)–Cl(2) 89.80(2).

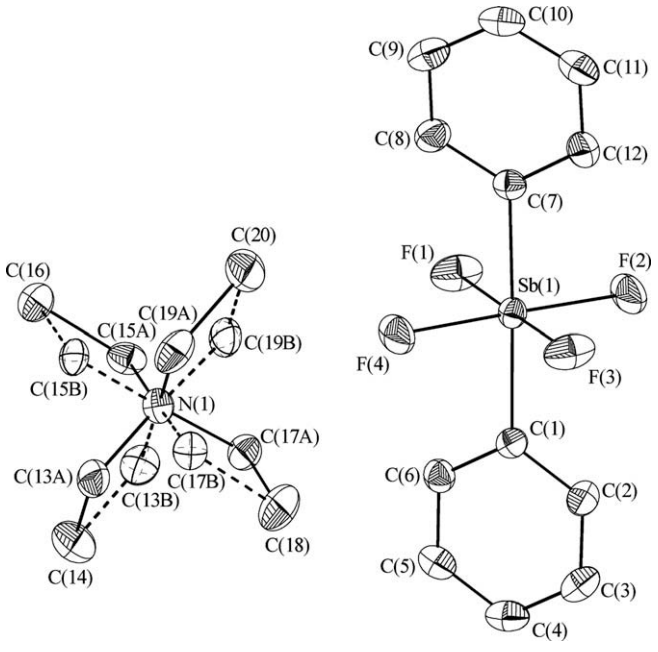

Fig. 2. ORTEP representation at 30% probability and atom numbering scheme for **7** (hydrogen atoms are omitted for clarity). Selected distances (Å) and angles (°): Sb(1)–C(1) 2.114(4), Sb(1)–C(7) 2.116(4), Sb(1)–F(1) 1.960(2), Sb(1)–F(2) 1.960(3); Sb(1)–F(3) 1.957(2), Sb(1)–F(4) 1.960(3), C(1)–Sb(1)–C(7) 177.76(14), C(1)–Sb(1)–F(1) 90.27(13), C(1)–Sb(1)–Fl(2) 90.42(13), C(1)–Sb(1)–F(3) 90.24(13), C(1)–Sb(1)–F(4) 88.70(13), C(7)–Sb(1)–F(1) 90.77(13), C(7)–Sb(1)–F(2) 91.56(13), C(7)–Sb(1)–F(3) 88.74(13), C(7)–Sb(1)–F(4) 89.31(13), F(1)–Sb(1)–F(3) 179.22(13), F(2)–Sb(1)–F(4) 178.98(12), F(1)–Sb(1)–F(2) 90.13(15), F(1)–Sb(1)–F(4) 90.39(14), F(2)–Sb(1)–F(3) 89.28(15), F(3)–Sb(1)–F(4) 90.21(14).

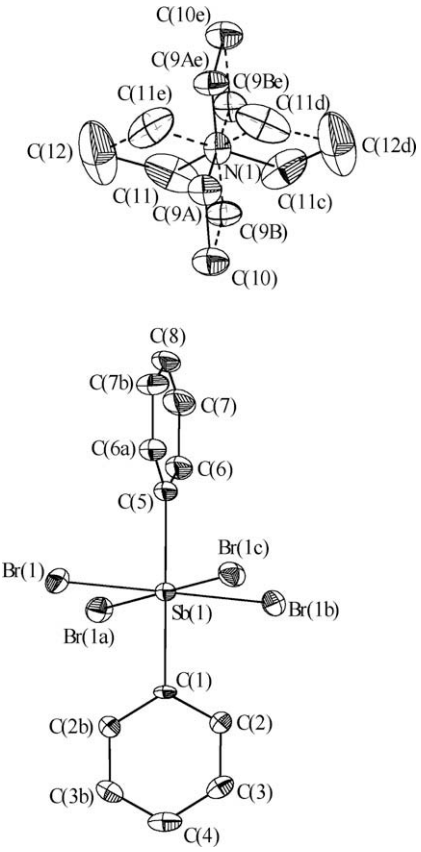

Fig. 3. ORTEP representation at 30% probability and atom numbering scheme for **8** [symmetry equivalent positions $(x, y, 0.5 - z)$, $(1 - x, y, 0.5 - z)$ and $(1 - x, y, z)$ are given by "a", "b" and "c" for the anion, and $(1 - x, -y, 1 - z)$ and $(x, -y, 1 - z)$ by "d" and "e" for the cation; hydrogen atoms are omitted for clarity]. Selected distances (Å) and angles (°):Sb(1)–C(1) 2.145(9), Sb(1)–C(5) 2.152(11), Sb(1)–Br(1) 2.6462(12), C(1)–Sb(1)–C(5) 180.000(2), C(1)–Sb(1)–Br(1) 89.898(18), C(5)–Sb(1)–Br(1) 90.102(18), Br(1)–Sb(1)–Br(1b) 179.80(4), Br(1)–Sb(1)–Br(1a) 89.81(5), Br(1)–Sb(1)–Br(1c) 90.19(5).

compare well with those observed in Me_4SbI [2.043(2), 2.070(1) Å] [21] and Ph_4SbBr [2.092(9)–2.151(9) Å] [22].

Interesting aspects emerge when the packing of the ions is inspected in the crystals of compounds containing tetraorganostibonium cations. Weak cation–anion interactions are observed in the crystals of **5** and **6**, resulting in different associations. In **5** all the chlorine atoms of a $[Ph_2SbCl_4]^-$ anion are involved in interactions with the metal center from four different $[Me_4Sb]^+$ cations [Sb(2)···Cl(1) 3.66, Sb(2)···Cl(2) 3.89 Å; cf. $\sum r_{vdW}$(Sb,Cl) ca. 4.0 Å] [23] thus resulting in a 3D architecture (Fig. 4). In addition, $C–H_{methyl}\cdots\pi$ ($Ph_{centroid}$) contacts [2.89 Å] between anions and cations are also present. The vectors of the Sb···Cl interactions are directed towards the capping positions of the tetrahedral SbC_4 core of the cation. By contrast, in the crystal of **6** only one of the three independent anions, i.e. **6c**, is involved in two Sb···Cl interactions [Sb(5d)···Cl(8) 3.93 Å] through halogen atoms placed in *trans* position, thus leading to discrete cation–anion–cation units (see Supplementary material). In $[Ph_4Sb]^+[Me_2SbCl_4]^-$ (**11**) where the cation is sterically protected close cation–anion contacts through Sb···Cl interactions were not observed. No significant distortions were noted in the cation coordination sphere of compounds **5** [Sb–C 2.097(3)/2.098(3) Å; C–Sb–C range 107.3(2)–111.4(1)°], **6** [Sb–C range 2.065(19)–2.150(19)/2.07(2)–2.115(19) Å; C–Sb–C range 105.6(6)–112.1(7)/105.3(15)–114.3(9)°] and **11** [Sb–C 2.104(5) Å; C–Sb–C range 103.8(3)–112.4(1)°].

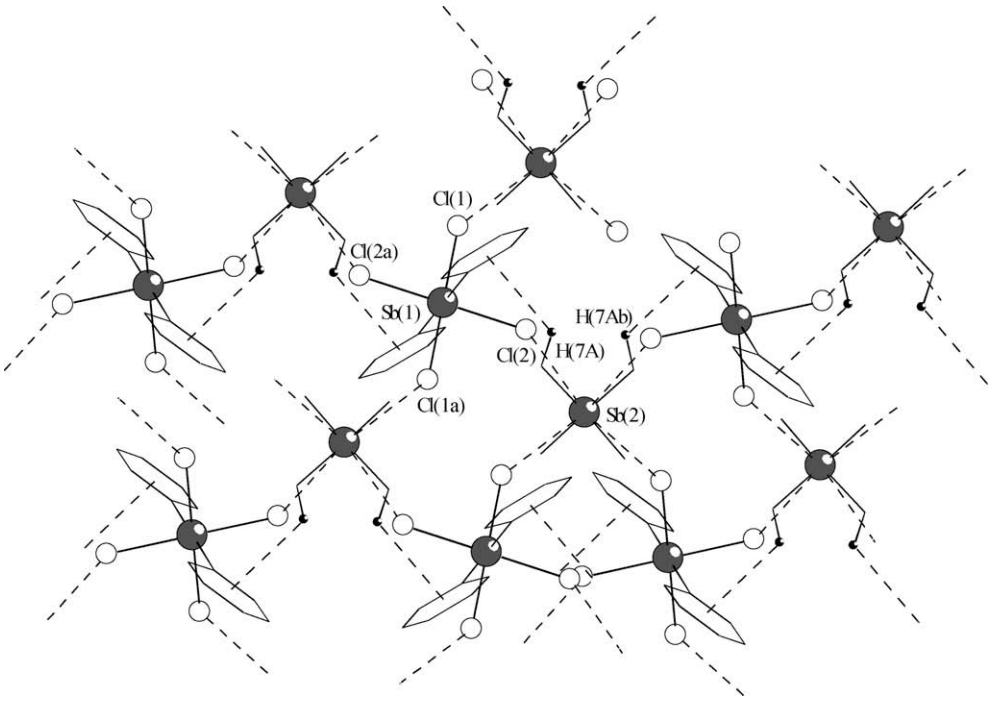

Fig. 4. View of a fragment of the 3D architecture based on antimony–chlorine and C–$H_{methyl}\cdots\pi$ ($Ph_{centroid}$) contacts between anions and cations in the crystal of **5** [only hydrogens involved in anion–cation C–$H_{methyl}\cdots\pi$ contacts are shown].

3. Conclusions

The onium diorganotetrafluoro-, -chloro- and -bromoantimonates reported here represent a large family of easily accessible, stable organoantimony compounds. The ionic nature and the almost uniform structure of the tetrahedral cations and the octahedral antimony anions with the organic groups in *trans* positions are clearly demonstrated. Applications of this class of compounds in organoantimony syntheses, e.g. the preparation of stibinic acids have a long tradition. The antimonates are certainly useful for the formation of salts with a variety of inorganic or organic cations. Other potential applications include, among others, the use as organic–inorganic materials, ionic solvents or analytical standards for antimony analyses or antimony-containing medicines.

4. Experimental

4.1. Materials and procedures

The starting materials such as Et_4NCl, Et_4NBr, $Bu_4NCl{\cdot}H_2O$, Ph_4PCl, Ph_4PBr, NaF and NaBr were commercially available. Me_2SbCl_3 [24], Ph_2SbCl_3 [25], $Ph_2SbCl_3{\cdot}H_2O$ [19], Ph_2SbBr_3 [13], Me_4SbI [26], Et_3MeSbI [26], Ph_4SbBr [21] were prepared according to published methods. Room-temperature ^1H, ^{13}C and ^{19}F spectra were recorded in DMSO-d_6 or $CDCl_3$ with BRUKER DPX 200 or Bruker Avance DRX 300 instruments. The chemical shifts are reported in ppm relative to the residual peak of the solvent (ref. $CHCl_3$: ^1H 7.26, ^{13}C 77.0 ppm; DMSO-d_5: ^1H 2.50, ^{13}C 39.43 ppm) and relative to $CFCl_3$ for ^1H, ^{13}C and ^{19}F NMR spectra, respectively. Mass spectra were recorded with a FINNIGAN MAT 8200 spectrometer.

4.2. Synthesis of $[Ph_4P]^+[Me_2SbCl_4]^-$ (**1**)

A solution of Me_2SbCl_3 (1.0 g, 3.9 mmol) in 50 ml methanol was added dropwise to Ph_4PCl (1.45 g, 4.2 mmol) in 30 ml methanol and a white solid is formed. Filtration and crystallization from acetonitrile by slow evaporation in the open atmosphere gave **1** as colorless crystals. Yield: 1.9 g (78%). M.p. 225 °C. Anal. Calc. for $C_{26}H_{26}Cl_4PSb$: C, 49.33; H, 4.14. Found: C, 48.33; H, 4.52%. ^1H NMR (200 MHz, DMSO-d_6): δ 2.82s (6H, $SbCH_3$), 7.77 m (16H, PC_6H_5-*meta* + *ortho*), 7.97 m (4H, PC_6H_5-*para*). ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 61.24 ($SbCH_3$), 117.59d (PC_6H_5-*ipso*, $^1J_{PC}$ 89.2 Hz), 130.36d (PC_6H_5-*meta*, $^3J_{PC}$ 12.8 Hz), 134.47d (PC_6H_5-*ortho*, $^2J_{PC}$ 10.5 Hz), 135.24d (PC_6H_5-*para*, $^4J_{PC}$ 2.7 Hz). ^{31}P NMR (81.0 MHz, DMSO-d_6): δ 23.7. MS (ESI, CH_3CN), *m/z* (%), pos.: 339 (100) [Ph_4P^+]; neg.: 292 (72) [$Me_2SbCl_4^-$], 242 (100) [$MeSbCl_3^-$].

4.3. Synthesis of $[Me_4Sb]^+[Me_2SbCl_4]^-$ (**2**)

A solution of Me_4SbI (0.5 g, 1.6 mmol) in 20 ml methanol was added dropwise to Me_2SbCl_3 (0.42 g, 1.6 mmol) in 50 ml methanol and the mixture was stirred for 1 h. The color changed to yellow and a white precipitate formed. After filtration the solid was solved in CH_3CN. Slow evaporation of the solvent in the open atmosphere gave crystals of **2**. Yield: 0.55 g (71%). M.p. 95 °C. ^1H NMR (200 MHz, DMSO-d_6): δ 1.61s (6H, $SbCH_3$), 1.75s (12H, $SbCH_3$). MS (ESI, CH_3CN), *m/z* (%), pos.: 181 (100) [Me_4Sb^+]; neg.: 292 (30) [$Me_2SbCl_4^-$], 242 (100) [$MeSbCl_3^-$].

4.4. Synthesis of $[Et_4N]^+[Ph_2SbCl_4]^-$ (**3**)

A solution of Et_4NCl (1.20 g, 7.3 mmol) in 30 ml methanol was added dropwise to a stirred solution of $Ph_2SbCl_3{\cdot}H_2O$ (2.92 g, 7.3 mmol) in 20 ml methanol at room temperature. After 24 h of stirring the solvent was removed in vacuum and a white powder was isolated. The title compound was recrystallized from acetonitrile to give a colorless microcrystalline product. Yield: 3.6 g (90%). M.p. 268–269 °C. ^1H NMR (200 MHz, DMSO-d_6): δ 1.12 m (12H, NCH_2CH_3), 3.15q (8H, NCH_2CH_3, $^3J_{HH}$ 7.1 Hz), 7.42 m (6H, SbC_6H_5-*meta* + *para*), 8.22d (4H, SbC_6H_5-*ortho*, $^3J_{HH}$ 7.2 Hz). ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 6.96 (NCH_2CH_3), 51.28 m (NCH_2CH_3), 127.38 (SbC_6H_5-*meta*), 128.87 (SbC_6H_5-*para*), 130.41

(SbC_6H_5-*ortho*), 167.34 (SbC_6H_5-*ipso*). MS (ESI, CH_3CN), *m/z* (%), pos.: 130 (100) [Et_4N^+]; neg.: 417 (100) [$Ph_2SbCl_4^-$].

4.5. Synthesis of $[Bu_4N]^+[Ph_2SbCl_4]^-$ (**4**)

To a solution of $Bu_4NCl{\cdot}H_2O$ (0.89 g, 3.0 mmol) in 50 ml methanol was added dropwise, under stirring, a solution of $Ph_2SbCl_3{\cdot}H_2O$ (1.20 g, 3.0 mmol) in 50 ml methanol, at room temperature. The resulted suspension was stirred for 1 h, then filtered and the solid was washed with 5 ml methanol. The solid was dissolved in 20 ml acetonitrile and the solution, left in open atmosphere, deposited within 24 h air stable, colorless crystals which were filtered off. Yield: 1.94 g (98%). M.p. 169 °C. Anal. Calc. for $C_{28}H_{46}Cl_4NSb$: C, 50.94; H, 7.02. Found: C, 51.11; H, 6.96%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.85t [12H, $NCH_2(CH_2)_2CH_3$, $^3J_{HH}$ 7.0 Hz], 1.89 m [16H, $NCH_2(CH_2)_2CH_3$], 2.84t [8H, $NCH_2(CH_2)_2CH_3$, $^3J_{HH}$ 8.0 Hz], 7.32 m (6H, SbC_6H_5-*meta* + *para*), 8.39d (4H, SbC_6H_5-*ortho*, $^3J_{HH}$ 8.0 Hz). ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 13.60 (C_δ), 19.51 (C_γ), 23.82 (C_β), 58.57 (C_α), 127.44 (SbC_6H_5-*meta*), 128.75 (SbC_6H_5-*para*), 131.04 (SbC_6H_5-*ortho*), 167.89 (SbC_6H_5-*ipso*). MS (ESI, CH_3CN), *m/z* (%), pos.: 242 (100) [Bu_4N^+]; neg.: 417 (100) [$Ph_2SbCl_4^-$].

4.6. Synthesis of $[Me_4Sb]^+[Ph_2SbCl_4]^-$ (**5**)

A suspension of Me_4SbI (1.43 g, 4.6 mmol) in 30 ml methanol was added dropwise to a solution of $Ph_2SbCl_3{\cdot}H_2O$ (1.85 g, 4.6 mmol) in 50 ml of a 1:1 mixture of HCl (37% in water) and methanol and the mixture was stirred for 2 h. The color changed from yellow to brown and a white solid precipitated. The solid was filtered off and then solved in CH_3CN. The solution, left in the open atmosphere at room temperature, deposited air stable, colorless crystals of **5**. Yield: 1.85 g (72%). M.p. 247 °C. Anal. Calc. for $C_{16}H_{22}Cl_4Sb_2$: C, 32.05; H, 3.70. Found: C, 32.26; H, 4.33%. ^{1}H NMR (200 MHz, DMSO-d_6): δ 1.49s (12H, $SbCH_3$), 7.39 m (6H, SbC_6H_5-*meta* + *para*), 8.21d (4H, SbC_6H_5-*ortho*, $^3J_{HH}$ 7.2 Hz). ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 2.23 ($SbCH_3$), 127.37 (SbC_6H_5-*meta*), 128.86 (SbC_6H_5-*para*), 130.42 (SbC_6H_5-*ortho*), 167.34 (SbC_6H_5-*ipso*). MS (ESI, CH_3CN), *m/z* (%), pos.: 181 (100) [Me_4Sb^+]; neg.: 417 (100) [$Ph_2SbCl_4^-$].

4.7. Synthesis of $[Et_3MeSb]^+[Ph_2SbCl_4]^-$ (**6**)

A solution of Et_3MeSbI (0.87 g, 2.5 mmol) in 10 ml methanol was added dropwise to $Ph_2SbCl_3{\cdot}H_2O$ (1.0 g, 2.5 mmol) in 15 ml of methanol and the mixture was stirred for 1 h. The color changed from yellow to dark brown and a light yellow precipitate formed. The solid was filtered off and then solved in CH_3CN. Slow evaporation of the solvent in the open atmosphere gave colorless crystals of **6**. Yield: 0.8 g (43%). M.p. 152 °C. ^{1}H NMR (200 MHz, DMSO-d_6): δ 1.30t (9H, $SbCH_2CH_3$, $^3J_{HH}$ 7.9 Hz), 1.38s (3H, $SbCH_3$), 2.17q (6H, $SbCH_2CH_3$, $^3J_{HH}$ 7.9 Hz), 7.41 m (6H, SbC_6H_5-*meta* + *para*), 8.22 m (4H, SbC_6H_5-*ortho*). ^{13}C NMR (50.3 MHz, DMSO-d_6): δ −4.63 ($SbCH_3$), 9.09 ($SbCH_2CH_3$), 11.83 ($SbCH_2CH_3$), 127.34 (SbC_6H_5-*meta*), 128.83 (SbC_6H_5-*para*), 130.39 (SbC_6H_5-*ortho*), 167.32 (SbC_6H_5-*ipso*). MS (ESI, CH_3CN), *m/z* (%), pos.: 223 (100) [Et_3MeSb^+]; neg.: 417 (100) [$Ph_2SbCl_4^-$].

4.8. Synthesis of $[Et_4N]^+[Ph_2SbF_4]^-$ (**7**)

A solution of NaF (0.3 g, 7.1 mmol) in 20 ml acetonitrile was added dropwise to a stirred solution of $[Et_4N]^+[Ph_2SbCl_4]^-$ (**3**) (0.5 g, 0.9 mmol) in 20 ml acetonitrile at room temperature. After 24 h of stirring the solvent was removed in vacuum and a white powder was isolated. The title compound was recrystallized from acetonitrile to give a colorless microcrystalline product. Yield: 0.34 g (78%). M.p. 151–153 °C. Anal. Calc. for $C_{20}H_{30}F_4NSb$: C, 49.82; H, 6.27. Found: C, 49.72; H, 6.78%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.11 m (12H, NCH_2CH_3), 3.14q (8H, NCH_2CH_3, $^3J_{HH}$ 7.2 Hz), 7.38 m (6H, SbC_6H_5-*meta* + *para*), 7.81 m (4H, SbC_6H_5-*ortho*). ^{13}C NMR (75.4 MHz, DMSO-d_6): δ 6.90 (NCH_2CH_3), 51.30 m (NCH_2CH_3), 127.63 (SbC_6H_5-*meta*), 128.75 (SbC_6H_5-*para*), 133.02qv (SbC_6H_5-*ortho*, $^3J_{FC}$ 2.0 Hz), 149.92 (SbC_6H_5-*ipso*, $^2J_{FC}$ 37.0 Hz). ^{19}F NMR (282.4 MHz, DMSO-d_6): δ −103.2. MS (ESI, CH_3CN), *m/z* (%), pos.: 611 (30) [M+Et_4N^+], 130 (100) [Et_4N^+]; neg.: 351 (100) [$Ph_2SbF_4^-$].

4.9. Synthesis of $[Et_4N]^+[Ph_2SbBr_4]^-$ (**8**)

A solution of Et_4NBr (0.09 g, 0.44 mmol) in 15 ml acetonitrile was added dropwise to a stirred solution of Ph_2SbBr_3 (0.23 g, 0.44 mmol) in 15 ml acetonitrile. After 24 h of stirring at room temperature the solvent was removed in vacuum and a white powder was isolated. The title compound was recrystallized from acetonitrile to give a colorless microcrystalline product. Yield: 0.25 g (88%). M.p. 245–247 °C. ^{1}H NMR (200 MHz, DMSO-d_6): δ 1.15 m (12H, NCH_2CH_3), 3.20q (8H, NCH_2CH_3, $^3J_{HH}$ 7.3 Hz), 7.45 m (6H, SbC_6H_5-*meta* + *para*), 8.06d (4H, SbC_6H_5-*ortho*, $^3J_{HH}$ 7.4 Hz). ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 7.02 (NCH_2CH_3), 51.29 m (NCH_2CH_3), 128.10 (SbC_6H_5-*meta*), 129.28 (SbC_6H_5-*para*), 129.85 (SbC_6H_5-*ortho*), 161.59 (SbC_6H_5-*ipso*). MS (ESI, CH_3CN), *m/z* (%), pos.: 130 (100) [Et_4N^+]; neg.: 595 (100) [$Ph_2SbBr_4^-$].

4.10. Reaction of Et_4NBr and $Ph_2SbCl_3{\cdot}H_2O$

A solution of Et_4NBr (0.17 g, 0.82 mmol) in 20 ml methanol was added dropwise to a solution of $Ph_2SbCl_3{\cdot}H_2O$ (0.33 g, 0.82 mmol) in 20 ml methanol, under stirring, at room temperature. After 24 h the solvent was removed in vacuum and a white powder was obtained. The product was recrystallized from acetonitrile to give colorless crystals (0.27 g, 56%). Anal. Calc. for $C_{20}H_{30}BrCl_3NSb$: C, 40.54; H, 5.10. Found: C, 40.38; H, 5.82%. MS (ESI, CH_3CN), *m/z* (%), pos.: 130 (100) [Et_4N^+]; neg.: 595 (80) [$Ph_2SbBr_4^-$], 550 (100) [$Ph_2SbBr_3Cl^-$], 506 (24) [$Ph_2SbBr_2Cl_2^-$], 461 (2) [$Ph_2SbBrCl_3^-$].

4.11. Reaction of Ph_4PBr and $Ph_2SbCl_3{\cdot}H_2O$

A solution of Ph_4PBr (2.2 g, 5.2 mmol) in 30 ml methanol was added dropwise to a solution of $Ph_2SbCl_3{\cdot}H_2O$ (2.0 g, 5.0 mmol) in 50 ml methanol, under stirring, at room temperature. The reaction mixture was stirred for 2 h, then the white solid formed was filtered off and solved in acetonitrile. Exposure of the solution to the open atmosphere gave white crystals (1.61 g, 41%). MS (ESI, CH_3CN), *m/z* (%), pos.: 339 (100) [Ph_4P^+]; neg.: 506 (8) [$Ph_2SbBr_2Cl_2^-$], 461 (32) [$Ph_2SbBrCl_3^-$], 417 (100) [$Ph_2SbCl_4^-$].

4.12. Reaction of Ph_4SbBr and Me_2SbCl_3

A solution of Ph_4SbBr (0.4 g, 0.7 mmol) in 25 ml methanol was added dropwise to Me_2SbCl_3 (0.2 g, 0.7 mmol) in 30 ml methanol. The mixture was stirred for 1 h at room temperature and the solvent was removed in vacuum. The remaining solid was solved in acetonitrile and the solution was exposed to the atmosphere to produce white crystals which were separated by filtration (0.52 g, 37%).

4.13. Reaction of Ph_4SbBr and Ph_2SbCl_3

A solution of Ph_4SbBr (0.5 g, 0.9 mmol) in 20 ml methanol was added dropwise to Ph_2SbCl_3 (0.37 g, 0.9 mmol) in 30 ml methanol. The mixture was stirred for 1 h at room temperature and the solvent was removed in vacuum. The remaining solid was solved in acetonitrile and the solution was exposed to the atmosphere to

Table 1
X-ray crystal data and structure refinement for compounds **1**, **3**–**6**.

	1	**3**	**4**	**5**	**6**
Empirical formula	$C_{26}H_{26}Cl_4PSb$	$C_{20}H_{10}Cl_4NSb$	$C_{28}H_{46}Cl_4NSb$	$C_{16}H_{22}Cl_4Sb_2$	$C_{19}H_{28}Cl_4Sb_2$
Formula weight	632.99	527.84	660.21	599.64	641.71
T (K)	297(2)	297(2)	173(2)	173(2)	173(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Tetragonal	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P4/n*	*C2/c*	$P2_1/n$	*C2/c*	$P2_1/c$
Unit cell dimension					
a (Å)	13.2796(19)	9.780(3)	16.6892(7)	11.8797(11)	7.903(3)
b (Å)	13.2796(19)	13.863(5)	9.2874(3)	13.5320(11)	20.699(9)
c (Å)	7.601(2)	17.770(6)	20.6957(8)	13.3885(13)	29.369(17)
α (°)	90.00	90	90	90	90
β (°)	90.00	92.732(6)	103.326(3)	94.196(12)	94.04(4)
γ (°)	90.00	90	90	90	90
Volume (Å^3)	1340.4(4)	2406.6(14)	3121.4(2)	2146.5(3)	4792(4)
Z	2	4	4	4	8
D_{calc} (g cm^{-3})	1.568	1.457	1.405	1.856	1.779
Absorption coefficient (mm^{-1})	1.501	1.594	1.243	3.018	2.702
F(0 0 0)	632	1024	1360	1152	2496
Crystal size (mm)	0.31 × 0.24 × 0.24	0.28 × 0.22 × 0.17	0.29 × 0.08 × 0.06	0.60 × 0.50 × 0.50	0.60 × 0.60 × 0.15
θ Range for data collection (°)	2.17–24.99	2.29–25.00	3.41–26.37	2.68–25.50	2.58–5.00
Reflections collected	9336	11 419	33 158	4760	11 050
Independent reflections	1187 [R_{int} = 0.0434]	2120 [R_{int} = 0.0474]	6362 [R_{int} = 0.1120]	1995 [R_{int} = 0.0339]	8348 [R_{int} = 0.0786]
Data/restraints/parameters	1187/0/75	2120/0/140	6362/0/307	1995/0/105	8348/0/482
Absorption correction	Multi-scan [29]	Multi-scan [29]	Multi-scan [29]	DIFABS [30]	DIFABS [30]
GOF on F^2	1.201	1.143	1.002	1.186	1.081
Final R indices[a]					
R_1	0.0336	0.0379	0.0453	0.0195	0.0803
wR_2	0.0767	0.0979	0.0817	0.0492	0.2022
R indices (all data)					
R_1	0.0369	0.0398	0.0954	0.0200	0.1057
wR_2	0.0785	0.0993	0.0989	0.0494	0.2197
Largest difference peak and hole (e Å^{-3})	0.353 and −0.787	0.686 and −0.922	0.823 and −0.750	0.494 and −0.382	1.577 and −1.575

[a] $I > 2\sigma(I)$.

Table 2
X-ray crystal data and structure refinement for compounds **7**–**11**.

	7	**8**	**9**	**10**	**11**
Empirical formula	$C_{20}H_{30}F_4NSb$	$C_{20}H_{10}Br_4NSb$	$C_{20}H_{10}Br_{1.24}Cl_{2.76}NSb$	$C_{20}H_{10}Br_{2.92}Cl_{1.08}NSb$	$C_{26}H_{26}Cl_4Sb_2$
Formula weight	482.20	705.68	582.97	657.64	723.77
T (K)	297(2)	297(2)	297(2)	297(2)	173(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Tetragonal
Space group	$P2_1/n$	*Cmcm*	*Cmcm*	*Cmcm*	*P4/n*
Unit cell dimension					
a (Å)	7.1770(13)	9.960(5)	9.826(3)	9.8945(19)	13.349(3)
b (Å)	32.264(6)	14.134(8)	13.882(4)	14.006(3)	13.349(3)
c (Å)	9.1454(17)	18.142(10)	17.853(5)	17.988(4)	7.919(3)
α (°)	90.00	90	90	90	90
β (°)	99.344(3)	90	90	90	90
γ (°)	90.00	90	90	90	90
Volume (Å^3)	2089.6(7)	2554(2)	2435.3(11)	2492.8(9)	1411.1(7)
Z	4	4	4	4	2
D_{calc} (g cm^{-3})	1.533	1.835	1.590	1.673	1.703
Absorption coefficient (mm^{-1})	1.358	7.341	3.474	4.904	2.306
F(000)	976	1312	1114	1186	704
Crystal size (mm)	0.51 × 0.44 × 0.28	0.35 × 0.30 × 0.25	0.42 × 0.31 × 0.17	0.33 × 0.25 × 0.16	0.42 × 0.27 × 0.22
θ Range for data collection (°)	1.26–25.00	2.25–24.99	2.28 to 25.00	3.12 to 25.00	2.16 to 25.00
Reflections collected	19 810	8999	8648	8821	6504
Independent reflections	3683 [R_{int} = 0.0453]	1234 [R_{int} = 0.0842]	1183 [R_{int} = 0.0436]	1205 [R_{int} = 0.0486]	1249 [R_{int} = 0.0353]
Data/restraints/parameters	3683/0/272	1234/0/92	1183/0/95	1205/28/95	1249/0/75
Absorption correction	Multi-scan [29]	Multi-scan [29]	Multi-scan [29]	Multi-scan [29]	Multi-scan [29]
GOF on F^2	1.239	1.116	1.218	1.079	1.263
Final R indices[a]					
R_1	0.0381	0.0438	0.0555	0.0334	0.0423
wR_2	0.0778	0.0994	0.1293	0.0844	0.0966
R indices (all data)					
R_1	0.0402	0.0528	0.0623	0.0396	0.0451
wR_2	0.0796	0.1036	0.1331	0.0874	0.0978
Largest difference peak and hole (e Å^{-3})	0.491 and −0.823	1.953 and −0.526	0.862 and −1.369	0.452 and −0.513	0.674 and −0.838

[a] $I > 2\sigma(I)$.

produce colorless crystals which were separated by filtration (0.71 g, 85%). Anal. Calc. for $C_{36}H_{30}BrCl_3Sb_2$: C, 48.45; H, 3.39. Found: C, 48.61; H, 3.66%. MS (ESI, CH_3CN), *m/z* (%), pos.: 429 (100) [Ph_4Sb^+]; neg.: 506 (2) [$Ph_2SbBr_2Cl_2^-$], 461 (18) [$Ph_2SbBrCl_3^-$], 417 (100) [$Ph_2SbCl_4^-$].

4.14. X-ray structure determination

Data were collected on Bruker SMART APEX (**1**, **3**, **8–11**), Bruker KAPPA APEX II (**4**) and Bruker P4 (**5**, **6**) diffractometers, using graphite-monochromated Mo Kα radiation. For **1**, **3** and **8–11** the data were collected at room temperature, while for compounds **4–6** the crystals were cooled under a nitrogen stream at low temperature. The details of the crystal structure determination and refinement for compounds **1** and **3–11** are given in Tables 1 and 2.

The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used [27]. The hydrogen atoms from methyl groups of compounds **1** and **2** are disordered over four positions with 25% occupancy for each. The cations of compounds **3** and **7–10** are disordered; the CH_2 fragments of the ethyl groups were modeled over two positions with occupancy of 0.50/0.50 for **3** and **8**, 0.58/0.42 for **7**, and 0.50/0.50 for one CH_2 and 0.40/0.60 for the other one in **9** and **10**. Further attempts to model the disorder for the whole ethyl groups did not resulted in better results. Due to the disorder and crystal symmetry no hydrogen atoms were calculated for the cations in the above compounds except compound **7**. Compounds **9** and **10** exhibit substitutional disorder of the halide atoms bonded to antimony, with Br/Cl in the ratio 0.31/0.69 for **9** and 0.73/0.27 for **10**, respectively. In compound **6** the antimony atoms of the cations are disordered over two positions with occupancy of 0.10/0.90 and 0.13/0.87, respectively. The drawings were created with the Diamond program [28].

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Appendix A. Supplementary material

CCDC 753670, 753673, 753676, 753678, 753677, 753675, 755367, 753672, 753674 and 753671 contain the supplementary crystallographic data for compounds **1**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10** and **11**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.02.016.

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