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Synthesis and characterization of the heteroaromatic MF_6^- (M = As, Sb) salts of the 1,2,4-trithiolanylium dication $[Ph\overline{CSSC(Ph)S}]^{2+}$†

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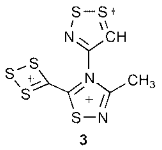
$Ph\overline{CSSC(Ph)S}(MF_6)_2$ (M = As, Sb), (X-ray crystal structure, FT Raman, ^1H, ^{13}C NMR and theoretical calculations) containing the first example of a dicationic 6π five-membered C–S heterocycle and sulfur were formed on disproportionation of $Ph\overline{CSSS}(MF_6)$ in liquid SO_2 solution.

We previously prepared **3** in low yield, containing the first structurally characterized example of the $R\overline{CSSS}^+$ ring.[1] In an attempt to prepare a simple derivative of this ring system in good yield we reacted the previously reported[2] $PhCS_3Cl$ with $AgSbF_6$ and to our surprise obtained $Ph\overline{CSSC(Ph)S}(SbF_6)_2$ **2**$(SbF_6)_2$. On further investigation we obtained $Ph\overline{CSSS}(SbF_6)_2$ **1**SbF_6 and found that it disproportionates in SO_2 solution to give **2**$(SbF_6)_2$ and elemental sulfur. **2** is the first example of a dicationic 6π five-membered C–S heterocycle. RCS_3Cl (R = Ph, p-MeOC$_6$H$_4$, 1-naphthyl) are known.[2] Therefore the synthesis of $R\overline{CSSC(R)S}(MF_6)_2$ is likely general, although it may require an R group onto which some of the +2 positive charge on the C_2S_3 ring can be delocalized. There are many examples of five- and six-membered C–S containing heteroaromatic rings,[3,4] however the only aromatic dication previously reported is **10**. Related analogues of **2** are **6** (R = Et, Bu), in which the $C_2S_3^{2+}$ ring is non-planar and charges are largely localized on the exocyclic N atoms as drawn.[5] The other C–S containing 6π five-membered cyclic heterocylcles are thiophene, 1,2-dithiolium **7**, and 1,3-dithiolium **8**.[3] **2** is isolobal to $\overline{SNSSN}^{2+}$ **9** in $(\overline{SNSSN})^{2+}(MF_6^-)_2$ (M = As, Sb).[6] However unlike the $S_3N_2^{2+}$ ring, which dissociates to SNS^+ and SN^+, **2** retains its identity in SO_2 solution. The isomeric 1,2,4-trithiolanylium dication $R\overline{CSSSC}R^{2+}$ has not been reported, although the 7π 1,2,3-trithiolynium monocation radical **11** is known.[7]



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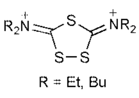

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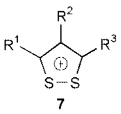

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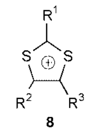

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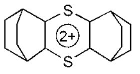

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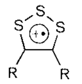

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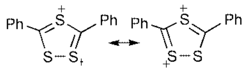

12 **13**

2$(SbF_6)_2$ was first prepared by adding the soluble product (0.586 g, 1.697 mmol) of the $PhCS_2H/SCl_2$ reaction to $AgSbF_6$ (1.331 g, 3.874 mmol) in liquid SO_2.‡ The mixture was stirred for 2 h in bulb 1 of a two-bulb Pyrex glass vessel incorporating a medium sintered-glass frit (see ref. 8). A solution over a precipitate was obtained in bulb 2 by repeatedly extracting the soluble material into bulb 2 leaving the insolubles (including AgCl) in bulb 1. The solvent in bulb 2 was then condensed back to bulb 1. About 2 ml SO_2 was condensed back (three times) onto the precipitate (in bulb 2) and the obtained solution containing the most soluble components (*e.g.* unreacted $AgSbF_6$ and other impurities) filtered to bulb 1. **2**$(SbF_6)_2$ was recovered with a trace of S_8 (Raman) from bulb 2 as an orange solid (0.446 g, 0.600 mmol, 35% yield). Single crystals of **2**$(SbF_6)_2$§ were grown from SO_2 solution. This implies the presence of $[Ph\overline{CSSC(Ph)S}]Cl_2$ as a main component of the soluble product of the $PhCSSH/SCl_2$ reaction. Crystals of **2**$(AsF_6)_2$ were obtained similarly by using $AgAsF_6$. An ORTEP diagram of **2** in **2**$(SbF_6)_2$ (−60 °C) is shown in Fig. 1. The observed and calculated (MPW1PW91/3-21G*)¶ bond distances and angles are in reasonable agreement. The structure of **2** in **2**$(AsF_6)_2$ (−100 °C)§ is similar. The FT Raman spectrum of **2**$(SbF_6)_2$ in the 50–800 cm^{-1} region is shown in Fig. 2 (full Raman spectra of **2**$(SbF_6)_2$ is shown in S-Fig. 1†). The observed and calculated Raman frequencies and ^{13}C, ^1H chemical shifts are in good agreement (Fig. 2, Table 1 and S-Table 1†).

The precipitate in the $PhCSSH/SCl_2$ reaction was found to be $PhCS_3Cl$.‖ $PhCS_3Cl$ (0.570 g, 2.59 mmol) was reacted with $AgSbF_6$ (0.953 g, 2.79 mmol) in liquid SO_2 (9.1 g) to give **1**SbF_6 (0.492 g, 1.17 mmol, 45% yield). The procedure was the same as described above except that the reaction time was < 30 min and light was excluded. The initial failure to obtain **1**SbF_6 is because the soluble rather than the insoluble product of the $PhCSSH/SCl_2$ reaction was reacted with $AgSbF_6$. ^1H (Fig. 3) and ^{13}C NMR spectra of **1**SbF_6 in liquid SO_2 were studied as a function of time. Observed and calculated chemical shifts of **1** are in good agreement and are given in Table 1 (Similar ^1H NMR spectra found for **1**AsF_6).** Peaks due to **1** decreased over time with the appearance of those of **2** and precipitation of

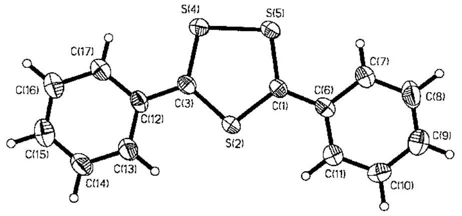

Fig. 1 ORTEP of **2** in **2**$(SbF_6)_2$ (−60 °C) drawn at the 50% probability level. Selected bond lengths (Å), bond angles (°); and calculated results (MPW1PW91/3-21G*) are given in parentheses and in bold: C(3)–C(12) 1.424(10) (**1.418**), C(12)–C(17) 1.397(12) (**1.427**), C(12)–C(13) 1.392(11) (**1.426**), C(13)–C(14) 1.351(12) (**1.378**), C(17)–C(16) 1.365(12) (**1.378**), C(16)–C(15) 1.363(14) (**1.403**), C(15)–C(14) 1.359(14) (**1.404**), C(3)–S(4) 1.680(8) (**1.710**), S(4)–S(5) 2.024(3) (**2.062**), S(5)–C(1) 1.683(7) (**1.710**), C(1)–S(2) 1.699(7) (**1.729**), C(1)–C(6) 1.412(10) (**1.418**); C(3)–S(2)–C(1) 100.8(4) (**100.7**), S(2)–C(3)–S(4) 119.4(4) (**119.2**), C(3)–S(4)–S(5) 100.4(3) (**99.8**), S(4)–S(5)–C(1) 99.8(3) (**99.8**), S(5)–C(1)–S(2) 119.5(4) (**119.2**), C(12)–C(3)–S(4) 121.8(6) (**120.1**), C(12)–C(3)–S(2) 118.8(6) (**120.6**).

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† Electronic supplementary information (ESI) available: S-Table 1: FT-Raman data for **2**$(MF_6)_2$ (M = As, Sb). S-Table 2: calculated/observed bond distances and angles for **2**. S-Table 3: FT-Raman data for **1**MF_6 (M = As, Sb). S-Fig. 1: FT-Raman spectrum of **2**$(SbF_6)_2$ in the 50–4000 cm^{-1} region. S-Fig. 2: calculated Pauling bond orders of **2** in **2**$(SbF_6)_2$. S-Fig. 3: FT-Raman spectrum of **1**SbF_6 in the 50–800 cm^{-1} region. See http://www.rsc.org/suppdata/cc/b1/b100001m/

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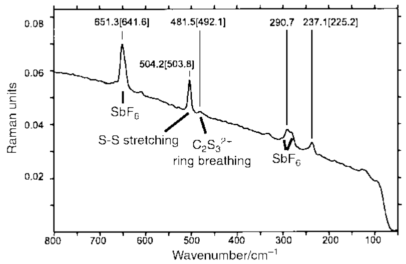


Fig. 2 FT-Raman spectrum of **2**$(SbF_6)_2$ in the 50–800 cm^{-1} region. Data in square brackets are the calculated frequencies (MPW1PW91/3-21G*).

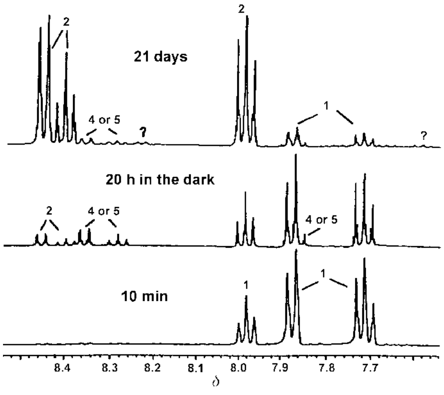
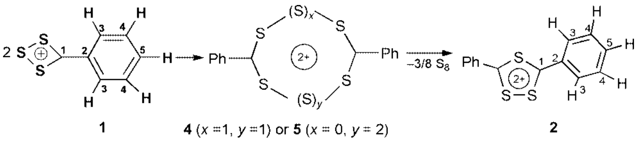


Fig. 3 *In situ* ^1H NMR study of **1**SbF_6 in liquid SO_2.

S_8 (Raman) and an intermediate we propose could be either **4** or **5** (see Scheme 1), the mechanism of which warrants further study. Light was found to facilitate this process.



Scheme 1 Proposed mechanisms for the rearrangement of **1** to **2** in liquid SO_2.

The phenyl and C_2S_3 ring of **2** are planar [Σ angles for C_2S_3 rings: 539.9° (25 °C), 540.1° (−60 °C) in **2**$(SbF_6)_2$, 540.0° in **2**$(AsF_6)_2$ (−100 °C)]. The benzyl rings and the dication ring are nearly coplanar in **2**$(MF_6)_2$ (M = Sb, As) with $Ph_1/\overline{\text{CSCSS}}^{2+}$, $Ph_2/\overline{\text{CSCSS}}^{2+}$ and Ph_1/Ph_2 torsion angles of 3.4° (12.6°), 7.0° (168.3°) and 3.8° (176.7°) respectively in **2**$(SbF_6)_2$ (25 °C) and **2**$(AsF_6)_2$ (−100 °C) (angles in parentheses). This implies the π electrons and charges are delocalized over the three rings, supported by the short Ph–C bond distance†† and the significant F–H and F–S contacts. The sum of the Pauling bond orders (BOs)‡‡ for the C_2S_3 ring is 6.8–6.9 in both salts (S-Fig. 2†) and the π bonding mostly in the C–S region, *cf.* **12** and **13**. The S–S bond distance of 2.024(3) [in **2**$(SbF_6)_2$, −60 °C] and 2.032(3) [in **2**$(AsF_6)_2$ (−100 °C)] implies the BO is slightly greater than 1 (*cf.* S–S distance: 2.05 Å in S_8 and 2.08 Å in C–SS–C containing compounds with C–S–S–C dihedral angle of 0°[10]). Consistently, the S–S stretching frequency at 504 cm^{-1} (see Fig. 2) is greater than that of S_8 (473 cm^{-1}).

Table 1 Observed[a] [in **1**SbF_6 and **2**$(SbF_6)_2$] and calculated[b] (in parentheses) ^1H and ^{13}C NMR chemical shifts of **1** and **2**

δ_H	C1-H	C2-H	C3-H	C4-H	C5-H
1	—	—	7.87 d (7.88)	7.71 t (7.91)	7.98 t (8.44)
2	—	—	8.44 d (8.28)	7.98 t (8.37)	8.39 t (9.14)
δ_C	C1	C2	C3	C4	C5
1	204.9 (213.7)	133.8 (135.2)	123.6 (125.6)	130.7 (135.6)	139.5 (153.3)
2	216.4 (218.8)	131.0 (135.0	133.2 (140.0)	134.4 (140.9)	148.2 (167.6)

[a] Chemical shifts were obtained at room temperature in liquid SO_2, using TMS in liquid SO_2 as external standard. [b] Isotropic NMR shielding tensors were calculated at the MPW1PW91/6-311G(2DF)//MPW1PW91/3-21G* level and referenced against calculated TMS values; d = doublet, t = triplet.

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Notes and references

‡ Filtration of the $PhCS_2H/SCl_2$ reaction mixture about 10 min after initial $PhCS_2H$ addition, followed by immediate removal of solvent *in vacuo*, gave the soluble product as a mixture of yellow powder and some red sticky material. (Campaine *et al.*[2] obtained red sticky oil as the soluble product, as they did not immediately remove the solvent.) The product was reacted with $AgSbF_6$ according to: $[Ph\overline{\text{CSSC(Ph)S}}]Cl_2 + 2\ AgSbF_6 \rightarrow \mathbf{2}(SbF_6)_2 + 2$ AgCl and assuming it was all $[Ph\overline{\text{CSSC(Ph)S}}]Cl_2$.

§ *Crystal data*: for **2**$(SbF_6)_2$ (room temp.): $C_{14}H_{10}S_3F_{12}Sb_2$, M = 745.89, monoclinic, space group $P2_1/n$ (no. 14), a = 9.359(5), b = 15.148(2), c = 15.762(2) Å, β = 104.56(2)°, U = 2162.8(9) Å^3, Z = 4, D_c = 2.291 g cm^{-3}, T = 296.0 K, F(000) = 1408.00, μ(Mo-Kα) = 28.85 cm^{-1}. 6923 reflections measured, 6564 independent reflections, $R(R_w)$ = 0.051 (0.202), $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

For **2**$(SbF_6)_2$ (−60 °C): $C_{14}H_{10}S_3F_{12}Sb_2$, M = 745.89, monoclinic, space group $P2_1/n$ (no. 14), a = 9.345(4), b = 15.005(5), c = 15.745(4) Å, β = 104.71(3)°, U = 2135(1) Å^3, Z = 4, D_c = 2.320 g cm^{-3}, T = 213 K, F(000) = 1408.00, μ(Mo-Kα) = 29.22 cm^{-1}. 6683 reflections measured, 6334 independent reflections, $R1$ ($wR2$) = 0.0391 (0.1487).

For **2**$(AsF_6)_2$ (−100 °C): $C_{14}H_{10}S_3F_{12}As_2$, M = 652.24, monoclinic, space group $P2_1/c$ (no. 14), a = 9.1371(9), b = 14.850(2), c = 15.427(2) Å, β = 107.747(7)°, U = 1993.6(4) Å^3, Z = 4, D_c = 2.173 g cm^{-3}, T = 173(1) K, F(000) = 1264.00, μ (Mo-Kα) = 37.77 cm^{-1}. 5041 reflections measured, 5041 independent reflections, R (R_w) = 0.076 (0.214). CCDC 156699–15670. See http://www.rsc.org/suppdata/cc/b1/b100001m/ for crystallographic data in CIF or other electronic format.

¶ GAUSSIAN 98W, Revision A. 3, Gaussian, Inc., Pittsburgh PA, 1998.

|| $PhCS_3Cl$ was prepared by a modification of the reported method.[2] The molar ratio of $PhCSSH:SCl_2$ was changed from 1:2 to 1:1 and the solvent from diethyl ether-CCl_4 to diethyl ether. The melting point (90–93 °C) and Raman spectrum are identical to the product obtained following the procedure of Campaine *et al.*.[2]

** **1**(SbF_6) was characterized also by Raman and elemental analysis [found (calc): C, 19.63 (19.90); H, 1.26 (1.20); S, 24.65 (22.80); Sb, 29.39 (28.90), F, 28.63 (27.10)%]. The observed and calculated (MPW1PW91/3-21G*) Raman frequencies are in good agreement (S-Fig. 3, S-Table 3†). A preliminary X-ray crystal structure confirms the atom connectivity [a = 6.899(3), b = 6.905(2), c = 14.651(4) Å, α = 88.78(1), β = 88.44(1), γ = 60.34(1)°].

†† The average Ph–C bond distance is 1.41(1) Å in **2**$(SbF_6)_2$ and 1.44(1) Å in **2**$(AsF_6)_2$, which are slightly shorter than a C_{sp^2}–C_{sp^2} single bond distance (1.48 Å).

‡‡ The Pauling bond order is given by $D_b = D_1 - 0.71 \log b$ where D_b is the observed bond distance and D_1 is the single bond distance [D_1(S–S) 2.05; D_1(C–S) 1.81, D_1(C_{sp^2}–C_{sp^2}) 1.48 Å]; see ref. 9.

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