# The Crystal Structures of the Hexachloroantimonate Salts of $(CH_3)_2SS(CH_3)^+$ $(CH_3S)_3^+$, and $(CH_3Se)_3^+$ ‡

**Risto Laitinen** *† **and Ralf Steudel** *
*Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, Str. des 17. Juni 135, D-1000 Berlin 12, West Germany*
**Robert Weiss**
*Institut für Organische Chemie der Universität, D-8520 Erlangen, West Germany*

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The crystal structures of $[(CH_3)_2SS(CH_3)]SbCl_6$ (**1**), $[(CH_3S)_3]SbCl_6$ (**2**), and $[(CH_3Se)_3]SbCl_6$ (**3**) have been determined by *X*-ray crystallography at 170 K. Compound (**1**) is triclinic, space group $P\bar{1}$ with $a$ = 701.3(3), $b$ = 1 415.1(8), $c$ = 689.9(3) pm, $\alpha$ = 94.97(4), $\beta$ = 91.19(4), $\gamma$ = 91.43(4)°, $Z$ = 2. Though (**2**) and (**3**) are analogous to each other and both are monoclinic, space group $P2_1/c$, they are not isomorphous. For (**2**), $a$ = 1 395.3(4), $b$ = 928.9(3), $c$ = 1 145.2(4) pm, $\beta$ = 94.31(3)°, $Z$ = 4; for (**3**), $a$ = 701.8(4), $b$ = 1 970.7(9), $c$ = 1 197.8(5) pm, $\beta$ = 113.45(4)°, $Z$ = 4. Each cation involves a three-co-ordinated chalcogen atom. The S–S bond length in (**1**) is relatively long while in (**2**) and (**3**) the chalcogen–chalcogen bonds have almost normal single bond lengths. $(CH_3)_2SS(CH_3)^+$ has an all-*cis* conformation with the approximate site symmetry $C_s$. The conformations of $(CH_3S)_3^+$ and $(CH_3Se)_3^+$ are fairly similar with the chain-end methyl groups in *trans* positions to each other. The packing of the ions is, however, different. This is also reflected by the drastically differing colours of these two compounds, (**2**) is practically colourless while (**3**) is deep red. In all three compounds the $SbCl_6^-$ anion is almost a regular octahedron with Sb–Cl 236.1(1)—239.3(4) pm and Cl–Sb–Cl 88.4(1)—91.1(1)°. The Raman spectra of (**2**) and (**3**) are reported.

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The $(CH_3)_2SS(CH_3)^+$ and $(CH_3S)_3^+$ ions have been established as important reagents in synthetic organic chemistry. Though their chemical properties have been investigated extensively (for some examples, see ref. 1), the structural information on them is surprisingly sparse consisting of a few theoretical studies carried out on analogous model compounds.[2] There are interesting features in the bonding of these ions because of a three-co-ordinated sulphur atom of the type found recently in homocyclic sulphur–halogen and selenium–halogen cations[3] as well as in neutral homocyclic sulphur oxides $S_nO$ and sulphane oxides $R_2S_nO$ ($n$ = 2—4).[4] We report here the crystal structure determinations of $[(CH_3)_2SS(CH_3)]SbCl_6$ (1), $[(CH_3S)_3]SbCl_6$ (2), and $[(CH_3Se)_3]SbCl_6$ (3) which have been carried out to obtain further experimental evidence about this novel bonding configuration of the chalcogen atoms. The Raman spectra of (2) and (3) have been measured for the first time.

## Experimental

The preparations of the compounds have been described elsewhere.[5] They were recrystallized from methylene chloride. Compound (1) was obtained as thin pale yellow plates, (2) as almost colourless needles, and (3) as dark red, almost spherical crystals.

The crystal data for the three compounds studied in this work as well as the details of the structure determinations are given in Table 1. A Syntex P2$_1$ four-circle diffractometer equipped with a LT-1 low-temperature device was used in all *X*-ray measurements using graphite-monochromated Mo-$K_\alpha$ radiation, $\lambda$ = 0.710 69 Å. The unit-cell parameters in each case were determined by the least-squares refinement of 15 automatically centred reflections. Two reference reflections were used to monitor the stability of each crystal. The intensities of these standard reflections were measured periodically after each batch of 48 data. The decay in all crystals appeared to be negligible during the data collection. Empirical absorption correction was made from the $\psi$-scan data after which the net intensities were corrected for Lorentz and polarization effects. Of the reflections collected those with $I \geqslant 3\sigma(I)$ were considered observed.

The positions of the antimony atoms in (1) and (2) were solved by the heavy-atom method, the subsequent difference Fourier syntheses revealing the positions of all remaining non-hydrogen atoms. The structure of (3) was solved by direct methods combined with subsequent difference Fourier synthesis. After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters the hydrogen atoms were placed geometrically around the carbon atoms and the resulting methyl groups were refined as rigid bodies (C–H 108.0 pm, H–C–H 109.5°). All hydrogen atoms in each compound were given a common isotropic thermal parameter which was refined along with other parameters. The final values of these common thermal parameters were 0.056(10), 0.057(7), and 0.039(16) Å$^2$ for (1), (2), and (3), respectively. The function minimized was $\sigma w \Delta F^2$ with $w = m[\sigma^2(F_o) + nF_o]^{-1}$ (see Table 1 for the numerical values of the coefficients $m$ and $n$). An empirical extinction correction $F_c(\text{corr.}) = F_c(1 - \varepsilon F_c^2/\sin\theta)$ was applied to all compounds in the last cycles of the refinement with $\varepsilon$ refined along with the other variables. Neutral atom scattering factors were used, and corrected for anomalous dispersion in the case of non-hydrogen atoms.[6] All calculations were performed with a CYBER 175-825 computer using the crystallographic program packages MULTAN 80,[7] SHELX 76,[8] and *X*-RAY 76.[9]

The Raman spectra were recorded at −100 °C with a Varian

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† *Present address:* Department of Chemistry, Helsinki University of Technology, SF-02150 Espoo 15, Finland.

‡ Dimethyl(methylthio)sulphonium, methylbis(methylthio)sulphonium, and methylbis(methylseleno)selenonium hexachloroantimonate respectively.

*Supplementary data available* (No. SUP 56485, 8 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

**Table 1.** Details of the structure determinations *

| (*a*) Crystal data | (**1**) | (**2**) | (**3**) |
|---|---|---|---|
| Compound | $[(CH_3)_2SS(CH_3)]SbCl_6$ | $[(CH_3S)_3]SbCl_6$ | $[(CH_3Se)_3]SbCl_6$ |
| Relative molecular mass | 443.7 | 475.8 | 616.5 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ (no.2) | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) |
| $a$/pm | 701.3(3) | 1 395.3(4) | 701.8(4) |
| $b$/pm | 1 415.1(8) | 928.9(3) | 1 970.7(9) |
| $c$/pm | 689.9(3) | 1 145.2(4) | 1 197.8(5) |
| $\alpha$/° | 94.97(4) | | |
| $\beta$/° | 91.19(4) | 94.31(3) | 113.45(4) |
| $\gamma$/° | 91.43(4) | | |
| $U$/nm$^3$ | 0.681 7(4) | 1.480 1(6) | 1.519 8(8) |
| $Z$ | 2 | 4 | 4 |
| $F$(000) | 424 | 912 | 1 128 |
| $D_c$/g cm$^{-3}$ | 2.16 | 2.13 | 2.69 |
| $\mu$(Mo-$K_\alpha$)/cm$^{-1}$ | 32.3 | 31.1 | 96.6 |
| (*b*) Data collection and structure refinement | | | |
| Crystal size (mm$^3$) | 0.016 | 0.020 | 0.032 |
| Reflections measured | $+h, \pm k, \pm l$ | $+h, +k, \pm l$ | $+h, +k, \pm l$ |
| Standard reflections | $1,0,\bar{1}$; $\bar{1},2,0$ | $2,2,\bar{3}$; $4,0,2$ | $0,1,\bar{2}$; $0,0,4$ |
| Number of reflections collected | 4 264 | 4 756 | 4 878 |
| Number of unique reflections | 3 964 | 4 318 | 4 435 |
| Number of observed reflections | 3 106 | 2 917 | 2 195 |
| $R_{INT}$ | 0.032 | 0.025 | 0.077 |
| $R$ | 0.054 | 0.035 | 0.059 |
| $R'$ | 0.058 | 0.040 | 0.060 |
| Weighting scheme: | | | |
| $m$ | 1.6633 | 0.8204 | 0.9614 |
| $n$ | 0.001 695 | 0.001 070 | 0.002 932 |
| Ratio of max. least-squares shift to error | 0.002 | 0.013 | 0.001 |
| Max. and min. heights in final difference Fourier synthesis (e Å$^{-3}$) | 0.7—(−0.9) | 0.6—(−0.8) | 0.5—(−0.9) |
| Extinction correction, ε | 1.1(17) × 10$^{-8}$ | 2.5(11) × 10$^{-8}$ | 5.4(13) × 10$^{-8}$ |

* Common data for (**1**)—(**3**): $T$ = 170 K, 2θ range 5—60°, ω scan, scan speed 1.0—29.3° min$^{-1}$; scan range: symmetrically over 1.0° about $K_{\alpha(1,2)}$ maximum; background measurement: offset 1.0 and −1.0° in ω from $K_{\alpha(1,2)}$ maximum; absorption correction: empirical from ψ-scan data, range of minimum transmission factor as a function of 2θ taking the maximum transmission factor as unity, 0.41—0.57 (**1**), 0.71—0.75 (**2**), 0.37—0.40 (**3**).

**Table 2.** Atomic co-ordinates for (**1**)—(**3**) with estimated standard deviations given in parentheses

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| $[(CH_3)_2SS(CH_3)]SbCl_6$ (**1**) | | | | | | | |
| Sb(1) | 0 | 0 | 0 | Cl(6) | 0.019 3(2) | 0.409 8(1) | 0.272 8(2) |
| Sb(2) | 0 | 0.5000 | 0 | S(1) | 0.395 5(2) | 0.258 4(1) | 0.371 9(2) |
| Cl(1) | 0.187 4(2) | 0.022 8(1) | 0.291 9(2) | S(2) | 0.560 2(3) | 0.182 8(1) | 0.563 2(2) |
| Cl(2) | −0.019 6(2) | 0.167 5(1) | −0.005 4(2) | C(1) | 0.500 2(10) | 0.378 7(5) | 0.399 3(11) |
| Cl(3) | 0.279 4(2) | 0.004 4(1) | −0.184 5(2) | C(2) | 0.477 3(10) | 0.219 9(5) | 0.127 0(10) |
| Cl(4) | 0.180 3(3) | 0.385 6(1) | −0.183 2(3) | C(3) | 0.803 9(10) | 0.212 3(5) | 0.509 5(10) |
| Cl(5) | −0.286 1(2) | 0.417 0(1) | −0.104 9(3) | | | | |
| $[(CH_3S)_3]SbCl_6$ (**2**) | | | | | | | |
| Sb(1) | 0 | 0 | 0 | Cl(6) | 0.397 3(1) | 0.167 3(1) | 0.085 2(1) |
| Sb(2) | 0.5000 | 0 | 0 | S(1) | 0.805 3(1) | 0.983 9(1) | 0.590 8(1) |
| Cl(1) | 0.024 8(1) | 0.243 0(1) | 0.056 9(1) | S(2) | 0.756 1(1) | 0.954 8(1) | 0.418 7(1) |
| Cl(2) | −0.167 4(1) | 0.029 8(2) | 0.010 5(1) | S(3) | 0.713 2(1) | 1.120 5(2) | 0.665 8(1) |
| Cl(3) | 0.015 5(1) | −0.074 0(2) | 0.198 2(1) | C(1) | 0.782 9(4) | 0.813 0(5) | 0.653 1(5) |
| Cl(4) | 0.607 8(1) | 0.014 3(1) | 0.170 2(1) | C(2) | 0.821 0(4) | 1.100 0(6) | 0.358 3(5) |
| Cl(5) | 0.420 2(1) | −0.193 2(1) | 0.086 3(1) | C(3) | 0.598 5(4) | 1.034 8(7) | 0.630 4(5) |
| $[(CH_3Se)_3]SbCl_6$ (**3**) | | | | | | | |
| Sb | 0.439 0(1) | 0.391 1(1) | 0.215 5(1) | Se(1) | 0.968 0(2) | 0.425 0(1) | 0.650 0(1) |
| Cl(1) | 0.801 1(5) | 0.414 3(2) | 0.324 0(3) | Se(2) | 1.294 3(2) | 0.382 9(1) | 0.665 6(1) |
| Cl(2) | 0.378 8(6) | 0.441 0(2) | 0.378 4(3) | Se(3) | 0.770 9(2) | 0.326 9(1) | 0.640 4(1) |
| Cl(3) | 0.512 3(6) | 0.341 3(2) | 0.056 0(3) | C(1) | 1.061 6(25) | 0.449 4(8) | 0.820 3(11) |
| Cl(4) | 0.394 8(5) | 0.497 7(2) | 0.117 2(3) | C(2) | 1.191 9(24) | 0.316 0(8) | 0.536 2(13) |
| Cl(5) | 0.487 9(6) | 0.283 7(2) | 0.313 4(3) | C(3) | 0.950 5(22) | 0.280 6(7) | 0.786 4(11) |
| Cl(6) | 0.081 0(5) | 0.367 7(2) | 0.111 3(3) | | | | |

**Table 3.** Bond lengths (pm), bond angles (°), and torsion angles (°) in the cations

| | | | | | |
|---|---|---|---|---|---|
| $(CH_3)_2SS(CH_3)^+$ | | | | | |
| S(1)–S(2) | 211.3(2) | C(1)–S(1)–S(2) | 104.3(2) | C(1)–S(1)–S(2)–C(3) | −48.1(3) |
| S(1)–C(1) | 183.0(7) | C(2)–S(1)–S(2) | 105.3(2) | C(2)–S(1)–S(2)–C(3) | 56.2(3) |
| S(1)–C(2) | 183.8(7) | C(3)–S(2)–S(1) | 104.5(2) | | |
| S(2)–C(3) | 180.2(7) | C(1)–S(1)–C(2) | 99.5(3) | | |
| $(CH_3S)_3^+$ | | | | | |
| S(1)–S(2) | 205.6(2) | S(2)–S(1)–S(3) | 108.0(1) | S(2)–S(1)–S(3)–C(3) | 52.5(2) |
| S(1)–S(3) | 204.1(2) | S(2)–S(1)–C(1) | 102.2(2) | S(3)–S(1)–S(2)–C(2) | 90.5(2) |
| S(1)–C(1) | 177.8(5) | S(3)–S(1)–C(1) | 104.5(2) | C(1)–S(1)–S(2)–C(2) | −159.6(3) |
| S(2)–C(2) | 179.2(5) | S(1)–S(2)–C(2) | 97.4(2) | C(1)–S(1)–S(3)–C(3) | −55.8(3) |
| S(3)–C(3) | 180.6(6) | S(1)–S(3)–C(3) | 101.9(2) | | |
| $(CH_3Se)_3^+$ | | | | | |
| Se(1)–Se(2) | 237.2(2) | Se(2)–Se(1)–Se(3) | 104.3(1) | Se(2)–Se(1)–Se(3)–C(3) | 55.1(5) |
| Se(1)–Se(3) | 235.4(2) | Se(2)–Se(1)–C(1) | 95.3(5) | Se(3)–Se(1)–Se(2)–C(2) | 47.1(5) |
| Se(1)–C(1) | 193.8(12) | Se(3)–Se(1)–C(1) | 101.6(5) | C(1)–Se(1)–Se(2)–C(2) | 150.5(7) |
| Se(2)–C(2) | 194.2(14) | Se(1)–Se(2)–C(2) | 97.8(5) | C(1)–Se(1)–Se(3)–C(3) | −43.4(7) |
| Se(3)–C(3) | 193.0(12) | Se(1)–Se(3)–C(3) | 100.7(4) | | |

**Table 4.** Selected bond parameters in some ions and molecules containing a three-co-ordinated chalcogen atom[a]

| Parameter | $S_7I^+$ [b] | $S_8O$ [c] | $S_{19}^{2+}$ [d] | $Se_6I^+$ [e] | $Se_{10}^{2+}$ [f] | $(S)_2S–B$ [g] |
|---|---|---|---|---|---|---|
| $r(YX_1)$/pm | 234 | 148 | 206 | 274 | 243 | 204 |
| $r(X_1X_2)$/pm | 210 | 220 | 212 | 237 | 241 | 204 |
| $r(X_1X_3)$/pm | 239 | 220 | 230 | 237 | 242 | 203 |
| $\alpha(YX_1X_2)$/° | 108 | 106 | 105 | 104 | 101 | 98 |
| $\alpha(YX_1X_3)$/° | 100 | 106 | 94 | 103 | 101 | 98 |
| $\alpha(X_1X_2X_3)$/° | 102 | 102 | 103 | 100 | 98 | 109 |

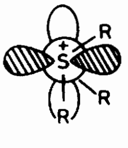
[a] The configuration studied is $-X_2-\overset{\overset{Y}{|}}{X_1}-X_3-$, where X = S or Se and Y = O, I, S, Se, or B. [b] Data from $[S_7I]SbF_6$ (ref. 3*a*). The corresponding bond lengths in $S_7$ (ref. 13) are: $r(X_1X_2) = 205$, $r(X_1X_3) = 210$ pm. [c] P. Luger, H. Bradczek, R. Steudel, and M. Rebsch, *Chem. Ber.*, 1976, **109**, 180. In $S_8$, $r(X_1X_2) = r(X_1X_3) = 205$ pm (ref. 10*a*). [d] From ref. 14. The corresponding bond lengths in $S_7$ (ref. 13) are: $r(X_1X_2) = 200$, $r(X_1X_3) = 218$ pm. [e] From ref. 3*d*. In $Se_6$, $r(X_1X_2) = r(X_1X_3) = 236$ pm (ref. 10*b*). [f] R. C. Burns, W-L. Chan, R. J. Gillespie, W-C. Luk, J. F. Sawyer, and D. R. Slim, *Inorg. Chem.*, 1980, **19**, 1432. [g] From ref. 15.

Cary 82 spectrometer equipped with a triple monochromator and krypton laser (647.1 nm).

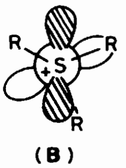
## Results and Discussion

*Crystal Structures.*—The atomic co-ordinates for (**1**)—(**3**) are given in Table 2. The structures of the cations indicating the numbering of the atoms are shown in Figure 1. The bond parameters involving the cations are given in Table 3.

Each structure consists of discrete cations and hexachloroantimonate anions. $(CH_3)_2SS(CH_3)^+$ has an approximate site symmetry $C_s$ with the sole methyl group on S(2) bisecting the angle formed by the two methyl groups on S(1). This is a consequence of the minimized lone-pair repulsion.[2] There are two possible equilibrium structures, (**A**) and (**B**).* The energies of the two conformers are expected to be rather similar. $(CH_3)_2SS(CH_3)^+$ assumes the conformation (**A**), possibly due to the more efficient packing in the lattice. The S–S bond length (211.3 pm) is slightly longer than what is expected for the S–S single bond length (*ca.* 205 pm)[10a] and may be the result of the steric crowding of the methyl groups.



(**A**)



(**B**)

The cations $(CH_3S)_3^+$ and $(CH_3Se)_3^+$ have very similar structures with the chain-end methyl groups in *trans* positions with respect to the plane defined by the three chalcogen atoms. The most notable difference between the two ions is that the torsional angle X(3)–X(1)–X(2)–C(2) (X = S or Se) is 90.5(2)° in (**2**) while in (**3**) the corresponding angle is 47.1(5)°. Consequently the $(CH_3S)_3^+$ cation has a more open structure than $(CH_3Se)_3^+$ (see Figure 1). The chalcogen–chalcogen bond lengths [204.1 and 205.6 pm in (**2**) and 235.4 and 237.2 pm in (**3**)] are close to the single bond lengths.[10] The C–S bond lengths of 180.2(7)—183.8(7) pm in (**1**) and 177.8(5)—180.6(6) pm in (**2**) agree with the C–S bond length of *ca.* 181 pm observed in $(CH_3)_2S_2$ by both microwave spectroscopy and electron diffraction.[11] Also, the C–Se bond lengths of 193.0(12)—194.2(14) pm in (**3**) are near to the corresponding bond length of 195.4 pm in $(CH_3)_2Se_2$.[12] According to the covalent radii of C, S, and Se (77, 104, and 117 pm, respectively) all C–S and C–Se bond lengths in (**1**), (**2**), and (**3**) correspond to quite normal single bonds.

The three-co-ordinated chalcogen atom in each of the three cations lies at the apex of a trigonal pyramid with all bond

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**Table 5.** Interionic contacts ($\leqslant$380 pm)

| | | | | | |
|---|---|---|---|---|---|
| [(CH$_3$)$_2$SS(CH$_3$)]SbCl$_6$[a] | | | | | |
| S(1)–Cl(1) | 359.9(2) | C(1)–Cl(4$^{\mathrm{i}}$) | 368.4(8) | C(2)–Cl(1) | 368.4(7) |
| S(1)–Cl(4$^{\mathrm{i}}$) | 378.3(2) | C(1)–Cl(5$^{\mathrm{iv}}$) | 369.7(8) | C(2)–Cl(2) | 362.6(7) |
| S(1)–Cl(6) | 353.3(2) | C(1)–Cl(6) | 351.4(7) | C(2)–Cl(2$^{\mathrm{v}}$) | 373.9(7) |
| S(2)–Cl(1) | 377.3(2) | C(1)–Cl(6$^{\mathrm{v}}$) | 378.5(7) | C(2)–Cl(3) | 379.1(7) |
| S(2)–Cl(1$^{\mathrm{ii}}$) | 364.5(2) | C(1)–C(1$^{\mathrm{vi}}$) | 359.0(10) | C(2)–Cl(3$^{\mathrm{iii}}$) | 368.8(7) |
| S(2)–Cl(3$^{\mathrm{i}}$) | 373.3(2) | | | C(2)–Cl(5$^{\mathrm{v}}$) | 370.7(7) |
| S(2)–Cl(3$^{\mathrm{iii}}$) | 376.6(2) | | | | |
| [(CH$_3$S)$_3$]SbCl$_6$[b] | | | | | |
| S(1)–Cl(1$^{\mathrm{i}}$) | 375.5(2) | S(3)–Cl(4$^{\mathrm{iv}}$) | 369.9(2) | C(2)–Cl(1$^{\mathrm{viii}}$) | 379.6(6) |
| S(1)–Cl(3$^{\mathrm{ii}}$) | 344.7(2) | S(3)–Cl(5$^{\mathrm{ii}}$) | 357.4(2) | C(2)–Cl(3$^{\mathrm{ix}}$) | 375.3(6) |
| S(2)–Cl(1$^{\mathrm{i}}$) | 362.9(2) | S(3)–Cl(5$^{\mathrm{v}}$) | 374.0(2) | C(2)–Cl(4$^{\mathrm{iii}}$) | 362.8(6) |
| S(2)–Cl(4$^{\mathrm{iii}}$) | 343.5(2) | S(3)–C(2$^{\mathrm{vi}}$) | 365.6(6) | C(3)–Cl(5$^{\mathrm{ii}}$) | 359.0(6) |
| S(2)–Cl(6$^{\mathrm{i}}$) | 342.0(2) | C(1)–Cl(1$^{\mathrm{i}}$) | 379.3(6) | C(3)–Cl(5$^{\mathrm{v}}$) | 353.7(6) |
| | | C(1)–Cl(2$^{\mathrm{vii}}$) | 367.0(5) | C(3)–Cl(6$^{\mathrm{ii}}$) | 375.6(6) |
| [(CH$_3$Se)$_3$]SbCl$_6$[c] | | | | | |
| Se(1)–Cl(1) | 360.9(4) | Se(3)–Cl(5) | 371.8(3) | C(1)–Cl(6$^{\mathrm{vii}}$) | 379.3(15) |
| Se(1)–Cl(1$^{\mathrm{i}}$) | 351.5(4) | Se(3)–C(2$^{\mathrm{vi}}$) | 375.2(16) | C(2)–Cl(1) | 349.1(14) |
| Se(1)–Cl(2$^{\mathrm{ii}}$) | 351.4(5) | C(1)–Cl(1$^{\mathrm{i}}$) | 352.9(17) | C(2)–Cl(2$^{\mathrm{iii}}$) | 365.2(18) |
| Se(2)–Se(3$^{\mathrm{iii}}$) | 364.6(2) | C(1)–Cl(2$^{\mathrm{ii}}$) | 374.5(15) | C(2)–Cl(3$^{\mathrm{iv}}$) | 378.2(17) |
| Se(2)–Cl(4$^{\mathrm{i}}$) | 354.3(4) | C(1)–Cl(4$^{\mathrm{ii}}$) | 371.8(19) | C(2)–Cl(5$^{\mathrm{iv}}$) | 370.3(14) |
| Se(2)–Cl(5$^{\mathrm{iv}}$) | 372.1(4) | C(1)–Cl(4$^{\mathrm{i}}$) | 373.2(18) | C(2)–C(3$^{\mathrm{viii}}$) | 337.8(19) |
| Se(3)–Cl(3$^{\mathrm{v}}$) | 372.1(4) | C(1)–Cl(4$^{\mathrm{vii}}$) | 352.1(12) | C(3)–Cl(5$^{\mathrm{v}}$) | 361.7(17) |

[a] The superscripts refer to the following symmetry operations: i $x,y,1+z$; ii $1-x,-y,1-z$; iii $1-x,-y,-z$; iv $1+x,y,1+z$; v $1+x,y,z$; vi $1-x,1-y,1-z$. [b] The superscripts refer to the following symmetry operations: i $1-x,\frac{1}{2}+y,\frac{1}{2}-z$; ii $1-x,1-y,1-z$; iii $x,1+y,z$; iv $x,\frac{3}{2}-y,\frac{1}{2}+z$; v $1-x,\frac{3}{2}+y,\frac{1}{2}-z$; vi $x,\frac{5}{2}-y,\frac{1}{2}+z$; vii $1+x,\frac{1}{2}-y,\frac{1}{2}+z$; viii $1+x,\frac{3}{2}-y,\frac{1}{2}+z$; ix $1+x,1+y,1+z$. [c] The superscripts refer to the following symmetry operations: i $2-x,1-y,1-z$; ii $1-x,1-y,1-z$; iii $1+x,y,z$; iv $1+x,\frac{1}{2}-y,\frac{1}{2}+z$; v $x,\frac{1}{2}-y,\frac{1}{2}+z$; vi $-1+x,y,z$; vii $1+x,y,1+z$; viii $x,\frac{1}{2}-y,\frac{1}{2}+z$.

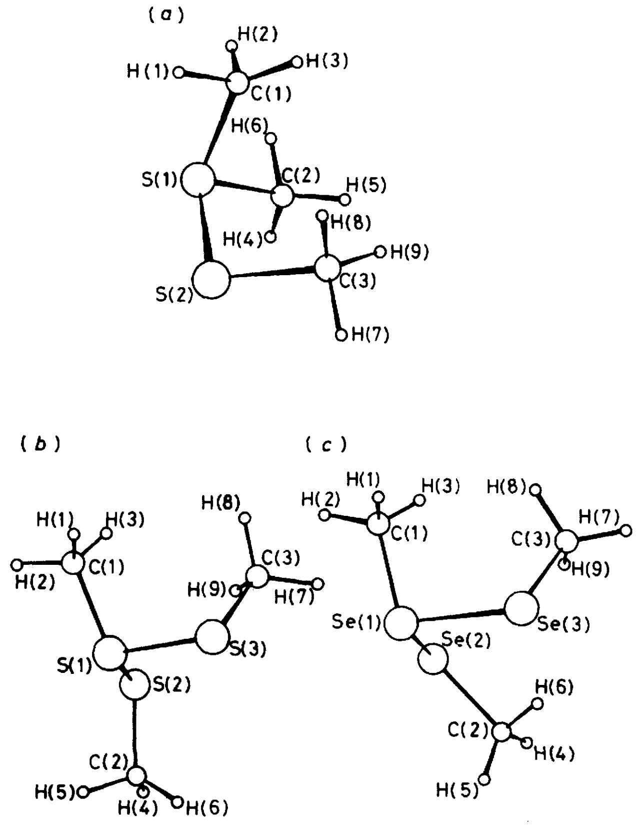

**Figure 1.** The structure of the cations. (*a*) (CH$_3$)$_2$SS(CH$_3$)$^+$, (*b*) (CH$_3$S)$_3$$^+$, (*c*) (CH$_3$Se)$_3$$^+$

angles between 95.3(5) and 108.0(1)° (see Table 3). It is interesting to compare the geometries around the three-co-ordinated chalcogen atoms in various molecular surroundings. An exocyclic halogen or a chalcogen atom attached to a homocyclic chalcogen ring molecule (as in S$_7$Br$^+$, S$_7$I$^+$, Se$_6$I$^+$, Se$_6$I$_2$$^{2+}$, S$_{19}$$^{2+}$, and Se$_{10}$$^{2+}$; see Table 4) has a profound effect on the bonds throughout the ring. The ring bonds originating from the three-co-ordinated atom are considerably longer than the corresponding bonds between the two-co-ordinated chalcogen atoms. The adjacent bonds become shorter than normal. This alternation in the bond lengths is carried over the whole ring molecule. For example, in the S$_7$I$^+$ cation [3a,b] the exocyclic I–S bond length is near to that expected for a single bond. The two S–S bonds originating from the three-co-ordinated sulphur atom are significantly longer (*ca.* 234 and 210 pm) than the corresponding bonds in the S$_7$ molecule (210 and 205 pm).[13] The lengths of the next-nearest bonds in the cation are *ca.* 200 and 190 pm while the corresponding bonds in S$_7$ are 205 and 199 pm, respectively. As iodine moves further away (like the bridging atom in Se$_6$I$^+$ [3d]), the perturbation in the ring molecule is expectedly smaller. Burns *et al.*[14] have provided a model to account for this alternation in terms of charge delocalization within the ring molecule. This type of delocalization is, however, not possible in the cations studied in this work because the carbon atoms of the methyl groups are lacking lone pairs for the propagation of the charge. Consequently quite normal single bond lengths are observed for both chalcogen–chalcogen and chalcogen–carbon bonds. The situation is analogous to the adduct of 4,6-dibromo-1,2,3,5,4,6-tetrathiadiborinane with 1,2,3-trimethyl-1,3,2-diazaborolidine in which all three bonds of the (S)$_2$S–B unit are quite normal single bonds[15] (see Table 4).

In each compound the hexachloroantimonate ions form almost regular octahedrons with Sb–Cl bonds ranging from 236.1(1) to 238.1(1) pm in (1), from 236.4(1) to 237.5(1) pm in

**Table 6.** Raman spectra (cm$^{-1}$) of (**2**) and (**3**) recorded at −100 °C*

| $[(CH_3S)_3]SbCl_6$ (100—1 000 cm$^{-1}$) | $[(CH_3Se)_3]SbCl_6$ (50—1 000 cm$^{-1}$) | Assignment |
|---|---|---|
| 690wm<br>684wm | | $\nu$(C–S) |
| | 591m<br>582w<br>568m | $\nu$(C–Se) |
| 498w<br>461ms | | $\nu$(S–S) |
| 338vs<br>299w | 331vs | $\nu_1(SbCl_6^-)$ |
| 288 (sh)<br>282m,br | 288 (sh)<br>278m | $\nu_2(SbCl_6^-)$ |
| | 257vs | $\nu$(Se–Se) |
| 239w | 220w,br | |
| 183wm<br>175ms | 178m<br>174m | $\nu_5(SbCl_6^-)$ |
| | 124ms | |
| | 109w | |
| | 78m | |
| | 58w | |

* Notation: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, br = broad.

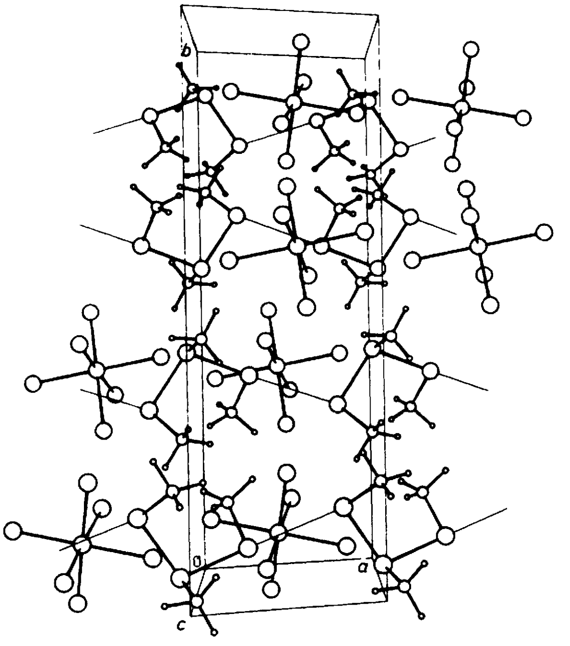

**Figure 2.** The packing of ions in $[(CH_3Se)_3]SbCl_6$ The shortest Se···Se contact of 364.6 pm is indicated by a thin line

(**2**), and from 236.3(1) to 239.3(4) pm in (**3**). The Cl–Sb–Cl angles lie in the ranges 89.3(1)—90.3(1), 89.3(1)—90.7(1), and 88.4(1)—91.1(1)° in (**1**), (**2**), and (**3**), respectively. In both (**1**) and (**2**) there are two antimony atoms in special positions with site symmetry $C_i$. Therefore each antimony atom is bonded to three crystallographically independent chlorine atoms, the full co-ordination sphere being completed by symmetry. As a consequence all *trans* angles are restricted to 180.0°. In (**3**) there is one antimony in a general position surrounded by six crystallographically independent chlorine atoms. The *trans* angles range from 178.0(1) to 179.1(1)°.

All three crystal structures are composed of alternating layers of cations and anions. Interionic distances less than 380 pm are listed in Table 5. The shortest S···Cl contact in (**1**) is 359.9(2) pm and in (**2**) 342.0(2) pm. Both these values are slightly shorter than the sum of van der Waals radii of these elements (*ca.* 365 pm). In (**3**) the shortest Se···Cl contact is 351.4(5) pm which is *ca.* 30 pm shorter than the sum of van der Waals radii for chlorine and selenium. However, the most notable difference in the packing of (**3**) as compared to both (**1**) and (**2**) is one short intercationic Se···Se contact of 364.6(2) pm (see Figure 2), which while somewhat longer than the Se···Se contacts in selenium allotropes (334—348 pm),[10b] is still *ca.* 40 pm shorter than the sum of the van der Waals radii of two selenium atoms. Possibly this is the origin of the deep red colour of (**3**) while (**1**) and (**2**) are practically colourless.

*Raman Spectra.*—The low-temperature Raman spectra of (**2**) and (**3**) are reported in Table 6. As the C–S, C–Se, S–S, and Se–Se bond distances correspond to single bonds the related stretching vibrations are located in their normal regions[16] and can thus easily be identified in the spectra. The Raman-active vibrations of the octahedral $SbCl_6^-$ anion can be assigned by comparison with the wavenumbers reported earlier.[17] The vibrations ($\nu_2$ and $\nu_5$), degenerate in the free anion, occur as broad or split lines due to the low anion site symmetries of $C_i$ and $C_1$ in (**2**) and (**3**) respectively. We were unsuccessful in obtaining a good Raman spectrum of (**1**) as only $\nu_1(SbCl_6^-)$ was observed at 335 cm$^{-1}$.

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