Preparation and Crystal Structure of the Paramagnetic Solid $F_3CCSSSCCF_3AsF_6$: Implications for the Identity of $RCSSCR^{\bullet+}$ †

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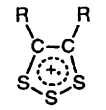
4,5-Bis(trifluoromethyl)-1,2,3-trithiolylium hexafluoroarsenate, which contains the 7π $F_3CCSSSCCF_3{}^{\bullet+}$ radical cation, the first example of a cationic carbon–sulfur heterocycle, has been prepared and characterised. It was prepared as a purple solid in 90% yield by the reaction of F_3CCCCF_3 with a 1:1 mixture of $S_4(AsF_6)_2$ and $S_8(AsF_6)_2$ in SO_2 at 50 °C for 2 weeks. Small amounts of a homopolyatomic sulfur cation (probably $S_8{}^{2+}$) were removed by work-up with fresh F_3CCCCF_3 and AsF_5 in SO_2 at 50 °C for 8 d. The $F_3CCSSSCCF_3AsF_6$ was characterised in the solid state by chemical analyses, IR, mass spectrometry [M^+ at m/z 258 (100%)] and X-ray crystallography. The crystal structure consists of layers containing both monomeric, planar $F_3CCSSSCCF_3{}^{\bullet+}$ radical cations *and* $AsF_6{}^-$ anions [space group *Pnma*, a = 12.241(4), b = 8.232(5), c = 37.39(3) Å, Z = 12 and R = 0.086]. A powder photograph of the bulk product correlated with the single-crystal data, and a variable-temperature magnetic susceptibility study indicated that $F_3CCSSSCCF_3AsF_6$ is a paramagnetic solid, exhibiting ordinary Curie–Weiss behaviour, μ = 1.68, θ = −0.6 K (μ = 2.1 in SO_2 solution at room temperature). The ESR spectrum of $F_3CCSSSCCF_3{}^{\bullet+}$ in SO_2 is identical to that previously reported for $F_3CCSSCCF_3{}^{\bullet+}$ [g = 2.014, $a(^{19}F)$ = 1.3 G, '$a(^{33}S)$' = 8.6 G], which suggested that spectra long assigned to 1,2-dithiete cations are in fact due to 1,2,3-trithiolylium cations. This is supported by the ESR spectrum of $MeO_2CCSSSCCO_2Me^{\bullet+}$, which consisted of a singlet at g = 2.017, with two sets of ^{33}S satellites in a 2:1 intensity ratio, with very similar ^{33}S coupling constants (8.0 and 8.9 G). The salt $F_3CCSSSCCF_3AsF_6$ is reduced by KI to give a mixture of neutral cyclic polysulfides including $F_3CCSSCCF_3$ (43%) and the previously unknown $F_3CCSSSCCF_3$ (23%). Attempts to oxidise $F_3CCSSSCCF_3{}^{\bullet+}$ with AsF_5 were unsuccessful.

Our recent investigations into the 7π carbon–sulfur–nitrogen radicals $RCSNSCR^{\bullet}$ [1–3] and $RCNSNS^{\bullet}$ [3–5] revealed some interesting and unusual physical properties. For example some $RCNSNS^{\bullet}$ are isolable, and all undergo an unprecedented rearrangement to the thermodynamically more stable $RCNSSN^{\bullet}$ isomer,[4,5] and $F_3CCSNSCCF_3{}^{\bullet}$ is a thermally stable (but photochemically unstable), deep green, paramagnetic liquid (ΔH for dimerisation is zero or positive) under a blue gas at room temperature.[1] We report the synthesis and characterisation of the $F_3CCSSSCCF_3{}^{\bullet+}$ cation **1**, which is a 7π radical related to $F_3CCSNSCCF_3{}^{\bullet}$ by the isovalent substitution of S^+ for N, and is the first example of a CS_xC^+ ring system to be isolated.

The $AsF_6{}^-$ salt of **1** was prepared in 90% yield by the reaction of F_3CCCCF_3 with a 1:1 mixture of $S_8(AsF_6)_2$ and $S_4(AsF_6)_2$. Its ESR spectrum in SO_2 is the same as that previously reported for the cation $F_3CCSSCCF_3{}^{\bullet+}$.[6,7] It is likely that spectra previously assigned to this and over 30 other 1,2-dithiete cations, which have been extensively studied by ESR spectroscopy during the past twenty years in dilute solution,[6–13] are in fact due to 1,2,3-trithiolylium cations. This is supported by the high-resolution spectrum of $MeO_2CCSSSCCO_2Me^{\bullet+}$ **2**, which shows two sets of ^{33}S satellites in 1:2 intensity ratio with very similar coupling constants. We rationalise these observations in terms of the singly occupied molecular SOMO of **1** which is uniformly distributed over the $S_3{}^+$ moiety. In the solid state the crystal structure consists of planes containing both monomeric **1** cations and $AsF_6{}^-$ anions. The $AsF_6{}^-$ salt behaves as an ordinary Curie–Weiss paramagnet, and may be classified, like O_2AsF_6[14] and $I_2Sb_2F_{11}$,[15] as a 'paramagnetic solid'.[4]



1 R = CF_3
2 R = CO_2Me

The stability of cation **1** is in marked contrast to neutral cyclic trisulfides, which are known to be highly labile and to equilibrate rapidly giving mixtures.[16] In this respect **1**, like $S_4{}^{2+}$, $Te_6{}^{4+}$ and $S_2I_4{}^{2+}$, is an example of the stabilisation of an unusual molecular framework by cation formation.[17,18] The neutral cyclic trisulfide $F_3CCSSSCCF_3$ given on reduction of the $AsF_6{}^-$ salt of **1** with KI undergoes rapid partial

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† *Supplementary data available* (No. SUP 56874, 9 pp.): spectra and details of other reactions performed. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI units employed: G = 10^{-4} T; emu = SI × $10^6/4\pi$.

disproportionation to several known cyclic sulfides (including $F_3C\overline{CSSC}CF_3$) and S_8. A preliminary communication of part of this work has been published.[19]

Experimental

The apparatus, techniques and chemicals, unless specified, have been previously described.[20] The compounds F_3CCCCF_3 (PCR), HCCH (Canadian Liquid Air), MeCCMe and MeO_2CCCCO_2Me (dmad) (Aldrich) and AsF_5 (Ozark-Mahoning) were used as received. Bromine (Anachemia) was dried over P_4O_{10}, SO_2ClF (Aldrich) over molecular sieves, and SO_2 over CaH_2; S_8 and KI were vacuum dried prior to use.

The ^{19}F NMR spectra were acquired at 188.15 MHz on a Varian Associates XL-200 spectrometer and referenced externally to $CFCl_3$ in SO_2. Samples were contained in thick-walled 5 (sealed) or 10 mm (fitted with J. Young O-Ringlette type valves) precision NMR tubes (Wilmad). Infrared spectra were obtained as Nujol mulls (for solid samples) or films (liquids) between KBr or CsI plates on a Perkin-Elmer 683 instrument. Samples for mass spectrometry were contained in sealed glass capillaries under dry nitrogen, and introduced into the spectrometer by direct inlet. All spectra were obtained at room temperature in the electron-impact mode using 27 eV (*ca.* 4.3×10^{-18} J) ionising voltage on a Kratos MS-50TC instrument. Powder photographs were obtained of finely ground samples contained in soda glass capillaries (Supper, outside diameter 0.5 mm) using copper X-rays with a nickel filter and exposure time of 3 h, and indexed with the aid of the DISPOW routine in the PC version of the NRCVAX suite of programs.[21]

The ESR spectra were recorded with a custom-built spectrometer, equipped with a 12 in. Varian Associates electromagnet controlled by a V-FR2503 Fieldial regulating unit and a Hall probe. The magnetic field was calibrated by a Bell 640 incremental gaussmeter. The klystron beam and reflector voltages were powered by two Power Designs high-stability power supplies, and the microwave frequency locked to the cavity by a Micronow Instruments model 210 automatic frequency-control stabiliser. When extra stability of the klystron frequency was required it was phase-locked, *via* a feedback loop, to a quartz oscillator thermostatted in the oven of a Frequency Engineering Laboratories model 137A synchroniser. This enabled spectra to be obtained at high power levels while eliminating the frequency modulation noise which is usually a problem under these conditions. The microwave bridge has been previously described.[22] The detection unit consisted of a Stanford Research Systems SRS 530 computer-controlled lock-in amplifier. The frequency of the spectrometer was measured by a calibrated wavemeter attached to the reference arm of the bridge *via* a directional coupler.

Elemental analyses were carried out by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Synthesis of $F_3C\overline{CSSSC}CF_3AsF_6$.—Sulfur dioxide (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) in a rigorously dried two-bulb vessel incorporating a medium sintered-glass frit, and equipped with a J. Young Teflon valve. After stirring the deep blue solution [containing $S_8(AsF_6)_2$ and $S_4(AsF_6)_2$] for 20 h at room temperature (r.t.) F_3CCCCF_3 (1.059 g, 6.53 mmol) was condensed onto the reaction mixture, which became dark purple after stirring at r.t. for 4 d. The mixture was then heated to 50 °C for 2 weeks. Removal of the volatiles {SO_2, F_3CCCCF_3 (0.6 mmol), AsF_3 (2.4 mmol) and SOF_2 (0.9 mmol), plus minor amounts (*ca.* 0.08 mmol) of CF_3-containing side products [$\delta(^{19}F)$ -63 and a group of resonances around δ -74]} to constant weight by dynamic vacuum for 15 h left a dark purple solid (2.250 g). In addition to the AsF_6^- salt of **1**, chemical analysis* suggested $S_8(AsF_6)_2$ as a possible impurity (*ca.* 10% by weight), and the mass spectrum was not inconsistent with this. Mass spectral peaks corresponding to the higher-molecular-weight species $C_8F_{14}S_{4-n}^+$ (n = 0–2) were also observed. The product (2.234 g) was purified by reaction with AsF_5 (0.229 g, 1.34 mmol) and F_3CCCCF_3 (0.208 g, 1.28 mmol) in SO_2 (4.571 g) at 50 °C for 8 d. The solvent was slowly removed from the reaction mixture overnight, yielding, after complete removal of the volatiles by dynamic vacuum (15 h), purple microcrystalline AsF_6^- salt of **1** (2.214 g, 90% yield). The most direct method for purity assessment is mass spectrometry, and in other reactions (see SUP 56874) purification steps were repeated until the intensities of the peaks due to S_8^+ and $C_8F_{14}S_{4-n}^+$ (n = 0–2) were less than 2.5% (see Table 1).

The AsF_6^- salt of **1** hydrolyses quickly in moist air emitting a foul odour. It was characterised in the solid state by elemental analysis [Found: (Calc.): C, 10.60 (10.75); As, 16.70 (16.75); F, 50.7 (51.00); S, 21.65 (21.50%)], mass spectrometry (Table 1), IR spectroscopy (Table 2), X-ray crystallography and variable-temperature magnetic susceptibility (μ = 1.68, see below). It is very soluble in SO_2 giving a purple solution. The magnetic moment (determined on a 0.14 mol dm^{-3} solution in SO_2 by Evans' NMR method,[24] employing 1.24 mol dm^{-3} CH_2Cl_2 in SO_2 as the internal shift standard) was 2.1 and 2.3 at r.t. and -60 °C respectively. Fluorine-19 NMR spectroscopy showed only a contact-shifted[25] AsF_6^- resonance at δ -40 ($\Delta\nu$ = 1500 Hz) with trace contaminants at δ -51 and -60, possibly arising from minor hydrolysis. Except for a slight narrowing of the resonance at δ -40 to 1300 Hz the spectrum was unchanged on cooling to -70 °C. The ESR spectrum of a 10^{-2} mol dm^{-3} solution using a modulation amplitude of 12 mG consisted of a central binomial septet [6 F, $a(^{19}F)$ = 1.3 G] and one set of weak ^{33}S satellites [apparent $a(^{33}S)$ = 8.6 G], with g = 2.014 (a copy of the spectrum has been deposited). The AsF_6^- salt was recovered unchanged from solutions in SO_2 (IR spectrum).

By reaction of $S_4(AsF_6)_2$ *with* F_3CCCCF_3, *studied* in situ *by ESR and NMR spectroscopy.* Sulfur dioxide (0.456 g), AsF_5 (30 mg, 0.16 mmol) and Br_2 (3 mg) were successively condensed onto S_8 (6 mg, 0.002 mol) in a 3 mm ESR tube equipped with a J. Young Teflon valve. The reaction mixture became initially pale blue and then pale orange. The compound F_3CCCCF_3 (30 mg, 0.17 mmol) was then condensed onto the frozen reaction mixture. The ESR spectrum after 15 min showed only the septet due to **1** [g = 2.014, $a(^{19}F)$ = 1.3 G]. It was unchanged after 2 d.

Sulfur dioxide (0.916 g), AsF_5 (0.194 g, 1.14 mmol) and Br_2 (0.8 mg) were successively condensed onto S_8 (0.063 g, 0.2 mmol) in a 5 mm NMR tube fitted with a J. Young valve. After 45 min at r.t. the compound F_3CCCCF_3 (0.117 g, 0.7 mmol) and SO_2ClF (an internal concentration standard; 0.058 g, 0.49 mmol) were condensed onto the blue solution and the tube sealed off. The ^{19}F NMR spectra after 17 h and 13 d at r.t. showed SOF_2 [0.08 (17 h), 0.15 mmol (13 d)], F_3CCCCF_3 (0.41, 0.19 mmol), a broad resonance assignable to $AsF_3/AsF_5/AsF_6^-$, SiF_4 (0.02, 0.02 mmol) and two peaks at δ -71.7 and -72.6 [each of which correspond to 0.30 (0.48 mmol) of fluorine atoms, or 7% of an impurity containing four CF_3 groups, see below]. In both spectra the presence of **1** likely caused the resonances to be contact-shifted by *ca.* 2–5 ppm to high frequency of their usual positions.

Attempted Preparation of Other Derivatives of Cation **1**.—Related reactions using HCCH or MeCCMe instead of

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* Analysis (%): C, 9.75; As, 16.40; F, 49.70; S, 24.15. Although it was surprising that the colour of the solution of the AsF_6^- salt 10% contaminated with $S_8(AsF_6)_2$ was dark purple, and not blue-black, a sample of the pure salt artificially contaminated with $S_8(AsF_6)_2$ was also dark purple in SO_2. The intense colour of $S_8(AsF_6)_2$ is due to the presence of the $S_5^{\cdot+}$ cation,[23] which may be scavenged by **1** in these solutions.

F_3CCCCF_3 in equation (1) produced only intractable brown tars which were not further characterised.

The reaction between dmad (1.158 g, 8.1 mmol), $S_8(AsF_6)_2$ and $S_4(AsF_6)_2$ [prepared *in situ* from S_8 (0.776 g, 3.0 mmol)] according to the procedure described above gave a hard black amorphous solid (2.729 g recovered yield) and S_8 (0.231 g, mass spectrum). The IR spectrum of the black solid consisted of several broad bands including ν(C=O) 1750, $\nu_3(AsF_6^-)$ 700 and $\nu_4(AsF_6^-)$ 398 cm^{-1},[26] but was otherwise inconclusive. The mass spectrum exhibited a peak at *m*/*z* 238 (due to **2**), although additional peaks at 316 and 285 strongly suggested the presence of $\overline{RCC(R)SC(R)C}R^{\cdot+}$ (R = CO_2Me). The ESR spectrum of a solution (*ca.* 10^{-3} mol dm^{-3}) of this material in SO_2 exhibited a singlet with *g* = 2.017, and *two* sets of ^{33}S satellites in 1:2 intensity ratio with $a(^{33}S)$ = 8.9 and 8.0 G (see Fig. 1), fully consistent with the presence of radical cation **2**. In the course of these studies four samples of this material were examined by ESR spectroscopy, and in one instance the spectrum showed a second singlet resonance with *g* = 2.0096, which we assign to the $\overline{RCSC(R)C(R)SC}R^{\cdot+}$ (R = CO_2Me) cation, by analogy with similar derivatives (typical range, 2.0079–2.0098[8]). No resonances were observed in the ^1H NMR spectrum of a *ca.* 0.4 mol dm^{-3} solution in SO_2. The mass and ESR spectra both indicated that the product from this reaction was a mixture, and the broad IR bands are consistent with this. Separation of the individual components was not attempted.

Crystal Structure Determination of the AsF_6^- *Salt of* **1**.—A solution of the AsF_6^- salt (0.358 g) in SO_2 (2.980 g)–SO_2ClF (1.331 g) contained in one bulb of a two-bulbed vessel (see above) was held at 0–5 °C, and the solvent slowly condensed into the second bulb, which was held at 0 °C, yielding after 2 months long (2–4 mm), purple, needle-like crystals suitable for X-ray crystallography. The crystals were carefully cut, then mounted and sealed in rigorously dried glass capillaries under dry nitrogen.

The data, 2995 unique reflections, were collected at 213 K on an Enraf-Nonius CAD-4 diffractometer with a ω–2θ scan. Collection and refinement data are given in Table 3. The data were reduced to a standard scale, and Lorentz polarisation[27] and absorption corrections[28] were applied. The structure was solved from the Patterson function, where the locations of the three As atoms were determined. All three As atoms, two fluorine atoms from each AsF_6^- group and the $C_4S_3F_2$ groups were all in, or very close to, the mirror plane in space group *Pnma*, or the false mirror in $Pna2_1$. The remaining fluorine atoms are thus related to the mirror (or false mirror). The structure was first refined[29] with large-block full-matrix least squares; in *Pnma* the refinement converged at *R* = 0.086 with one of the rings slightly disordered out of the mirror. Two of the AsF_6^- groups are also obviously disordered or librating and the system was refined with these two groups disordered, with the second portion of the group rotated 90° about the As atoms in the mirror plane. The refinement converged at *R* = 0.076 with *ca.* 80% of these groups in their original position. Refinement of the undisordered model in space group $Pna2_1$ reduced the *R* factor to 0.062 but with very strong correlations between the parameters of many pseudo-symmetry-related atoms. The refinement had to be strongly damped to achieve convergence. While the change from a centro- to a non-centrosymmetric space group lowers the *R* value, it also increases the number of variables by 198. The lowering of the *R* value is significant according to the Hamilton test,[30] even at the 0.5% probability level. However, the structure in space group $Pna2_1$ did not differ significantly from that in *Pnma*, and given the extreme conditions of the refinement it seems wise to report only the parameters for the centrosymmetric structure. One constant feature of all refinements was an indication of a slight buckling of ring 2 [S(21), *etc*]. This has been included as a disorder in the atomic parameters. During refinement all similar bonds were lightly restrained to be of similar lengths (As–F, S–S and C–S, *etc.*), but these lengths were also allowed to refine. Reported in Table 4 are the atomic parameters for the structure in space group *Pnma* without disorder in the AsF_6^- since this is the refinement which gives the clearest picture of the basic structure.

With three very similar $C_4S_3F_6{\cdot}AsF_6$ groups in the asymmetric unit there remains the concern that the chosen lattice is a sub-lattice of a higher-symmetry space group; this is particularly true when the *a* and *c* lengths are in the approximate ratio 1:3. However, the ratio is not exactly 1:3, and reflections $l \neq 3n$ are clearly present. Similarly, attempts to find a trigonal arrangement have failed, so far, for the lack of the correct Laue symmetry.

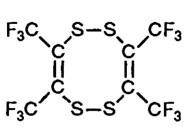
A powder photograph of the bulk product (see SUP 56874) correlated with that calculated from the single crystal data, showing the two to be the same material. Consistently, the IR spectrum of powdered crystals was identical to that given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Variable-temperature Magnetic Susceptibility Study of the AsF_6^- *Salt.*—The magnetisation, *M*, was measured with a SQUID magnetometer, at 1 kG, and the susceptibility obtained from $\chi = M/H$. A plot of $1/\chi$ *vs.* *T* shows Curie–Weiss behaviour over much of the temperature range (0–300 K) and the data between 25 and 200 K (given in Fig. 2) were fitted by least squares to a straight line, yielding an effective moment μ = 1.68 and a Curie–Weiss temperature $\theta = -0.6$ K. At low temperature short-range antiferromagnetic order develops with a rounded maximum at 3 K (illustrated in Fig. 3). Since the antiferromagnetic ordering temperature, T_N, occurs when $(\partial^2\chi/\partial T^2)_H = 0$, an upper limit of $T_N \leqslant 2$ K can be inferred from the available data, in rough agreement with the Curie–Weiss temperature.

Attempted Oxidation of the AsF_6^- *Salt.*—Sulfur dioxide (4.442 g), AsF_5 (0.381 g, 1.9 mmol) and Br_2 (10 mg) were successively condensed onto the AsF_6^- salt (0.450 g, 1.0 mmol) giving a purple solution, and the solution stirred for 2 months at r.t. with no change in appearance. Removal of the volatiles (SO_2, AsF_5 and small amounts of SiF_4 and AsF_3, IR spectrum) at −20 °C left the AsF_6^- salt (0.507 g, IR spectrum). An ESR spectrum at −70 °C of the AsF_6^- salt (10^{-2} mol dm^{-3} in SO_2) in the presence of a 16-fold excess of AsF_5 showed the expected septet due to **1**. The ^{19}F NMR spectrum of a solution containing the AsF_6^- salt (0.05 mmol) and AsF_5 (2.00 mmol) in SO_2 (0.867 g) in a 5 mm NMR tube showed only a broad resonance at δ −41 (Δν = 654 Hz) attributable to AsF_6^-/AsF_5.

Reduction of the AsF_6^- *Salt.*—Sulfur dioxide (6.027 g) was condensed onto a mixture of the AsF_6^- salt (1.341 g, 3.0 mmol) and KI (0.551 g, 3.3 mmol), contained in a two-bulbed vessel incorporating a sintered glass frit and a 10 mm NMR tube. The brown-black solution and a black precipitate given immediately on thawing was stirred for 17 h, and then filtered into the 10 mm NMR tube, leaving a black insoluble solid (1.190 g) identified as a mixture of $KAsF_6$, S_8 and I_2 (IR and mass spectra). The ^{19}F NMR spectrum of the solution showed resonances at δ −55.0 (integration 34 mm), −55.9 (4 mm, **3**),[31] −57.2 (28 mm, **4**),[31] −58.9 (8 mm), −59.4 (10 mm) and −61.8 (61 mm, **5**).[31] Removal of the volatiles through a U tube at −78 °C left a black solid (0.303 g) in the NMR tube, and a red oil (0.163 g) in the cold trap. The black solid contained compound **3** [IR ν(C=C) 1554m cm^{-1},[31] mass spectrum *m*/*z* = 451 (M^+, 33.9%)], **4** [IR ν(C=C) 1585mw cm^{-1},[31] mass spectrum *m*/*z* = 388 (M^+, 13.9%)] and I_2 [mass spectrum *m*/*z* = 254 (M^+, 100%)]. The red oil was similarly shown to be a mixture of compounds **5** [IR ν(C=C) 1622s cm^{-1},[31] mass spectrum *m*/*z* = 226 (M^+, 76.2%)] and **6** [IR (tentative) 1637(sh) cm^{-1}, mass spectrum *m*/*z* = 258



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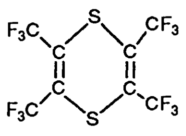

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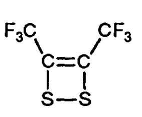

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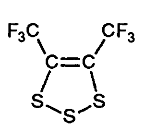

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(M^+, 63.7%)], contaminated with **3** and **4** (IR and mass spectra). The ^{19}F NMR spectrum of the red oil (65 mg) in SO_2 (3.822 g) showed only resonances at δ −54.9 and −61.6. Assignment of the ^{19}F NMR resonance at δ −55.0 to **6** gives the following product yields (with respect to the AsF_6^- salt on the basis of NMR integrations): **3**, 3, **4**, 20, **5**, 43 and **6**, 23%. This accounts for 89% of the product, but leaves the weak NMR resonances at δ −58.9 and −59.4 unassigned.

Molecular Orbital Calculations.—Molecular orbital calculations were performed at the 3-21G* and 6–31G* levels using the GAUSSIAN 86 suite of programs.[32] $\mathrm{H\overline{CSSSC}H^{\bullet+}}$ (with the geometry of the $\mathrm{\overline{CSSSC}}$ ring taken from the crystal structure of AsF_6^- salt of **1**) was used as a model for **1**. Use of the unrestricted Hartree-Fock (UHF) procedure led to heavy spin contamination ($\langle S^2 \rangle = 1.09$), and so the restricted open-shell Hartree-Fock (ROHF) procedure was preferred.[33] The same effects have been described for $\mathrm{R\overline{CNSSN}^{\bullet}}$ radicals,[34] for which similar calculations have been performed.

Discussion

Preparation of $\mathrm{F_3C\overline{CSSSC}CF_3AsF_6}$ *and its Characterisation in the Solid State. Attempted Syntheses of Other* $\mathrm{R\overline{CSSSC}R^{\bullet+}}$ *Cations.*—Cation **1** is the first isolated example of a 1,2,3-trithiolylium cation, and is related by the isovalent substitution of S^+ for N in the 7π systems $\mathrm{R\overline{CSNSC}R^{\bullet}}$,[1–3] $\mathrm{R\overline{CNSNS}^{\bullet}}$,[3–5] $\mathrm{R\overline{CNSSN}^{\bullet}}$,[34–36] $\mathrm{R\overline{CNSeSeN}^{\bullet}}$[37–39] and $S_xSe_{3-x}N_2^{\bullet+}$ (x = 0–3),[40–44] many derivatives of which are indefinitely stable and can be prepared on the gram scale as pure compounds. The AsF_6^- salt was prepared in 90% yield according to equation (1).

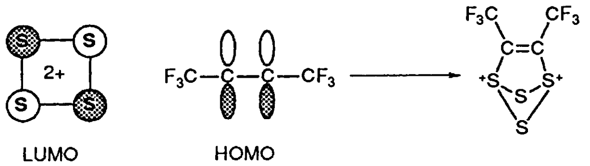
$$\tfrac{1}{2}S_8(AsF_6)_2 + \tfrac{1}{2}S_4(AsF_6)_2 + 2F_3CCCCF_3 \longrightarrow 2\mathrm{F_3C\overline{CSSSC}CF_3AsF_6} \quad (1)$$

A 1:1 mixture of $S_4(AsF_6)_2$ and $S_8(AsF_6)_2$ was prepared *in situ* by the bromine-facilitated oxidation of S_8 by AsF_5.[17,45] Colour changes and previous reactions at r.t. in which shorter times had been used showed that F_3CCCCF_3 reacted with this mixture very slowly, and it was necessary to heat at 50 °C for 2 weeks to drive the reaction to completion. Even under these conditions the product apparently still contained 10% S_8^{2+} as a possible impurity and some higher-molecular-weight species, but it was purified by further reaction with F_3CCCCF_3 and AsF_5 at 50 °C for 8 d, AsF_5 possibly converting the unreacted $S_8(AsF_6)_2$ into $S_4(AsF_6)_2$ [equation (2)]. The same products were obtained

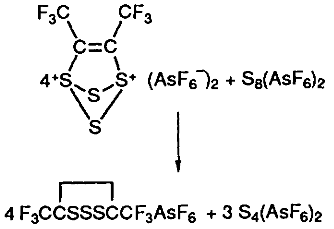
$$S_8(AsF_6)_2 + 3AsF_5 \longrightarrow 2S_4(AsF_6)_2 + AsF_3 \quad (2)$$

from the reaction of $S_4(AsF_6)_2$ with F_3CCCCF_3, which was studied *in situ* by ^{19}F NMR and ESR spectroscopy suggesting that the AsF_6^- salt is a highly stable 'thermodynamic sink' in this system.

Our data do not enable us to characterise intermediates in these reactions. Although a 1:1 mixture of S_4^{2+} and S_8^{2+} is stoichiometrically equivalent to $4S_3^+$ there is no evidence that this species is present. It is possible that these syntheses proceed initially *via* a reverse electron demand cycloaddition between S_4^{2+} and F_3CCCCF_3 [equation (3)]. The high ionisation potential of cation **1** (see below) implies that such a highly oxidised cycloadduct is likely to be short-lived under these reaction conditions, and it may be envisaged to react directly with S_8^{2+} [equations (4) and (5)] or *via* fluoride-ion transfer from AsF_6^- [equations (6)–(8)].



(3)



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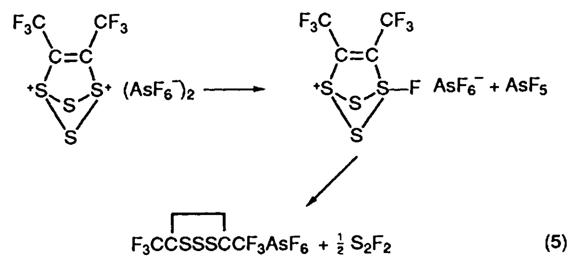

(5)

$$2S_2F_2 \longrightarrow \tfrac{3}{8}S_8 + SF_4{}^{*} \quad (6)$$

$$SF_4 + SO_2 \longrightarrow 2SOF_2 \quad (7)$$

$$S_8 + 6AsF_5 \longrightarrow 2S_4(AsF_6)_2 + 2AsF_3 \quad (8)$$

The AsF_6^- salt of **1** was characterised in the solid state by its satisfactory elemental analyses, IR and mass spectra, variable-temperature magnetic susceptibility and X-ray powder photography (which was consistent with the single-crystal data). The IR spectral data are compared to those of the isoelectronic 7π radical **7**[47] in Table 2. Although differences between the IR spectra of these two species are observed between 1220 and 800 cm^{-1}, which usually corresponds to SN stretching modes, they are otherwise similar [*e.g.* ν(C=C) at 1550 for **1** and 1580 for **7**, ν(CS) at 571 for **1** and 590 cm^{-1} for **7**], reflecting the similarity in their molecular and electronic structures.

The mass spectrum of the AsF_6^- salt of **1** is given in Table 1, and shows it to be essentially free of contaminants such as S_8, homopolyatomic sulfur cations or high-molecular-weight species, which all possess less than 2.5% of base intensity. The usual mode of volatilisation of AsF_6^- salts is *via* an initial fluoride-ion transfer [equation (9)], which is supported in this

$$\mathrm{F_3C\overline{CSSSC}CF_3AsF_6} \longrightarrow \mathrm{F_3C\overline{CSSSC}CF_3F} + AsF_5 \quad (9)$$

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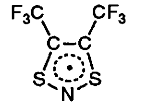
[*] This process is known to occur in the presence of acid catalysts such as BF_3 and HF,[46] AsF_5 or trace amounts of HF may act as the catalyst in this case.

Table 1 Mass spectrum of $F_3C\overline{CSSSC}CF_3AsF_6$

m/z	Intensity	Assignment
490	1.4	$C_8F_{14}S_4$
320	1.1	?$C_6F_8S_3$
298	5.8	^{34}S isotopomer of 296
297	2.6	$^{33}S/^{13}C$ isotopomer of 296
296	46.2	$C_4F_8S_3$
277	1.3	$C_4F_7S_3$
276	1.3	^{34}S isotopomer of 274. Plus ?
274	6.2	?$C_4F_6S_3O$ or C_7F_{10}
262	1.0	^{13}C or ^{33}S or ^{34}S isotopomers of 258. Plus?
261	1.9	
260	23.5	
259	11.8	
258	100	$C_4F_6S_3$
256	2.4	S_8
245	1.8	$C_4F_7S_2$
241	1.2	^{34}S isotopomer of 239. Plus ?
240	2.3	?
239	6.2	$C_4F_5S_3$
228	1.6	^{34}S isotopomer of 226
227	1.4	^{33}S, ^{13}C isotopomers of 226
226	19.4	$C_4F_6S_2$
213	3.3	C_4F_7S
207	4.6	$C_4F_5S_2$
196	3.3	^{34}S isotopomer of 194. Plus ?
195	4.6	$C_3F_5S_2$. Plus ^{33}S, ^{13}C isotopomers of 194
194	41.8	C_4F_6S
192	1.1	S_6
191	1.2	^{34}S isotopomer of 189. Plus ?
189	7.2	$C_3F_3S_3$
181	3.6	C_4F_7
175	5.3	C_4F_5S
164	2.8	$C_2F_4S_2$
163	2.4	C_3F_5S
160	1.3	S_5
159	2.0	^{34}S isotopomer of 157
158	1.0	$^{33}S/^{13}C$ isotopomer of 157
157	19.5	$C_3F_3S_2$
151	9.2	AsF_4
149	1.6	?
144	2.2	C_3F_4S
143	2.2	C_4F_5
132	12.5	AsF_3
131	1.1	C_3F_5
128	1.7	S_4
127	1.2	^{34}S isotopomer of 125. Plus ?
125	14.9	C_3F_3S
115	2.3	^{34}S isotopomer of 113. Plus ?
114	1.8	$^{33}S/^{13}C$ isotopomer of 113. Plus ?
113	45.3	AsF_2/C_2F_3S
106	4.2	C_3F_2S
102	1.0	S_2F_2
98	6.1	^{34}S isotopomer of 96. Plus ?
96	27.4	S_3
93	1.7	C_3F_3
88	1.1	CF_4 or C_2S_2
83	3.6	S_2F
78	1.7	^{34}S isotopomer of 76. Plus ?
76	1.7	CS_2
69	8.1	CF_3
66	3.7	^{34}S isotopomer of 64
65	1.6	^{33}S isotopomer of 64. Plus ?
64	41.1	S_2
63	4.3	CSF
48	1.4	? S_3^{2+}
46	4.8	? SN
32	2.1	S
28	7.7	N_2

All assignments refer to unipositive cations containing ^{12}C and ^{32}S, unless otherwise specified.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case by the peaks at *m/z* 277 (1.3%, $[F_3C\overline{CSSSC}CF_3F]^+$) and 151 (9.2%, $[AsF_4]^+$). However, a prominent peak at *m/z* 296 (I = 46.2%) implies that the alternative process in equation (10) may compete with (9), leading to a $[F_3C\overline{CSSSC}CF_3F_2]^+$ fragment.

$$F_3C\overline{CSSSC}CF_3AsF_6 \longrightarrow F_3C\overline{CSSSC}CF_3F_3 + AsF_3 \quad (10)$$

When attempts were made to prepare other derivatives of the 1,2,3-trithiolylium cation intractable brown tars were produced with HCCH and MeCCMe, possibly due to fluorination or polymerisation of the alkyne or its substituent. The reaction with dmad produced an undetermined amount of $MeO_2C\overline{CSSSC}CO_2Me^{\bullet +}$ **2**. The mass and ESR (Fig. 1) spectra of this product showed that it was a mixture consisting of at least one species in addition to **2**, although no evidence was observed for species analogous to the high-molecular-weight contaminants of the AsF_6^- salt of **1** (see above).

Tetrafluoroethene reacts with $S_4(Sb_2F_{11})_2$ and $S_8(AsF_6)_2$ to give a series of neutral polysulfides including $(C_2F_5)_2S_x$ (mostly, x = 3–5).[48] Analogously, the reaction with $F_3CC{\equiv}CCF_3$ would be expected to yield $F_3C(F)C{=}C(CF_3){-}S_x{-}C(CF_3){=}C(F)CF_3$, and the mass spectral peak at *m/z* 490 (which corresponds to x = 4) suggests that this occurs to a small extent. It is possible that the resonances at δ −71.7 and −72.6 observed in ^{19}F NMR spectra of reaction mixtures are due to species of this type, the small three-, four- and five-bond F–F couplings being lost through the broadening due to the presence of (paramagnetic) **1**. This polysulfide, if present, only constituted 7% of the reaction mixture, and the resonance due to the vinylic fluorine atoms is expected to be of very low intensity, and may be one of several very weak resonances observed in these spectra. Neutral polysulfides are liable to be quite volatile, and pumping to constant weight thus constitutes a purification step. The group of resonances around δ −74 in the ^{19}F NMR spectra of volatiles condensed from reaction mixtures correspond reasonably to those described above;[48,49] the resonance at δ −63 in these spectra is likely due to some compound **5**[31] arising from trace hydrolysis (H_2O acting as a reducing agent). The relative stability of the $\overline{CSSSC}^{\bullet +}$ ring may be due to the ability of the unsaturated F_3CCCCF_3 moiety to become involved in a delocalised π system over the trithiolylium ring. This is not possible in, say, $F_2C\overline{CSSSC}CF_2^{\bullet +}$ because the carbon centres are saturated.

When the reaction of C_2F_4 with $S_8(AsF_6)_2$ was carried out in SO_2, OSF_2 was observed as a by-product, and this has been associated with the formation of carbonyl fluorides[48,49] [*e.g.* $C_2F_5S_3CF_2C(O)F$]. Although OSF_2 is observed as a by-product in the synthesis of the AsF_6^- salt of **1**, at no stage were IR absorptions assignable to ν(CO) observed either for reaction volatiles or solid samples, and neither were resonances assignable to COF centres observed in the *in situ* ^{19}F NMR

Table 2 Infrared data (cm^{-1}) for $F_3CCSSSCCF_3AsF_6$ (Nujol mull) and $F_3CCSNSCCF_3^{\bullet}$ (gas phase)

$F_3CCSSSCCF_3AsF_6$	$F_3CCSNSCCF_3^{\bullet}$	Assignment
1550s	1580m	C=C stretch
1345sh	1350w	CF stretch
	1316w	
	1282vs	
1240vs	1263vs	
1205vs	1182vv	
1041m	1028m	SN stretch or CF_3 rock and/or C–C stretch or ring vibration
929m	917m	
865m	863m	
	843m	
820w		AsF_6^- (?)
729s	721s	SN stretch and/or ring vibration
700vs		ν_3 AsF_6^-
598w		
571mw	590w	CS stretch
	543w	
537w		
445w		
397vs		ν_3 AsF_6^-
367sh		
334w		
294s		
247m		

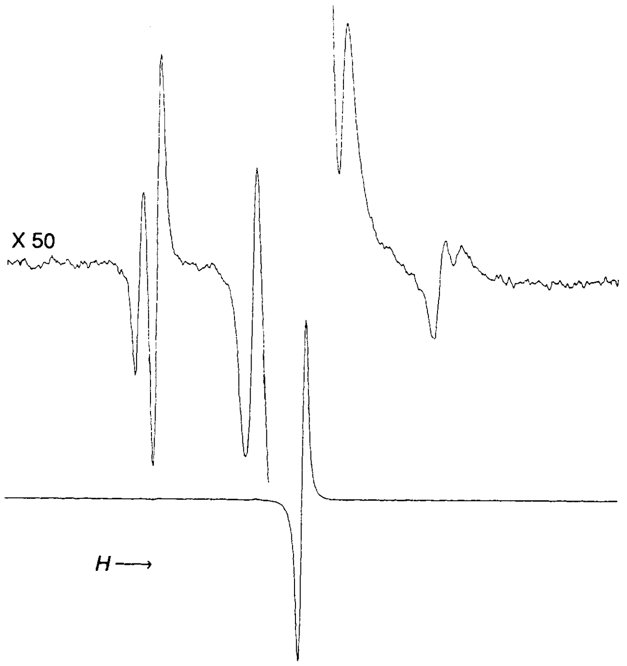


Fig. 1 The ESR spectrum of cation **2** (10^{-3} mol dm^{-3} in SO_2) at −70 °C. Modulation amplitude 12 mG, microwave power 40 mW. Increasing the signal gain by a factor of 50 reveals two sets of ^{33}S satellites; ^{33}S possesses a spin of $\frac{3}{2}$, and coupling of an electron to one ^{33}S gives rise to a 1:1:1:1 quartet in ESR spectra. Two such quartets can be seen here, although they are somewhat obscured by the main signal and by rotational broadening effects (see text)

study of reaction (1). Carbonyl fluorides must therefore only be present in very minor quantities if at all. Significant quantities of OSF_2 were observed in these studies, and they seem more likely to arise from processes such as equations (6)–(8) (see above).

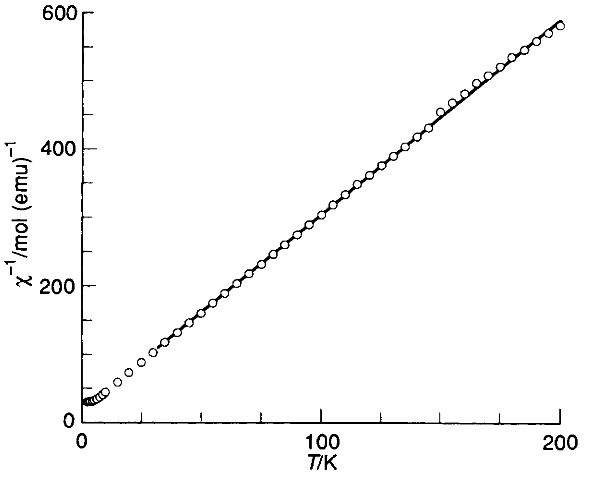


Fig. 2 Magnetic data for $F_3CCSSSCCF_3AsF_6$: plot of 1/χ *versus* *T* (0–200 K)

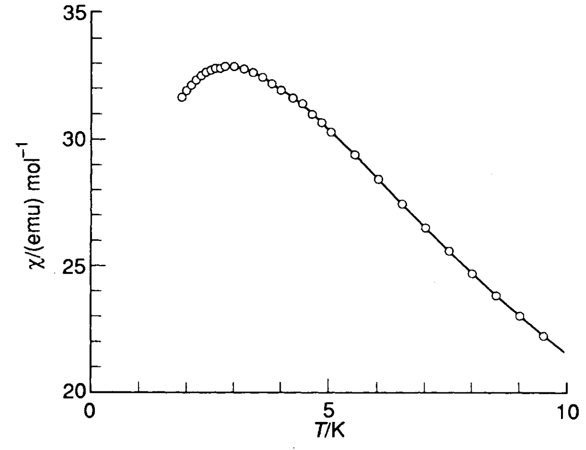


Fig. 3 Magnetic data for $F_3CCSSSCCF_3AsF_6$: χ *versus* *T* (2–10 K)

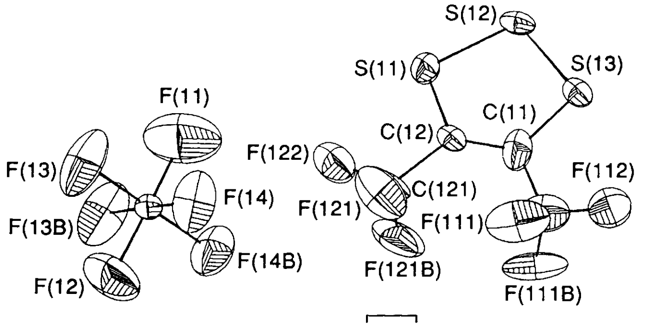


Fig. 4 The molecular structure of $F_3CCSSSCCF_3AsF_6$

The X-Ray Crystal Stucture and Magnetic Properties of $F_3CCSSSCCF_3AsF_6$.—The X-ray data show that the unit cell contains three independent, monomeric radical cations **1** (Fig. 4) and three independent AsF_6^- anions. The structure is composed of layers containing both cations and anions (Fig. 5) perpendicular to the *b* axis (at *b* = $\frac{1}{4}$ and $\frac{3}{4}$, interlayer distance 4.1 Å). Each cation or anion is surrounded by six anions or cations (four in plane, one above, one below), and the structure is related to that of NaCl.[50] A related packing regime exists in the structures of $SNSSNAsF_6$[43] and $F_3CCNSSSAsF_6$[51] (which respectively contain monomeric $S_3N_2^{\bullet +}$ and $F_3CCNSSS^{\bullet +}$ radical cations), although in the case of $S_3N_2AsF_6$ the anions are 1.46 Å from the planes of the cations. The observed lack of dimerisation of **1** is consistent with the very weak dimerisation observed for the isovalent

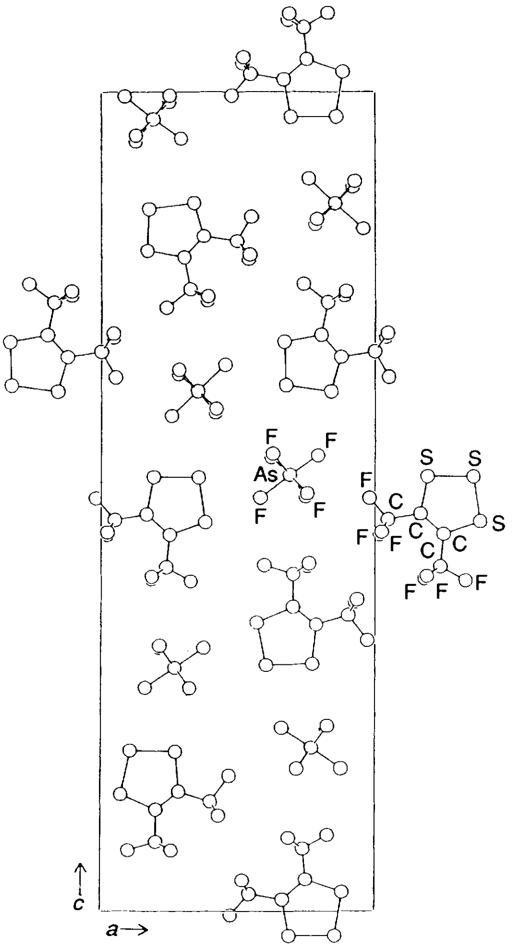
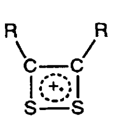


Fig. 5 Packing in the unit cell of $F_3CCSSSCCF_3AsF_6$ showing planes containing both cations and anions

Table 3 Crystal data for $F_3CCSSSCCF_3AsF_6$

Crystal system	Orthorhombic
Space group	*Pnma* (or *Pna*2$_1$)
a/Å	12.241(4)
b/Å	8.232(5)
c/Å	37.39(3)
U/Å^3	3767.7(4)
Z	12
M	447.126
D_c/Mg m^{-3}	2.364
Crystal dimensions (mm)	0.15 × 0.20 × 0.35
F(000)	2556
μ	33.08 cm^{-1}
Radiation	Mo-Kα (λ = 0.709 26 Å)
T/K	213
Ranges of h, k, l	0–9, 0–13, 0–41
$2\theta_{max}$/°	46
No. of unique reflections	2995
No. of observed reflections [$I > 2\sigma(I)$]	1175
No. of parameters	359
Weighting scheme	$0.9042/(\sigma^2F + 0.01509F^2)$(*Pnma*) $[(\sigma^2F + 0.01509F^2)^{-1}$(*Pna*2$_1$)]
R	0.086(*Pnma*) [0.066(*Pna*2$_1$)]
R'	0.90
Final difference synthesis maximum/e Å^{-3}	0.97 (in the region of disordered AsF_6^-)
Final difference synthesis minimum/e Å^{-3}	−0.79

$F_3CCSNSCCF_3^{\bullet}$ (which dimerises through the sulfur atoms, with S–S bond lengths of 3.27(7) and 3.07(7) Å; ΔH for dimerisation is zero or positive.[1,47] Formation of weak dimers will be electrostatically opposed by the positive charge on **1**, and hence the observed lack of dimerisation.



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Although the parallel alignment of the radical cations in the AsF_6^- salt of **1** has the potential of giving rise to unusual magnetic properties, in the temperature regime between 25 and 200 K ordinary Curie-Weiss paramagnetism was shown, with $\mu = 1.68$ and $\theta = -0.6$ K, and it is clear that coupling between the radical cation spins is very weak. In contrast to the related systems $RCSNSCR^{\bullet}$ (μ = 1.52, R = CF_3, neat liquid at r.t.[1]), $RCNSNS^{\bullet}$ (μ = 1.41, R = Bu^t, after melting) and $RCNSSN^{\bullet}$ (μ = 1.40, R = CF_3, after melting[47]), which are 'paramagnetic liquids' (i.e. diamagnetic in the solid state, but paramagnetic as liquids), the AsF_6^- salt of **1** can be described as a paramagnetic solid.[4] Other examples of this class of compounds are known (*e.g.* O_2, O_2AsF_6, and $I_2Sb_2F_{11}$), although they are rare amongst the heavier main-group elements (row three and higher), especially in cases where there is no steric hindrance to dimerisation.

Disorder in the structure precludes detailed discussion of the geometry of the cations. Bond distances and angles are presented in Tables 5 and 6, and the average bond lengths in the $CSSSC^{\bullet +}$ rings [C–C 1.34(4) (bond order 1.9), C–S 1.72(7) (1.3), S–S 2.03(4) Å (1)] are consistent with the 7π configuration of **1**, and similar to those of $F_3CCSNSCCF_3^{\bullet}$ [electron diffraction, C–C 1.324(14), C–S 1.749(5), S–N 1.634(4) Å].[1] Although the space group *Pnma* restricts the cations to planarity, they must at least be almost planar, implying that π bonding is delocalised around the ring, incorporating the weak $3p_\pi$–$3p_\pi$ S–S interactions suggested by our molecular orbital calculations (see Fig. 6).

The Characterization of Cations **1** *and* **2** *in Solution, and the Implications for the Nature of the Radicals previously designated* 1,2-*Dithiete Cations*.—The ESR spectrum of the AsF_6^- salt of **1** in SO_2 (10^{-2} mol dm^{-3}) at −60 °C (with modulation amplitude 1.0 G) consisted of a central binomial septet (6F, a = 1.36 G) with one set of weak ^{33}S satellites (natural abundance 0.76%, apparent 'a' = 8.6 G), g = 2.014. These parameters are practically identical with those quoted in the literature for derivatives of the 1,2-dithiete cation **8**[6–13] (typical ranges g = 2.0160–2.0144, $a(^{33}S)$ = 7.6–8.8 G; specifically for **8** (R = CF_3) $a(^{19}F)$ = 1.35 G, $a(^{33}S)$ = 8.6 G and g = 2.016.[6,7]

From the ESR spectrum, crystal structure, mass spectrum and chemical analyses of the AsF_6^- salt of **1** it seemed likely that the ESR spectra previously assigned to **8** (R = CF_3) (and therefore other 1,2-dithiete radical cations) were in fact due to 1,2,3-trithiolylium cations. Although trithiolylium cations contain two inequivalent sets of sulfur nuclei, only one set of ^{33}S satellites were observed for **1**. The reason for this apparent inconsistency was established from a high-resolution ESR study of the ^{33}S satellites of $MeO_2CCSSSCCO_2Me^{\bullet +}$ **2**.

Owing to the low natural abundance of ^{33}S (0.76%)[52] the signal intensity was at a premium, and while increasing the modulation amplitude increases the signal to noise ratio it decreases the spectral resolution, and this parameter was limited to 12 mG. Since these radicals did not saturate at high microwave power levels the sample was subjected to 40 mW of microwave power, frequency modulation noise being eliminated using the phase-locking circuit described above. In addition the temperature was lowered to −70 °C to reduce the rate of radical–radical encounters, a source of line broadening. The complex splittings of the ^{33}S satellites in the ESR spectrum of **1**

Table 4 Fractional atomic positional parameters with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
As(1)	−0.309 2(2)	0.250 00(0)	0.533 05(8)	F(121)	0.019(1)	0.119(2)	0.461 7(4)
As(2)	0.270 3(3)	0.250 00(0)	0.299 04(8)	F(122)	−0.013(2)	0.250 00(0)	0.505 5(6)
As(3)	0.355 9(3)	0.250 00(0)	0.635 89(8)	S(21)	0.841 9(7)	0.250 00(0)	0.634 3(2)
F(11)	−0.204(2)	0.250 00(0)	0.560 2(8)	S(22)	0.675 5(7)	0.250 00(0)	0.641 6(2)
F(12)	−0.420(2)	0.250 00(0)	0.506 4(7)	S(23)	0.668 9(7)	0.250 00(0)	0.695 1(2)
F(13)	−0.370(2)	0.102(2)	0.558 3(4)	C(21)	0.806 4(1)	0.250 00(0)	0.703 9(5)
F(14)	−0.249(1)	0.109(2)	0.507 7(4)	C(22)	0.879 1(1)	0.250 00(0)	0.677 8(5)
F(21)	0.382(2)	0.250 00(0)	0.324 1(7)	C(211)	0.830 6(2)	0.255 00(0)	0.743 9(7)
F(22)	0.161(2)	0.250 00(0)	0.272 6(8)	C(221)	1.005 6(2)	0.250 00(0)	0.682 6(8)
F(23)	0.209(2)	0.116(2)	0.324 7(5)	F(211)	0.741 5(2)	0.260 00(0)	0.762 7(5)
F(24)	0.329(2)	0.121(2)	0.272 1(4)	F(212)	0.888(2)	0.131(2)	0.753 7(3)
F(31)	0.256(2)	0.250 00(0)	0.604 5(5)	F(221)	1.038(1)	0.127(2)	0.701 8(5)
F(32)	0.458(2)	0.250 00(0)	0.666 7(5)	F(222)	1.050 8(1)	0.250 00(0)	0.651 5(8)
F(33)	0.286(1)	0.104(2)	0.658 5(3)	S(31)	0.571 60(7)	0.250 00(0)	0.355 2(2)
F(34)	0.424(1)	0.108(2)	0.612 1(4)	S(32)	0.609 24(7)	0.250 00(0)	0.302 8(2)
S(11)	0.193 4(7)	0.250 00(0)	0.531 1(2)	S(33)	0.774 45(7)	0.250 00(0)	0.304 8(2)
S(12)	0.359 4(7)	0.250 00(0)	0.530 0(2)	C(31)	0.701 7(1)	0.250 00(0)	0.372 5(5)
S(13)	0.383 8(7)	0.250 00(0)	0.476 3(2)	C(32)	0.790 3(1)	0.250 00(0)	0.350 8(6)
C(11)	0.251(2)	0.250 00(0)	0.461 6(5)	C(311)	0.705 8(2)	0.250 00(0)	0.414 0(7)
C(12)	0.170(1)	0.250 00(0)	0.486 1(5)	C(321)	0.910 2(2)	0.250 00(0)	0.363 1(7)
C(111)	0.235(2)	0.250 00(0)	0.420 3(7)	F(311)	0.605 8(2)	0.250 00(0)	0.425 8(5)
C(121)	0.048(2)	0.250 00(0)	0.477 5(7)	F(312)	0.759(1)	0.380(2)	0.425 1(3)
F(111)	0.184(1)	0.120(2)	0.409 4(3)	F(321)	0.937(1)	0.123(2)	0.381 2(4)
F(112)	0.330(1)	0.250 00(0)	0.405 8(5)	F(322)	0.973 6(1)	0.250 00(0)	0.333 4(7)

Table 5 Interatomic distances (Å) for $F_3C\overline{CSSSC}CF_3AsF_6$

As(1)–F(11)	1.64(2)	S(23)–S(22)	2.002(8)
As(1)–F(12)	1.68(2)	S(23)–C(21)	1.71(1)
As(1)–F(13)	1.71(2)	S(22)–S(21)	2.055(8)
As(1)–F(14)	1.67(2)	S(21)–C(22)	1.70(1)
As(2)–F(21)	1.66(2)	C(21)–C(22)	1.32(2)
As(2)–F(22)	1.66(2)	C(21)–C(211)	1.52(2)
As(2)–F(23)	1.64(2)	C(22)–C(221)	1.56(2)
As(2)–F(24)	1.63(2)	C(211)–F(211)	1.30(2)
As(3)–F(31)	1.70(1)	C(211)–F(212)	1.29(2)
As(3)–F(32)	1.70(1)	C(221)–F(221)	1.30(3)
As(3)–F(33)	1.70(1)	C(221)–F(222)	1.29(3)
As(3)–F(34)	1.69(2)	S(33)–S(32)	2.024(8)
S(13)–S(12)	2.030(7)	S(33)–C(32)	1.73(1)
S(13)–C(11)	1.72(1)	S(32)–S(31)	2.012(8)
S(12)–S(11)	2.033(8)	S(31)–C(31)	1.72(1)
S(11)–C(12)	1.71(1)	C(31)–C(32)	1.36(2)
C(11)–C(12)	1.35(2)	C(31)–C(311)	1.55(2)
C(11)–C(111)	1.56(2)	C(32)–C(321)	1.54(2)
C(12)–C(121)	1.52(2)	C(311)–F(311)	1.30(2)
C(111)–F(111)	1.30(2)	C(311)–F(312)	1.32(2)
C(111)–F(112)	1.28(2)	C(321)–F(321)	1.28(2)
C(121)–F(121)	1.28(2)	C(321)–F(322)	1.36(2)
C(121)–F(122)	1.29(2)		

(from the six ^{19}F nuclei) are absent in the spectrum of **2** (Fig. 1), and beside the main singlet line (g = 2.017) we were able to resolve the low-field ^{33}S satellite of **2** into *two* components with $a(^{33}S)$ = 8.9 and 8.0 G in 1 : 2 intensity ratio, consistent with the structure of a 1,2,3-trithiolylium radical cation. The high-field satellites were subject to the potent rotational broadening effects common in radicals of this nature.[53]

Thus, although derivatives of cation **1** contain two sets of inequivalent sulfur atoms the magnitudes of their ^{33}S hyperfine coupling constants are very similar, and individual resonances are not resolved unless conditions specially chosen to optimise resolution are used. This is consistent with an ROHF/6-31G* *ab initio* calculation on the model cation $H\overline{CSSSC}H^{\bullet +}$, which shows the π* SOMO to be uniformly distributed over the S_3 moiety (Fig. 6). Also consistent with these results, no S_8 was ever observed to be precipitated from solutions of **1**, discounting processes such as (11).

$$\mathbf{1} \longrightarrow \mathbf{8}\,(R = CF_3) + \tfrac{1}{8}S_8 \qquad (11)$$

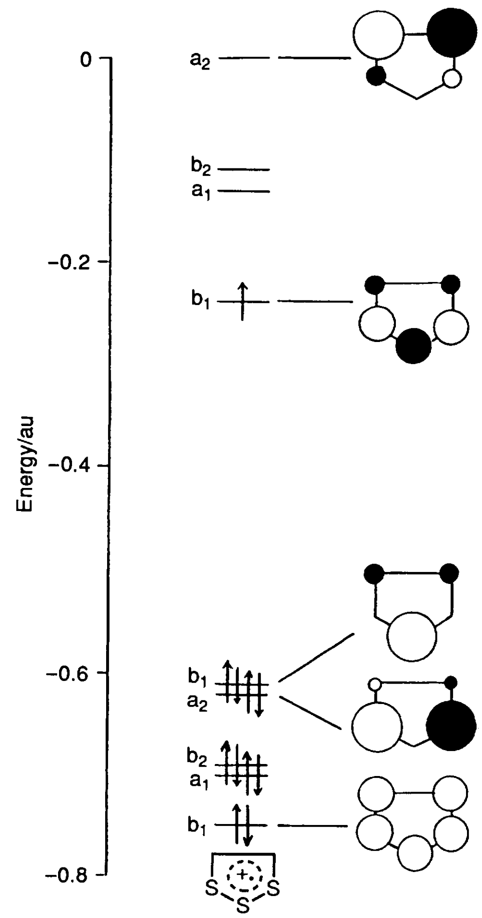

Fig. 6 The π bonding in $H\overline{CSSSC}H^{\bullet +}$ calculated at the ROHF/6-31G* level using the average geometry of $F_3C\overline{CSSSC}CF_3AsF_6$ from the crystal structure. The C–H distances were set at 1.09 Å. The valence orbital linear combination of atomic orbitals (LCAO) coefficients in the SOMO from the 6-31G* calculations are as follows: C, 2p −0.20, 3p −0.19; S(off axial), 3p 0.44, 4p 0.29; S(axial), 3p −0.42, 4p −0.29. The a_1 and b_2 MOs lie in the plane of the $\overline{CSSSC}$ ring, while a_2 and b_1 are out-of-plane π MOs; au ≈ 4.36 × 10^{-18} J

Table 6 Interbond angles (°)

F(11)–As(1)–F(12)	178.1(9)	F(32)–As(3)–F(34)	89.5(7)	F(121)–C(121)–F(121′)	115(2)	C(22)–C(221)–F(221)	112(2)
F(11)–As(1)–F(13)	90.1(9)	F(33)–As(3)–F(33′)	90.7(7)	F(121)–C(121)–F(122)	104(1)	C(22)–C(221)–F(222)	109(2)
F(11)–As(1)–F(14)	90.2(9)	F(33)–As(3)–F(34)	90.8(7)	F(121)–C(121)–F(122′)	101(1)	F(221)–C(221)–F(221′)	102(2)
F(12)–As(1)–F(13)	88.6(8)	F(33)–As(3)–F(34′)	178.2(7)	S(22)–S(23)–C(21)	98.8(5)	F(221)–C(221)–F(222)	112(2)
F(12)–As(1)–F(14)	91.1(8)	F(34)–As(3)–F(34′)	87.7(7)	S(23)–S(22)–S(21)	100.0(3)	S(32)–S(33)–C(32)	98.6(5)
F(13)–As(1)–F(13′)	90.7(8)	S(12)–S(13)–C(11)	100.2(5)	S(22)–S(21)–C(22)	98.0(5)	S(33)–S(32)–S(31)	101.1(3)
F(13)–As(1)–F(14)	90.6(8)	S(13)–S(12)–S(11)	99.6(3)	S(23)–C(21)–C(22)	121(1)	S(32)–S(31)–C(31)	98.9(5)
F(13)–As(1)–F(14′)	178.6(8)	S(12)–S(11)–C(12)	98.5(5)	S(23)–C(21)–C(211)	112(1)	S(31)–C(31)–C(32)	121(1)
F(14)–As(1)–F(14′)	88.0(8)	S(13)–C(11)–C(12)	119(1)	S(23)–C(21)–C(211′)	112(1)	S(31)–C(31)–C(311)	114(1)
F(21)–As(2)–F(22)	178.1(9)	S(13)–C(11)–C(111)	116(1)	C(22)–C(21)–C(211)	126(1)	C(32)–C(31)–C(311)	125(1)
F(21)–As(2)–F(23)	92.6(9)	C(12)–C(11)–C(111)	126(1)	C(22)–C(21)–C(211′)	126(1)	S(33)–C(32)–C(31)	120(1)
F(21)–As(2)–F(24)	89.3(9)	S(11)–C(12)–C(11)	123(1)	S(21)–C(22)–C(21)	122(1)	S(33)–C(32)–C(321)	114(1)
F(22)–As(2)–F(23)	89(1)	S(11)–C(12)–C(121)	112(1)	S(21)–C(22)–C(221)	112(1)	C(31)–C(32)–C(321)	126(1)
F(22)–As(2)–F(24)	89(1)	C(11)–C(12)–C(121)	125(1)	C(21)–C(22)–C(221)	126(1)	C(31)–C(311)–F(311)	108(1)
F(23)–As(2)–F(23′)	84(1)	C(11)–C(111)–F(111)	112(2)	C(21)–C(211)–F(211)	112(1)	C(31)–C(311)–F(312)	109(1)
F(23)–As(2)–F(24)	97(1)	C(11)–C(111)–F(112)	108(1)	C(21)–C(211)–F(211′)	112(1)	F(311)–C(311)–F(312)	111(2)
F(23)–As(2)–F(24′)	176(1)	F(111)–C(111)–F(111′)	110(2)	C(21)–C(211)–F(212)	112(2)	F(312)–C(311)–F(312′)	108(2)
F(24)–As(2)–F(24′)	81(1)	F(111)–C(111)–F(112)	109(2)	C(21)–C(211)–F(212′)	114(2)	C(32)–C(321)–F(321)	114(2)
F(31)–As(3)–F(32)	178.7(6)	F(111)–C(111)–F(112′)	106(2)	F(211)–C(211)–F(212)	109(2)	C(32)–C(321)–F(322)	108(1)
F(31)–As(3)–F(33)	89.4(6)	C(12)–C(121)–F(121)	112(1)	F(211)–C(211)–F(212′)	107(2)	F(321)–C(321)–F(321′)	109(2)
F(31)–As(3)–F(34)	89.6(7)	C(12)–C(121)–F(122)	114(1)	F(212)–C(211)–F(212′)	103(2)	F(321)–C(321)–F(322)	107(2)
F(32)–As(3)–F(33)	91.5(6)						

Primed atoms at symmetry-related position $x, \frac{1}{2} - y, z$.

The alternative possibilities that cation **8** is produced with another diamagnetic or paramagnetic species can be discounted from ^{19}F NMR spectra (which shows only a broad contact-shifted AsF_6^- resonance at δ −40, width (1500 Hz), the magnetic moment of the solution (determined by the Evans' NMR method at r.t. and −60 °C to be 2.1 and 2.3 respectively, implying that no dimerisation occurs in solution, consistent with the crystal structure results), and ESR spectra (which show no resonances other than that described above). Consistently the AsF_6^- salt of **1** may be recovered unchanged from solutions in SO_2.

At least 31 derivatives of 1,2-dithiete radical cations have been claimed since 1972.[6–13] Various methods of generation have been employed, although the most common appear to be *via* $RC{\equiv}CR' + S_2Cl_2 + AlCl_3$ in CH_2Cl_2[8] or oxidation of the neutral 1,2-dithiete in 98% sulfuric acid.[6] In all cases the radicals were characterised in dilute solution (often 10^{-6} mol dm^{-3}) by ESR spectroscopy. In many cases one set of ^{33}S satellites was observed, consistent with the dithiete assignment. Additional evidence lay in the ESR spectrum of '$H\overline{CSSC}H^{\bullet+}$' 48% enriched with ^{33}S,[8] which was shown to be consistent with the presence of two sulfur atoms.

In the case of $R\overline{CSSSC}R^{\bullet+}$ cations the similarity of the two ^{33}S hyperfine coupling constants likely led to the observation of only one set of satellites in ESR spectra. Even for the AsF_6^- salt of **1**, in spite of persistent attempts, we were unable to resolve more than one set of ^{33}S satellites. The individual ^{33}S splittings were resolved only when conditions of high power and low modulation amplitude were employed to record the ESR spectrum of **2**, which is uncomplicated by hyperfine coupling to the substituents. In this context the previous assignment of spectra to 1,2-dithiete radicals was quite reasonable, and it was only by the bulk characterisation of $F_3C\overline{CSSSC}CF_3AsF_6$ using several techniques that this possible assignment error was detected, although we can not formally rule out the possibility that 1,2,3-trithiolylium and 1,2-dithiete cations coincidentally possess the same ESR parameters. The characterisation of the number of sulfur atoms in a radical by ESR spectroscopy is notoriously difficult, and it is notable that the radicals $S_5^{\bullet+}$[25] and $S_3N_2^{\bullet+}$[54,55] 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.[55] The stability of **1** and **8** is consistent with the stabilities of numerous related 7π systems $R\overline{CSNSC}R^{\bullet}$, $R\overline{CNSNS}^{\bullet}$, $R\overline{CNSSN}^{\bullet}$, $R\overline{CNSeSeN}^{\bullet}$ and $S_xSe_{3-x}N_2^{\bullet+}$ (x = 0–3),[34–42] all of which are indefinitely stable and can be prepared on the gram scale as pure compounds in many cases quantitatively.

Attempted Oxidation and Reduction of $F_3C\overline{CSSSC}CF_3$-AsF_6.—Attempts made to oxidise cation **1** with excess of AsF_5 according to equation (12) (with and without the presence of Br_2) were unsuccessful, implying that the ionisation energy of **1** must be at least 1387 kJ mol^{-1}.* This is quite reasonable in terms of the recently reported i.p.s of the three electron–two centre sulfur-containing radical cations, *e.g.* $\overline{CH_2SCH_2CH_2S}^+$ (1186–1475 kJ mol^{-1}),[61] and the second i.p. of sulfur, 2300 kJ mol^{-1}.[57]

$$2F_3C\overline{CSSSC}CF_3AsF_6 + 3AsF_5 \longrightarrow 2F_3C\overline{CSSSC}CF_3(AsF_6)_2 + AsF_3 \quad (12)$$

The AsF_6^- salt may be reduced with potassium iodide according to equation (13). The ^{19}F NMR, IR and mass spectra show that compound **6** rapidly equilibrates with species **3**–**5** (see above) and S_8. This study constitutes the first observation of **6**, and its lability is consistent with the well known instability of other cyclic polysulfide derivatives described in ref. 16.

$$2F_3C\overline{CSSSC}CF_3AsF_6 + 2KI \longrightarrow 2F_3C\overline{CSSSC}CF_3 + 2KAsF_6 + I_2 \quad (13)$$

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* $\Delta H = 2U[F_3C\overline{CSSSC}CF_3AsF_6] + 2\text{i.p.}(\mathbf{1}) + 2\Delta H_f[AsF_6^-(g)] + \Delta H_f(AsF_3) - 3\Delta H_f(AsF_5) - 2U[F_3C\overline{CSSSC}CF_3(AsF_6)_2] > 0$. The lattice energy of $F_3C\overline{CSSSC}CF_3AsF_6$ estimated from its molar volume using Bartlett's equation[56] is 420 kJ mol^{-1}; $\Delta H_f[AsF_6^-(g)] = -1973$ $\{= \Delta H_f(AsF_5) + \Delta H_f[F^-(g)] + \text{f.a.}(AsF_5)$ where f.a. = fluoride-ion affinity; data taken from refs. 57–59$\}$, $\Delta H_f(AsF_3) = -858$[60] and $\Delta H_f(AsF_5) = -1237$ kJ mol^{-1},[58] give i.p.(**1**) − $U[F_3C\overline{CSSSC}CF_3(AsF_6)_2] > 127$ kJ mol^{-1}. Assuming that the monocation and dication possess similar thermochemical radii, the Kapustinskii equation[55] $[U = W\nu z_+z_-/(r_+ + r_-)$ where W = constant, z are the charges and r the thermochemical radii of the ions and ν is the number of ions in one molecule$]$ gives $3U(F_3C\overline{CSSSC}CF_3AsF_6) = U[F_3C\overline{CSSSC}CF_3(AsF_6)_2]$, and i.p.(**1**) > 1387.

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References

1 E. G. Awere, N. Burford, C. Mailer, J. Passmore, M. J. Schriver, P. S. White, A. J. Banister, H. Oberhammer and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1987, 66.

2 E. G. Awere, N. Burford, R. C. Haddon, S. Parsons, J. Passmore, J. W. Waszczak and P. S. White, *Inorg. Chem.*, 1990, **29**, 4821.

3 G. K. Maclean, J. Passmore, M. N. S. Rao, M. J. Schriver and P. S. White, *J. Chem. Soc., Dalton Trans.*, 1985, 1405.

4 W. V. F. Brooks, N. Burford, J. Passmore, M. J. Schriver and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1987, 69.

5 N. Burford, J. Passmore and M. J. Schriver, *J. Chem. Soc., Chem. Commun.*, 1986, 140.

6 G. A. Russell, R. Tanikaga and E. R. Talaty, *J. Am. Chem. Soc.*, 1971, **94**, 6125.

7 H. Bock, P. Rittmeyer, A. Krebs, K. Schultz, J. Vöss and B. Köpke, *Phosphorus Sulfur*, 1984, **19**, 131.

8 H. Bock, P. Rittmeyer and U. Stein, *Chem. Ber.*, 1986, **119**, 3766.

9 G. A. Russell, W. C. Law and M. Zaleta, *J. Am. Chem. Soc.*, 1985, **107**, 4175.

10 Z. Chen, H. Ge, G. A. Russell and W. C. Law, *Phosphorus Sulfur*, 1988, **35**, 121.

11 D. Buddensiek, B. Köpke and J. Vöss, *Chem. Ber.*, 1987, **120**, 575.

12 G. A. Russell and W. C. Law, *Heterocycles*, 1986, **24**, 321.

13 H. Bock, B. Hierholzer and P. Rittmeyer, *Z. Naturforsch., Teil B*, 1989, **44**, 1987.

14 N. Bartlett and D. H. Lohmonn, *Proc. Chem. Soc. London*, 1962, 115; *J. Chem. Soc.*, 1962, 5253.

15 C. G. Davies, R. J. Gillespie, P. R. Ireland and J. M. Sowa, *Can. J. Chem*, 1974, **52**, 2048.

16 B. L. Chenard, R. L. Harlow, A. L. Johnson and S. A. Vladuchick, *J. Am. Chem. Soc.*, 1985, **107**, 3871 and refs. therein.

17 N. Burford, J. Passmore and J. C. P. Sanders, *Molecular Structure and Energetics, Isoelectronic Relationships in Atoms to Polymers*, eds. J. Liebman and A. G. Greenberg, VCH, Deerfield Beach, FL, 1989, p. 53.

18 T. Klapötke and J. Passmore, *Acc. Chem. Res.*, 1989, **22**, 234.

19 T. S. Cameron, R. C. Haddon, S. M. Mattar, S. Parsons, J. Passmore and A. P. Ramirez, *J. Chem. Soc., Chem. Commun.*, 1991, 358.

20 M. Murchie and J. Passmore, *Inorg. Synth.*, 1986, **24**, 76.

21 E. J. Gabe, Y. Le Page, J. P. Chenard, F. L. Lee and P. S. White, *J. Appl. Crystallogr.*, 1989, **22**, 384.

22 S. M. Mattar and D. G. Sutherland, *J. Phys. Chem.*, 1991, **95**, 5129.

23 H. S. Low and R. A. Beaudet, *J. Am. Chem. Soc.*, 1976, **98**, 3849.

24 E. A. V. Ebsworth, D. W. H. Rankin and S. Cradock, *Structural Methods in Inorganic Chemistry*, Blackwell, Oxford, 1987; D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

25 R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy*, Longman, Harlow, 1986.

26 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley, New York, 1986.

27 T. S. Cameron and R. Cordes, *Acta Crystallogr., Sect. B*, 1979, **35**, 748.

28 N. Walker and D. Stewart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

29 G. M. Sheldrick, SHELX-76, A system of computer programs for X-ray structure determination, as locally implemented at Dalhousie and Oxford Universities, 1976.

30 W. C. Hamilton, *Acta Crystallogr.*, 1965, **18**, 502.

31 C. G. Krespan, *J. Am. Chem. Soc.*, 1961, **83**, 3434.

32 M. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, R. Martin, J. P. P. Stewart, D. Defrees, R. Seeger, R. Whiteside, D. Fox, E. Fludel and J. A. Pople, GAUSSIAN 86, Carnegie-Mellon University, Pittsburg, PA, 1986.

33 W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.

34 A. W. Cordes, J. D. Goddard, R. T. Oakley and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1989, **111**, 6147.

35 R. T. Boeré, R. T. Oakley, R. W. Reed and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1989, **111**, 1180.

36 R. T. Oakley, *Prog. Inorg. Chem.*, 1988, **36**, 299.

37 P. Del Bel Belluz, A. W. Cordes, E. M. Kristof, S. W. Liblong and R. T. Oakley, *J. Am. Chem. Soc.*, 1989, **111**, 9276.

38 A. W. Cordes, R. C. Haddon, R. T. Oakley, L. F. Schneemeyer, J. V. Waszczak, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc.*, 1991, **113**, 582.

39 M. P. Andrews, A. W. Cordes, D. C. Douglass, R. M. Fleming, S. H. Glarum, R. C. Haddon, P. Marsh, R. T. Oakley, T. M. M. Palstra, L. F. Schneemeyer, G. W. Trucks, T. Tycko, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc.*, 1991, **113**, 3559.

40 E. G. Awere, J. Passmore, K. F. Preston and L. H. Sutcliffe, *Can. J. Chem.*, 1988, **66**, 1776.

41 E. G. Awere, J. Passmore, P. S. White and T. M. Klapötke, *J. Chem. Soc., Chem. Commun.*, 1989, 1415.

42 E. G. Awere, Ph.D. Thesis, University of New Brunswick, 1992.

43 R. J. Gillespie, J. P. Kent and J. F. Sawyer, *Inorg. Chem.*, 1981, **20**, 3784.

44 R. J. Gillespie, J. P. Kent and J. F. Sawyer, *Inorg. Chem.*, 1981, **20**, 4053.

45 M. P. Murchie, J. Passmore, G. W. Sutherland and R. Kapoor, *J. Chem. Soc., Dalton Trans.*, 1992, 503; J. Passmore, G. Sutherland and P. S. White, *J. Chem. Soc., Chem. Commun.*, 1980, 330; J. Passmore, T. K. Whidden and P. S. White, *Inorg. Chem.*, 1981, **20**, 3839; R. J. Gillespie, J. Passmore, P. K. Ummat and O. C. Vaidya, *Inorg. Chem.*, 1971, **10**, 1327.

46 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984.

47 M. J. Schriver, Ph.D. Thesis, University of New Brunswick, 1989.

48 C. D. Desjardins and J. Passmore, *Can. J. Chem.*, 1977, **55**, 3136 and refs. therein.

49 C. D. Desjardins, Ph.D. Thesis, University of New Brunswick, 1976.

50 A. F. Wells, *Structural Inorganic Chemistry*, 5th edn., Oxford University Press, Oxford, 1984.

51 T. S. Cameron, S. Parsons and J. Passmore, *Inorg. Chem.*, in the press.

52 *Handbook of Chemistry and Physics*, 54th edn., CRC Press, Boca Raton, FL, 1973, p. B-248.

53 S. A. Fairhurst, R. S. Pilkington and L. H. Sutcliffe, *J. Chem. Soc., Faraday Trans.*, 1983, 439.

54 K. F. Preston, J. P. Charland and L. H. Sutcliffe, *Can. J. Chem.*, 1988, **66**, 1299.

55 K. F. Preston and L. H. Sutcliffe, *Magn. Reson. Chem*, 1990, **28**, 189 and refs. therein.

56 R. T. Richardson, F. L. Tanzella and N. Bartlett, *J. Am. Chem. Soc.*, 1986, **108**, 4937.

57 D. A. Johnson, *Some Thermodynamic Aspects of Inorganic Chemistry*, 2nd edn., Cambridge University Press, Cambridge, 1982.

58 P. A. G. O'Hare, B. M. Lewis, S. Susman and K. J. Volin, unpublished work; see P. A. G. O'Hare, E. G. Awere, S. Parsons and J. Passmore, *J. Chem. Thermodyn.*, 1989, **21**, 153.

59 T. E. Mallouk, G. L. Rosenthal, G. Müller, R. Brusasco and N. Bartlett, *Inorg. Chem.*, 1984, **23**, 3167.

60 A. A. Woolf, *J. Fluorine Chem.*, 1975, **5**, 172.

61 T. Drewello, C. B. Lebrilla, K. D. Asmus and H. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1275.

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