The Synthesis, Characterization, X-Ray Crystal Structure and Solution ESR Spectrum of the Paramagnetic Solid, 4,5-Bis(trifluoromethyl)-1,2,3-trithiolium Hexafluorarsenate: Implications for the Identity of '1,2-Dithiete' Cations

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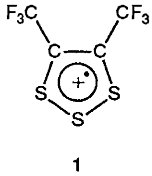
The 7π radical $CF_3\overline{CSSSC}CF_3^{+\cdot}$ **1**, which is the first isolated example of a $R\overline{CS_xC}R^{+\cdot}$ cation, is prepared by the reaction of $S_8(AsF_6)_2$, $S_4(AsF_6)_2$, AsF_5 and CF_3CCCF_3 in SO_2; the X-ray crystal structure consists of planes containing both monomeric radical cations and anions, the solid exhibiting Curie–Weiss paramagnetism between 25 and 200 K (μ = 1.68 μ_B).

We report the synthesis and characterization of the 7π $CF_3\overline{CSSSC}CF_3^{+\cdot}$ cation **1**,[1] formally derived from $CF_3\overline{CSNSC}CF_3$ **2** by the isovalent substitution of S^+ for N. This is the first preparative scale synthesis and characterization of a simple cationic $\overline{RCS_xC}R^{+\cdot}$ heterocycle. The ESR spectrum of **1** in SO_2 solution is the same as that previously reported for the cation $CF_3\overline{CSSC}CF_3^{+\cdot}$, **3** (R = CF_3).[2,3] It is probable that spectra previously assigned to **3** and other 1,2-dithiete radical cations, which have been extensively investigated[2–7] by ESR spectroscopy over the past twenty years in dilute solution (usually *ca.* 10^{-6} mol dm^{-3}), are in fact due to 1,2,3-trithiolium cations.

$$1/2S_8(AsF_6)_2 + 1/2S_4(AsF_6)_2 + 2CF_3CCCF_3 \rightarrow 2CF_3\overline{CSSSC}CF_3AsF_6 + AsF_3 \quad (1)$$



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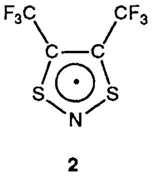

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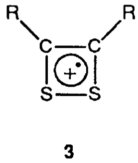

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$CF_3\overline{CSSSC}CF_3AsF_6$ was prepared in 90% yield according to eqn. (1). SO_2 (8.158 g), AsF_5 (1.6351 g, 9.62 mol) and Br_2 (13 mg) were successively condensed onto S_8 (0.522 g, 2.03 mmol). After stirring the deep-blue solution [containing

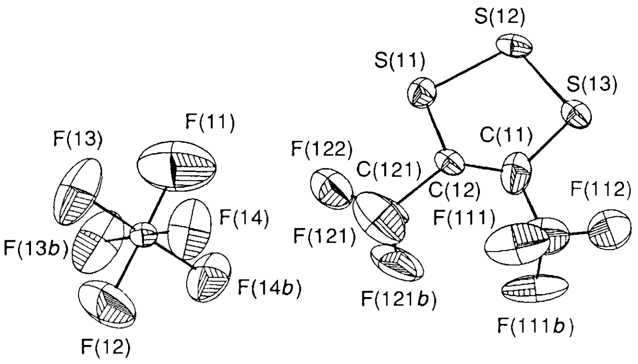

Fig. 1 The crystal structure of $1AsF_6$. Average bond lengths (in Å over three independent cations assuming C_{2v} symmetry): S–S 2.026(8), C–S 1.71(2), C–C 1.34(2), C–CF_3 1.54(2), C–F 1.30(2). Angles (°): S–S–S 100.2(3), C–S–S 98.8(5), S–C–C 121(1), S–C–CF_3 115(1), C–C–F 111(2), F–C–F 108(2).

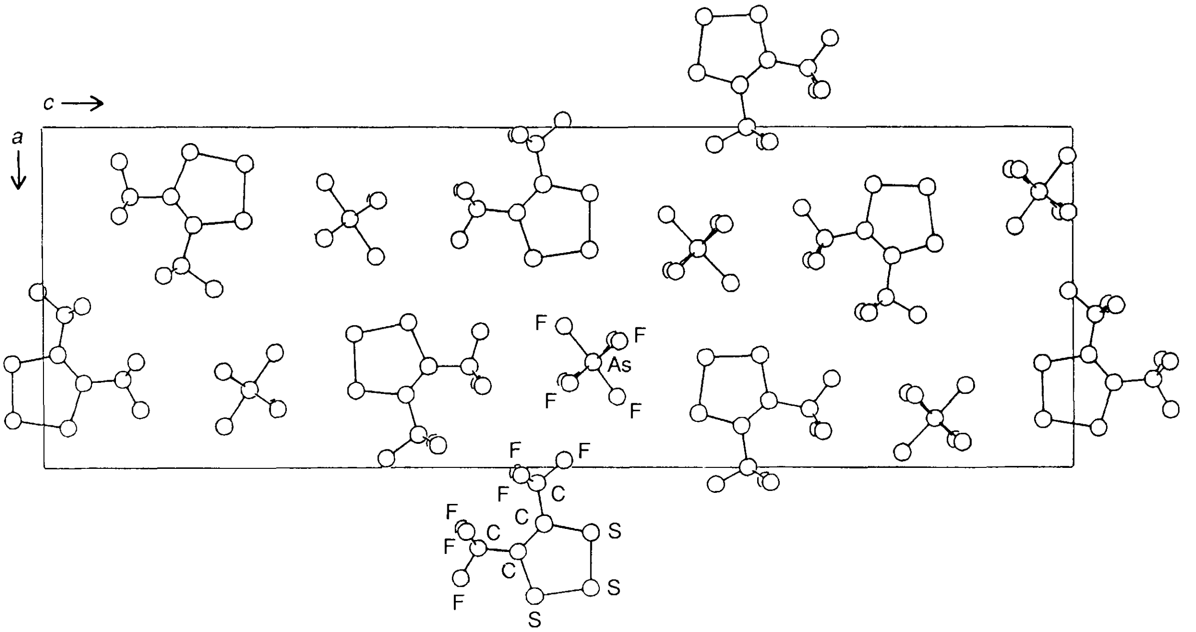

Fig. 2 The contents of the plane at $b = 0.25$. The plane at $b = 0.75$ is related to this by an inversion centre at 0.5, 0.5, 0.5. Two fluorines on either CF_3 group and four fluorines on each anion lie out of the plane, all other atoms lie in the plane.

$S_8(AsF_6)_2$ and $S_4(AsF_6)_2$[8]] for 20 h at room temp. CF_3CCCF_3 (1.059 g, 6.53 mmol) was condensed onto the reaction mixture, which became dark-purple after four days' stirring at room temp. The reaction mixture was then heated to 50 °C for 2 weeks. Removal of the volatiles (SO_2, CF_3CCCF_3 and SOF_2, ^{19}F NMR) left a dark-purple solid, consisting of **1**AsF_6, contaminated with $S_8(AsF_6)_2$ (*ca.* 10% by weight) and some higher molecular weight species (mass spectroscopy and chemical analysis). The product was purified by reaction with AsF_5 (0.229 g, 1.34 mmol) and CF_3CCCF_3 (0.208 g, 1.28 mmol) in SO_2 (4.571 g) at 50 °C for 8 days (eqns. 2 and 1), yielding 2.214 g of **1**AsF_6.

$$S_8(AsF_6)_2 + 3AsF_5 \rightarrow 2S_4(AsF_6)_2 + AsF_3 \qquad (2)$$

1AsF_6 was characterized by its IR spectrum (which was similar to that of **2**) and chemical analyses. The mass spectrum (electron impact, 27 eV) shows the molecular ion due to **1** at 258 (100% intensity), with no significant contamination by S_8^+ or its fragments. Slow evaporation of a solution of **1**AsF_6 in SO_2–SO_2ClF gave long, needle-like crystals† that were identical to the bulk product (correlation of X-ray powder and single crystal data, IR).

It is clear from the X-ray data that the cell contains three independent, monomeric $CF_3\overline{CSSSC}CF_3^{+\cdot}$ cations (Fig. 1) and three independent AsF_6^- anions. The structure is composed of layers containing both cations and anions (Fig. 2)

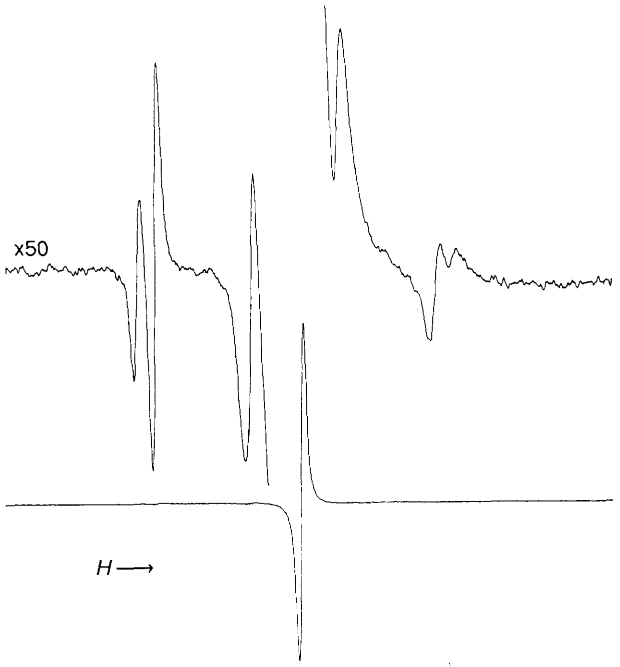

Fig. 3 High resolution ESR spectrum of $MeO_2C\overline{CSSSC}CO_2MeAsF_6$ in SO_2 (10^{-3} mol dm^{-3}) at −70 °C showing resolution of the ^{33}S satellites into two signals in 1 : 2 intensity ratio consistent with the structure of the 1,2,3-trithiolium ring being maintained in solution. The sample was subjected to 40 mW of microwave power to maximize the signal intensity, and a microwave frequency-phase locking circuit was used to minimize the FM noise produced at these power levels. The modulation amplitude was 12.0 mG.

perpendicular to the *b*-axis (interlayer distance 4.1 Å). It seems reasonable to infer that in the absence of dimerisation effects (which are expected to be negligible for **1**[1,12]), packing in the crystal is largely determined by electrostatics.

The possibility of unusual magnetic properties was explored in a variable temperature magnetization study using a Quantum Design SQUID magnetometer operating at 0.1 T. In the temperature regime between 25 and 200 K the material showed ordinary Curie–Weiss paramagnetism, with μ =

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† *Crystal data*: $C_4F_6S_3{\cdot}AsF_6$, $M_r = 447.126$, orthorhombic, space group *Pnma* (or *Pna*2_1), $a = 12.241(4)$, $b = 8.232(5)$, $c = 37.39(3)$ Å, $V = 3767.7(4)$ Å^3, $Z = 12$, $D_c = 2.364$ g cm^{-3}, Mo-Kα radiation (graphite monochromator), $\lambda = 0.70926$ Å, $\mu = 33.08$ cm^{-1}, $F(000) = 2556$, 1175 observed reflections with $I > 2\sigma(I)$. The data, 2995 unique reflections, were collected at 213 K with an ω-2θ the scan. The data were reduced to a standard scale;[9] Lorentz–polarization and absorption corrections were applied.[10] The structure was solved from the Patterson function, to determine the positions of the three As atoms. Refinement[11] in the centrosymmetric space group (*Pnma*) converged with $R = 0.076$ when some disorder in the AsF_6^- groups was introduced. The refinement in the equivalent non-centrosymmetric space group (*Pna*2_1) has not yet converged, $R = 0.066$, and calculations are continuing. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

1.68 μ_B and $\theta = -0.6$ K, and it is clear that the coupling between the radical cation spins is very weak.

The ESR spectrum of **1**AsF_6 in SO_2 (10^{-2} mol dm^{-3}) at −60 °C (with modulation amplitude 1.0 G; 1 G = 10^{-4} T) consisted of a central binomial septet (6F, a = 1.3 G) with one set of weak ^{33}S satellites (apparent 'a' = 8.6 G), g = 2.014. These parameters are practically identical to those quoted in the literature for derivatives of the 1,2-dithiete cation **3** [typical ranges: g = 2.0160–2.0144, $a(^{33}S)$ = 7.6–8.8 G;[2,7] specifically for **3** ($R = CF_3$): $a(^{19}F)$ = 1.35 G, g = 2.016 and $a(^{33}S)$ = 8.6 G[2,3]].

From the ESR spectrum, crystal structure, mass spectrum and chemical analyses of **1**AsF_6, it seemed probable that spectra previously assigned to **3** ($R = CF_3$) were in fact due to **1**. The ESR spectrum of $\mathrm{MeO_2C\overline{CSSSC}CO_2Me^{+\bullet}}$‡ (*ca.* 10^{-3} mol dm^{-3}) was also studied because the ^{33}S satellites are not complicated by the extra F hyperfine splittings (see Fig. 3). Beside the main singlet line (g = 2.017) we have been able to resolve the ^{33}S satellites of $\mathrm{MeO_2C\overline{CSSSC}CO_2Me^{+\bullet}}$ into two components with $a(^{33}S)$ = 8.9 and 8.0 G in a 1:2 intensity ratio, fully consistent with the structure of a 1,2,3-trithiolium radical cation. This result strongly suggests that the ESR spectra previously assigned to other derivatives of **3** are in fact due to derivatives of **1**, although we cannot rule out completely the possibility that derivatives of **1** and **3** possess identical ESR parameters.

Consistent with these results, no S_8 was ever observed to be precipitated from solutions of **1**, ^{19}F NMR spectra showed only a broad contact-shifted AsF_6^- resonance at δ −40, $\Delta\nu$ = 1747 Hz, the magnetic moment of the solution was 2.1 μ_B (at room temp.) and 2.3 μ_B (at −60 °C) (Evans' method[13]) and ESR spectra shows no resonances other than that described above. **1**AsF_6 was recovered unchanged from solutions in SO_2.

Although derivatives of **1** contain two sets of inequivalent sulphur atoms, the magnitudes of their ^{33}S hyperfine coupling constants are very similar. This is consistent with an MNDO calculation on the model cation $\mathrm{H\overline{CSSSC}H^{+\bullet}}$ (UHF, experimental geometry of **1**), which shows the b_1 (π^*) SOMO to be uniformally distributed over the S_3 moiety. While it is not impossible that derivatives of **1** and **3** coincidentally possess identical ESR parameters, we have shown that unless conditions of high power and low modulation amplitude are employed, ESR spectra of 1,2,3-trithiolium cations apparently exhibit only one set of ^{33}S satellites. It is possible that this has led to the assignment of the spectra of 1,2,3-trithiolium cations to 1,2-diethiete cations. The characterization by ESR spectroscopy of the number of sulphur atoms in a radical is notoriously difficult, and it is notable that $S_5^{+\bullet}$[14] and $S_3N_2^{+\bullet}$[15] were once thought to be $S_4^{+\bullet}$ and $S_2N_2^{+\bullet}$ on the basis of ESR studies which included 48% ^{33}S enrichment experiments. The stability of **1** over **3** is consistent with the stabilities of the related 7π radicals $\mathrm{R\overline{CSNSC}R}$,[1,16] $\mathrm{R\overline{CNSSN}^{\bullet}}$,[12,17] $\mathrm{R\overline{CNSeSeN}^{\bullet}}$[18] and $S_xSe_{3-x}N_2^{+\bullet}$ (x = 0–3).[19]

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‡ The reaction of $\mathrm{MeO_2CC{\equiv}CCO_2Me}$ with $S_8(AsF_6)_2$ and $S_4(AsF_6)_2$ [*cf.* eqn. (1)] gave a mixture containing an undetermined quantity of $\mathrm{MeO_2C\overline{CSSSC}CO_2MeAsF_6}$ (mass spectroscopy and ESR).

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