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An improved synthesis of $SF_5(CN)$ and its cycloaddition reaction with $SNSAsF_6$. Crystal structure of $F_5S\overline{CNSNS}AsF_6$ and electron spin resonance spectrum of $F_5S\overline{CNSNS}^{\bullet}$ †

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An improved synthesis of $SF_5(CN)$, by direct fluorination of $SF_3(CN)$, has been achieved. This product forms a stable adduct at low temperature with AsF_5, and addition of MeCN to this adduct led to very pure $SF_5(CN)$. The $SF_5(CN){\cdot}AsF_5$ adduct has been characterized by vibrational and ^{19}F Fourier-transform NMR spectroscopy and by its dissociation vapour-pressure curve. The salt $SNSAsF_6$ and an excess of $SF_5(CN)$ reacted in sulfur dioxide solution to give the stable salt $F_5S\overline{CNSNS}AsF_6$ which has been characterized by vibrational, ^{19}F NMR and mass spectroscopy and X-ray crystallography. The structure consists of discrete $F_5S\overline{CNSNS}^+$ cations and AsF_6^- anions. The mass spectrum of $F_5S\overline{CNSNS}AsF_6$ was consistent with loss of AsF_5 and fluoride ion transfer to give $F_5S\overline{CNSNS}F$ which dissociated to SF_4 and $F_2\overline{CNSNS}$. Reduction of a dilute solution of the salt in SO_2 led to identification (ESR spectroscopy) of the radical $F_5S\overline{CNSNS}^{\bullet}$

The synthesis of $SF_5(CN)$ has a long history.[1a] After several unsuccessful attempts at its synthesis and the first erroneous claim to its existence[1b] it was presumed that $SF_5(CN)$, if formed, immediately isomerizes to $CF_3{-}N{=}SF_2$.[1c] However, in 1989 we were able to demonstrate that $SF_5(CN)$ is formed in a yield of a few percent by direct fluorination of $(SCN)_2$ dissolved in $C_2Cl_3F_3$.[1d] Unexpectedly it proved to be a stable colourless gas at room temperature and was characterized by vibrational and ^{19}F NMR spectroscopy; its molecular weight, melting point and vapour-pressure curve were also determined. Subsequently, the synthesis of sulfur pentafluoride isocyanide, SF_5NC, was described, which isomerizes slowly at room temperature to $SF_5(CN)$.[1e] Finally the structure of $SF_5(CN)$ was determined in the gas phase by electron diffraction and microwave spectroscopy.[2]

In order to study further properties of $SF_5(CN)$ it was necessary to find a higher-yield synthesis from the precursor $SF_3(CN)$,[3] which is now reported. This made it possible to explore the chemistry of $SF_5(CN)$ and to determine its physical properties more accurately. The reactivity of the CN group in $SF_5(CN)$ is of special interest. The electronegativity of the SF_5 group is high, as is the molecule's ionization energy (12.98 eV)[4] [*cf.* MeCN (12.2 eV),[5] CF_3CN (14.3 eV)[6]]. Consistently, $SF_5(CN)$ forms only a weak σ complex with HF (estimated proton affinity, 689 kJ mol^{-1}).[7] We report its reaction with AsF_5 and the π acceptor SNS^+ (as the AsF_6^- salt), which has been shown to undergo symmetry-allowed concerted cycloaddition with a wide range of RCN (R = CF_3, Bu^t or NMe_2) and RCCR (R = H, Me or $SiMe_3$) molecules, the rate of which was shown to be inversely proportional to the ionization energy, with steric factors unimportant for nitriles.[8] Thus, the nitrile acts as a π donor and SNS^+ as a π acceptor in the formation of $R\overline{CNSNS}^+$. On this basis, we anticipated that $SF_5(CN)$ should cycloadd to SNS^+ at a rate slower than that with $CF_3C{\equiv}CCF_3$ [ionization potential (i.p.) 12.83 eV;[9] $k_{rel} = 0.1$ ‡],[8a] but faster than CF_3CN (i.p. 14.3 eV;[6] $k_{rel} = 0.01$).[8a] Reduction of $R\overline{CNSNS}^+$ has led to the synthesis of the corresponding $R\overline{CNSNS}^{\bullet}$ radical,[8b,10,11] which we show also occurs for R = SF_5.

Experimental

General procedures and reagents

All apparatus were carefully dried prior to use. Moisture-sensitive materials, crystals suitable for X-ray analysis and all solid products were manipulated in a dry-box (M. Braun, München) under a dry argon atmosphere. Volatile materials and gases were handled with standard vacuum-line techniques. Reactions were carried out inside Duran® glass vessels (10 or 50 cm^3) fitted with Teflon-stemmed Pyrex glass valves (diameter 10 mm; PTT/10/RA, J. Young, UK) and ground-glass cores (size NS 14.5). Vapour pressures were measured in a device ($V \approx 25$ cm^3) consisting of a capacitance pressure gauge (Setra Acton, MA, USA, Model 205-2, 0–1700 mbar), a glass tube (6 × 1 mm) connected to a glass sphere (outside diameter 10 mm) in contact with a Pt-100 temperature sensor (inside the vessel), and a valve connecting the device with the vacuum line. For vapour-pressure measurements, about 0.2 g of the compound were condensed at −196 °C into the glass vessel. The contents were warmed from one measuring temperature to the next in the range 180–250 K. The data were fitted by a least-squares method using the equation $\log(p/\text{mbar}) = (-A/T) + B$. Fluorine (Solvay, Hannover, Germany) was measured by

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† Dedicated to Professor M. Baudler on the occasion of her 75th birthday.

Non-SI units employed: eV ≈ 1.60×10^{-19} J, bar = 10^5 Pa, G = 10^{-4} T.

‡ k_{rel} is the relative rate constant (relative to the rate of cycloaddition of SNS^+ and Bu^tCN); for details see ref. 8(*a*).

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PVT in a stainless-steel vacuum line with a diaphragm pressure gauge (ME 235-65 Medas, Laichingen, Germany). Hydrogen fluoride was removed by passing the gaseous fluorine through an absorber (KF powder between SIPERM sintered Monel discs; Thyssen, Dortmund, Germany). The fluorine and nitrogen additions were controlled separately by mass-flow meters (Tylan, San Diego, CA, USA; model FC 260). The compounds $SiMe_3(CN)$ (Merck, >98%), $SbPh_3$ (Lancaster Synthesis), NMe_4Cl (Kodak), AsF_5 (Ozark-Mahoning) and SF_4 (Baker) were used as received; $C_2Cl_3F_3$ (Merck, >99.5%) and MeCN (Merck, > 99,8%) and SO_2 were dried over P_4O_{10} prior to use. Sulfur cyanide trifluoride, $SF_3(CN)$, was prepared by the reaction of sulfur tetrafluoride, SF_4, with trimethylsilyl cyanide, $Me_3Si(CN)$.[3] The compound $SNSAsF_6$ was prepared as described.[12]

Infrared spectra were recorded in the range 4000–400 cm^{-1} (resolution 2 and 4 cm^{-1}). The spectra of the adduct $SF_5(CN)\cdot AsF_5$ were obtained at low temperatures on a Nicolet MX-1 FTIR spectrometer equipped with a special vacuum chamber containing a silicon window as sample support at its centre. The adduct was condensed onto the window cooled to −196 °C. The spectra were measured after annealing to −100 °C and recooling the sample to −196 °C. The spectrum of $F_5S\overline{CNSNS}AsF_6$ was obtained from a ground sample between AgBr plates on an FTIR spectrometer (Bruker IFS 66v). Fourier-transform Raman spectra of $F_5S\overline{CNSNS}AsF_6$ and $SF_5(CN)\cdot AsF_5$ were recorded on an FTIR spectrometer (Bruker IFS 66v) equipped with a Fourier-transform Raman accessory (Bruker FRA 106) using a Nd-YAG laser (emission wavelength 1064 nm, maximum laser power 300 mW). The data were collected in the backscattering mode (180° excitation; resolution 4 and 2 cm^{-1}). The spectra of $F_5S\overline{CNSNS}AsF_6$ were obtained from a solid sample sealed under an argon atmosphere in melting-point tubes. For the low temperature (−196 °C) measurements of the $SF_5(CN)\cdot AsF_5$ adduct a special vacuum chamber was used containing a nickel-plated copper cold-finger, on which the adduct was deposited. The UV/VIS spectra of gaseous $SF_5(CN)$ were measured on a diode-array spectrometer (Spectroscopy International) using a glass cell of 100 mm path length equipped with Suprasil® windows. Mass spectra were recorded from solids sealed under an inert atmosphere in m.p. tubes on a Finnigan SJQ 7000 and a Kratos MS-50TC mass spectrometer at ionizing voltages of 70 (*ca.* 1.12×10^{-17}) and 27 eV (*ca.* 4.3×10^{-18} J), respectively, using the direct-inlet method. In addition, a few crystals of $F_5S\overline{CNSNS}AsF_6$ were mixed with an excess of CsF in a melting tube in order to facilitate removal of AsF_5 generated on warming the sample. The evaporated sample was immediately introduced into the mass spectrometer. The ESR spectra of SO_2 solutions in 3 mm (outside diameter) sealed quartz tubes were recorded on a modified version of a Varian E-4 spectrometer equipped with a variable-temperature control unit using diphenylpicrylhydrazyl (dpph) as field marker. After 10 d the spectrum was recorded again, however no signal was obtained. The NMR samples were contained in thick-walled 5 mm (sealed) precision NMR tubes (Wilmad Glass, Buena, NJ). The ^{19}F Fourier-transform spectra were acquired at −45 °C [$SF_5(CN)\cdot AsF_5$ adduct] and at room temperature ($F_5S\overline{CNSNS}AsF_6$) on a Bruker MSL-200 spectrometer operating at 188.3 MHz. Chemical shifts were referenced either externally [$SF_5(CN)\cdot AsF_5$ adduct] or internally ($F_5S\overline{CNSNS}AsF_6$) to $CFCl_3$ with the high-frequency direction positive.

Improved synthesis of $SF_5(CN)$

In a typical reaction $SF_3(CN)$ (1.4 g, 12 mmol) and CCl_2FCClF_2 (15 g) were transferred to a glass trap containing a stirring bar. A mixture of fluorine and nitrogen (1:10) was slowly passed above (not through!) this solution with an overall flow rate of about 230 mmol h^{-1} and continuous stirring at −30 °C. The volatile products were collected at −183 °C for 1 d and then purified by trap-to-trap condensation at −100, −128 and −196 °C. The amount of $SF_5(CN)$ collected in the middle trap was about 250 mg (1.6 mmol; 25% yield with a purity of 95%), which with AsF_5 (310 mg, 1.8 mmol) was condensed at −196 °C into a glass vessel (50 cm^3), warmed to room temperature for better mixing, and then recooled to −60 °C. All volatile impurities were removed *in vacuo* at this temperature. Acetonitrile (*ca.* 5 mmol) was condensed onto the solid residue and the resulting mixture warmed to room temperature and recooled to −196 °C several times. Subsequently the volatile products were passed through a series of cold traps held at −100, −128 and −196 °C. The middle trap contained 200 mg of $SF_5(CN)$ in high purity as determined by IR and ^{19}F NMR spectroscopy.

Synthesis of $F_5S\overline{CNSNS}AsF_6$ [equation (3)]

Several glass ampoules (outer diameter 6 mm, inner diameter 4 mm, length 100 mm) were filled with $SNSAsF_6$ (*ca.* 0.053 g, 0.2 mmol), $SF_5(CN)$ (0.061 g, 0.4 mmol) and SO_2 (0.2 g) and then flame sealed *in vacuo*. All ampoules were placed in an autoclave which was filled with some $CHCl_2F$ and then stored at 60 °C for 3 d. At 60 °C the internal pressure in the glass ampoules exceeds 10 bar and the external $CHCl_2F$ pressure prevents the glass ampoules from bursting. Subsequently the autoclave was slowly cooled to −30 °C and the $CHCl_2F$ transferred to a vacuum line. The glass ampoules were opened, volatile material removed, and finally flame sealed as described.[13] In the dry-box the 'cleanest' crystals were collected for spectroscopic studies. Infrared and Raman spectra of this material showed no bands of the starting materials. Some crystals were mounted in glass capillaries for single-crystal X-ray analysis.

Reduction of $F_5S\overline{CNSNS}AsF_6$ [equation (7)]

Sulfur dioxide (100 mg) and $CFCl_3$ (500 mg) were successively condensed onto a mixture of $F_5S\overline{CNSNS}AsF_6$ (*ca.* 7 mg), $SbPh_3$ (*ca.* 7 mg) and NMe_4Cl (*ca.* 7 mg) in an ESR tube, giving a red solution at room temperature. The ESR tube was flame sealed and stored at −196 °C prior to measuring the ESR spectrum at room temperature.

Crystal structure determination of $F_5S\overline{CNSNS}AsF_6$

A crystal of $F_5S\overline{CNSNS}AsF_6$ with approximate dimensions 0.30 × 0.20 × 0.40 mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo-Kα radiation and a 2.4 kW sealed-tube generator.

The data were collected at −60 ± 1 °C using the ω–2θ technique and a maximum 2θ value of 46°. The ω-scan width was $(1.68 + 0.35 \tan \theta)°$ and the ω-scan speed 8° min^{-1}. Weak reflections $[I < 15\sigma(I)]$ were rescanned up to a maximum of six scans and the counts were accumulated. Stationary background counts were recorded on each side of the reflections with a peak/background counting time ratio of 2:1. Of the 3263 reflections collected, 3067 were unique ($R_{int} = 0.063$) and equivalent reflections were merged. The intensities of three representative reflections measured after every 150 remained stable throughout the data collection. An empirical absorption correction, using ψ scans,[14] was applied, which resulted in absorption coefficients ranging from 0.64 to 1. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[15] which revealed the positions of all atoms refined anisotropically. Crystal data are summarized in Table 4. The largest parameter shift was 0.01 times its estimated standard deviation (e.s.d.) during the final cycle of full-matrix least-squares refinement.[15] The standard deviation of an observation of unit weight[6] was 2.082. The weighting scheme was based on counting statistics and included a factor ($p = 0.01$) to downweight the intense reflections. Plots of $w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. A correction for secondary extinction was applied (coefficient = 1.50×10^{-7}). The maximum and minimum peaks in the final Fourier-difference map corresponded to 0.99 and −0.91 e Å^{-3}, respectively. Scattering factors for the structure determination were taken from ref. 16 and effects of anomalous dispersion were included in F_c,[17] the values for $\Delta f'$ and $\Delta f''$ being those of Cromer.[18] All calculations were performed using the TEXSAN[19] crystallographic software package. The final atomic coordinates are listed in Table 5.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

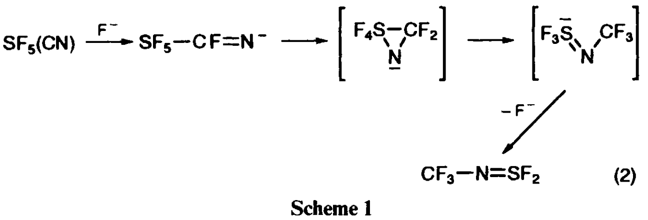
Physical properties of $SF_5(CN)$ and the adduct $SF_5(CN)\cdot AsF_5$

The fluorination of $SF_3(CN)$ in $C_2Cl_3F_3$ solution led to $SF_5(CN)$ in a yield of about 25%. Sulfur cyanide trifluoride, $SF_3(CN)$, is easily available on a gram scale by the metathesis of SF_4 and $SiMe_3(CN)$, at −30 °C.[3] In contrast to the synthesis of $SF_5(CN)$ described in ref. 1(*d*), samples produced by our new method are now available in larger quantities and are of higher purity because, by complexation with AsF_5 all impurities of similar boiling points are easily removed. The access to samples of high purity (checked by IR and ^{19}F NMR spectroscopy) enabled us to redetermine the physical properties of $SF_5(CN)$ and to study its chemical behaviour in more detail.

The melting point was −101 °C, and the boiling point extrapolated to −26 °C from equation (1). From the vapour-pressure curve the enthalpy of vaporization, ΔH_{vap}, was calculated to be 23.7 kJ mol^{-1} using the Clausius–Clapeyron relationship.[20] The value for ΔS_{vap} (= ΔH_{vap}/b.p.) is 96 J K^{-1} mol^{-1}, indicating some association between $SF_5(CN)$ molecules in the liquid phase since this value is higher than the expected value of ≈88 J K^{-1} mol^{-1} for non-associated molecules (Trouton's rule[20]). In the UV region $SF_5(CN)$ shows one unstructured band at $\lambda_{max} = 286$ nm with $\varepsilon_{max} = 3.1$ dm^3 mol^{-1} cm^{-1} and a half width of 39 nm.

$$\log(p/\text{mbar}) = -(1238/T) + 8.014 \qquad (1)$$

In the gas phase $SF_5(CN)$ is thermally stable for days at room temperature. However, the presence of ionic fluorides such as CsF causes isomerization to CF_3NSF_2 (Scheme 1)[21] and we believe that this process, in addition to S–C bond cleavage during fluorination, is responsible for the low yield in the synthesis of $SF_5(CN)$. The compound $SF_5(CN)$ has some hydrolytic stability, but in alkaline solution, it is quantitatively absorbed within a few minutes. With Lewis and protonic acids (*e.g.* HF, ref. 7) adduct formation is observed. The formation of the $SF_5(CN)\cdot AsF_5$ adduct is an important step in the purification of the crude $SF_5(CN)$. The vapour-pressure curve of this adduct (recorded between 220 and 280K) can be expressed as in equation (2), leading to a value of +44.3 kJ mol^{-1} for the enthalpy of dissociation, ΔH_{diss}. Gas-density measurements of 1:1 mixtures $SF_5(CN)$ and AsF_5 indicate that the molecules are not associated in the gas phase. Using the values for ΔH_{diss} [$SF_5(CN)\cdot AsF_5$], $\Delta_f H(AsF_5)$ −1234.2 kJ mol^{-1} [22] and $\Delta_f H[SF_5(CN)]$ −830.5 kJ mol^{-1},[4,23] the enthalpy of formation of the adduct $SF_5(CN)\cdot AsF_5$ is calculated to be −2109 kJ mol^{-1}. In contrast, the complex of MeCN with AsF_5 is stable at room temperature. This indicates weaker bonding of $SF_5(CN)$ to AsF_5. This behaviour can be explained by the base properties of the two compounds: $SF_5(CN)$ is a much weaker base than MeCN and consistently it also has a higher ionization potential and acts as a weaker base towards HF.



Scheme 1

$$\log(p/\text{mbar}) = -(2315/T) + 11.04 \qquad (2)$$

Spectroscopic characterization of $SF_5(CN)\cdot AsF_5$

The reaction between $SF_5(CN)$ and AsF_5 could lead in principle to a product with an ionic structure $[SF_4CN]^+[AsF_6]^-$ or a simple σ adduct $SF_5(CN)\rightarrow AsF_5$. The ionic structure should be discernible from the strong absorptions of the AsF_6^- ion, the strongest bands of which are at 699 cm^{-1} in the infrared and at 685 cm^{-1} in the Raman spectrum.[24a] Neither of these bands is found in the spectra (see Table 1) and therefore, the formation of $[SF_4CN]^+[AsF_6]^-$ can be excluded.

In the adduct $SF_5(CN)\rightarrow AsF_5$ the symmetry of $SF_5(CN)$ is unchanged in contrast to that of AsF_5. Therefore the vibrations of the $SF_5(CN)$ sub-molecule are assigned by comparison with the vibrations of the free molecule (see Table 1). In the adduct the CN and SC stretching vibrations are blue shifted by about 100 and 40 cm^{-1} respectively, because the lone electron pair of the CN group is antibonding (σ*). The SF modes are not much affected on complexation with AsF_5. The AsF_5 vibrations are assigned by comparison with the respective modes in the $MeCN\rightarrow AsF_5$ adduct.[24b] The ^{19}F NMR spectrum is consistent with the proposed structure of the $SF_5(CN)\rightarrow AsF_5$ adduct. In SO_2 solution at −45 °C it shows signals ($CFCl_3$ as external standard) at: δ 80.8 (SF_{eq}, doublet); 55.5 (SF_{ax}, quartet), $J(F_{ax}F_{eq}) = 162$ Hz; −43.7 (AsF_5, broad signal, $\Delta\nu_{\frac{1}{2}} = 170$ Hz). The intensity ratio of these three signals is 4:1:5.

Preparation and characterization of the salt $F_5S\overline{CNSNS}AsF_6$

The AsF_6^- salt of the cation $F_5S\overline{CNSNS}^+$ was prepared at 60 °C according to reaction (3). This reaction is a *reverse-electron-demand cycloaddition* of SNS^+ with an unconventional nitrile $SF_5(CN)$ and provides strong evidence for the generality of the SNS^+/nitrile cycloaddition reaction. The i.p. of $SF_5(CN)$ is 12.98 eV,[4] and a slow reaction with SNS^+ is expected by comparison with the analogous reactions of $CF_3C{\equiv}CCF_3$ and CF_3CN with SNS^+.[8] In fact the cycloaddition was not complete after 22 d at room temperature, and it was necessary to heat the mixture to 60 °C for 3 d in order to complete the reaction.

$$SNSAsF_6 + SF_5(CN) \xrightarrow{SO_2(l)} F_5S\overline{CNSNS}AsF_6 \qquad (3)$$

The ^{19}F NMR spectrum of $F_5S\overline{CNSNS}AsF_6$ in SO_2 solution shows resonances attributable to the SF_5 group and to the AsF_6^- anion in a 5:6 intensity ratio. From the AM_4 spin system of the SF_5 group resonances at δ 72.8 (doublet, split, SF_{eq}) and 61.5 (quartet, split, SF_{ax}), $J(F_{ax}F_{eq}) \approx 153$ Hz are easily identified. In the series $SF_5(CN)\cdot AsF_5$, $SF_5(CN)$, $F_5S\overline{CNSNS}AsF_6$ the difference in the chemical shifts (25.3, 18.7,[1d] 11.3 respectively) between the equatorial and axial

Table 1 Fourier-transform IR and Raman data (cm^{-1}) for the adduct $SF_5(CN)\cdot AsF_5$ at −196 °C and assignments

IR	Raman	IR [$SF_5(CN)$]*	Assignment
2346w	2338s		
2337w	2328 (sh)	2239m	$\nu(CN)\ (a_1)$
918vvs	917w	916vs	$\nu_{asym}(SF_{4\,eq})$ (e)
897vs		906s	$\nu(SF_{ax})\ (a_1)$
751vvs			$\nu(AsF_{4\,eq})$ (e)
736vs	739s	723m	$\nu(AsF_{ax})\ (a_1)/\nu_{sym}\ (SF_4)$ (e)
696m	698vs		$\nu(AsF_{4\,eq})\ (a_1)$
	653m		
623s	622m	628s	$\delta_{sym}(SF_5)\ (a_1)$
590s	591w	591s	$\delta_{asym}(SF_{eq/ax})$ (e)
526m	520m	479w	$\nu(SC)\ (a_1)$
	508 (sh)		$\delta_{asym}(SF_{4\,eq})\ (b_2)$
394s	397m		$F_{ax}AsF_{eq}$ wagging (e)
380vs			$\delta_{oop}(AsF_{4\,eq})\ (a_1)$
	263m		
	166vw		
	125m		

v = Very, s = strong, m = medium, w = weak, sh = shoulder, ax = axial, eq = equatorial, oop = out-of-plane.
* Neon-matrix, ref. 2.

Table 2 Vibrational data (cm^{-1}) for $F_5S\overline{CNSNS}AsF_6$ and tentative assignments

IR (solid)	Raman (solid)	Assignment*
1426m-w	1426w	$\nu(C{=}N)$
1052m	1050vw	$\nu_{asym}(NS_2)$
938m	934m	$\nu(SF_5)$
881vs	885	$\nu_{sym}(NS_2)$ and/or
849s	847m	$\nu\ (SF_5)$
785m-w	784m-s	
728 (sh)		$\nu(SF_5)$
690vs	696s	$\nu_3(AsF_6^-)$
	681s	$\nu_1(AsF_6^-)$
671s		
621m-s	623w-m	$\delta_{sym}(SF_5)$
586m	587m-s	$\nu(C{-}S)_{ring}$
568m-s	572m-s	$\nu_2(AsF_6^-)$
	502vw	$\delta_{asym}(SF_5)$
454s		$\nu(C{-}SF_5)$ and/or ring vibration
	431w	
	371m	$\nu_5(AsF_6^-)$
	293m	
	255s	
	132m	

* The tentative assignments were made by comparison with related $R\overline{CNSNS}AsF_6$ salts (R = SBr or Me),[10,26,27] $F_3C\overline{CSSSC}CF_3AsF_6$,[28] $SF_5(CN)$,[2] $CsAsF_6$[24] and using the relationship between $\nu_{asym}(S_2N)$ and $\nu_{sym}(S_2N)$ stretching vibrations (see ref. 25).

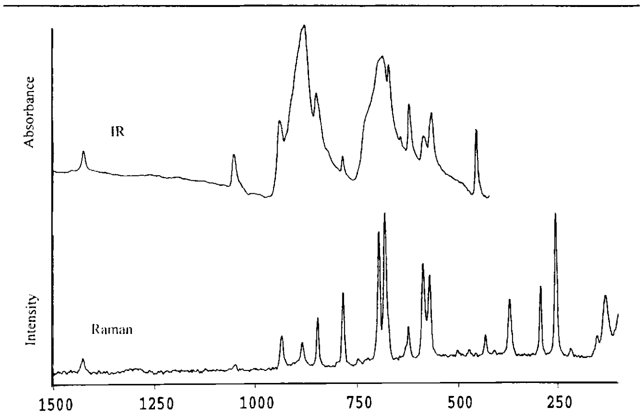


Fig. 1 Fourier-transform IR and Raman spectra of $F_5S\overline{CNSNS}AsF_6$

fluorine atoms decreases, because the fluorine atoms become more and more equivalent. As expected for the octahedral AsF_6^- anion, the fluorine resonance at δ −58 is a 1:1:1:1 quartet due to the coupling with the ^{75}As ($I = \frac{3}{2}$) nucleus, J(AsF) = 923 Hz.

The vibrational spectra of $F_5S\overline{CNSNS}AsF_6$ (Fig. 1 and Table 2) contain bands assignable to the AsF_6^- ion , the SF_5 group and the $\overline{CNSNS}$ ring of the cation. The ν(CN) stretching vibration at 1426 cm^{-1} is in the region expected for CN double bonds (C–N, 1020–1250; C=N, 1470–1690 cm^{-1}), consistent with the calculated CN bond order of 2.0 (see below). The bands at 1052 and 881/849 cm^{-1} are assigned to the asymmetric and symmetric SN stretching vibrations using Banister's SN bond length–stretching frequency correlation.† The assignment for the two CS stretching vibrations in the $F_5S\overline{CNSNS}^+$ cation was made by comparison with stretching frequencies found for related compounds. The bands at 586 and 454 cm^{-1} are assigned to the stretching vibrations of the C(1)–S(2) and C(1)–S(3) bonds, respectively.

The mass spectra of $R\overline{CNSNS}AsF_6$ salts[10] show ions derived from the neutral species $R\overline{CNSNS}F$ and AsF_5 produced *via* an initial fluoride-ion transfer according to equation (4). However, for $F_5S\overline{CNSNS}AsF_6$ this only occurred

$$F_5S\overline{CNSNS}AsF_6 \longrightarrow F_5S\overline{CNSNS}F + AsF_5 \quad (4)$$

on addition of CsF, evident by the presence of $F_5S\overline{CNSNS}^+$ [m/z 231 (64%)] and AsF_4^+ [m/z 151 (36%)]. The addition of CsF facilitates the removal of AsF_5 as $CsAsF_6$ is generated on electron impact, and/or a replacement reaction occurs [equation (5)]. In the absence of CsF the mass

$$F_5S\overline{CNSNS}AsF_6 + CsF \longrightarrow F_5S\overline{CNSNS}F + CsAsF_6 \quad (5)$$

spectra of $F_5S\overline{CNSNS}AsF_5$ (Table 3) imply dissociation into SF_4 (SF_3^+, SF_2^+, SF^+) and $F_2\overline{CNSNS}$ ($F_2\overline{CNSNS}^+$, $F\overline{CNSNS}^+$, SNS^+, *etc.*) and AsF_5 as shown in equation (6) as

$$F_5S\overline{CNSNS}AsF_6 \longrightarrow F_5S\overline{CNSNS}F\ (+AsF_5) \longrightarrow SF_4 + F_2\overline{CNSNS}^+ \quad (6)$$

well the isomerization of $SF_5(CN)$ to CF_3NSF_2, (Scheme 1). Presumably formation of $F_5S\overline{CNSNS}F$ occurs under milder

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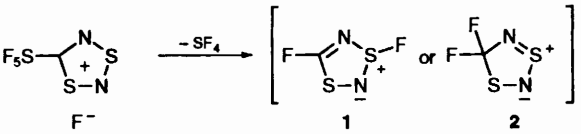
† λ(S–N) = 0.1941d(SN) − 20.66, where λ(S–N) is the S–N stretching wavelength in 10^{-4} cm and d(SN) the S–N bond distance in pm. For $F_5S\overline{CNSNS}^+$: d_{av}(SN) = 157.5 pm, λ(S–N) = 9.9707 × 10^{-4} cm and ν_{av}(SN) 1003 cm^{-1}.[25]

Table 3 Mass spectra of $F_5SCNSNCAsF_6$

m/*z* [Intensity (%)]

70 eV	27 eV	27 eV (+CsF)*	Assignment
		231 (64)	$CN_2S_3F_5^+$
		185 (3)	$CNS_3F_5^+$
		166 (3)	$CNS_3F_4^+$
151 (100)	151 (80)	151 (36)	AsF_4^+
	148 (6)	148 (22)	$CNS_3F_3^+$
142 (22)	142 (68)	142 (44)	$CN_2S_2F_2^+$
132 (14)	132 (32)	132 (44)	AsF_3^+
		127 (15)	SF_5^+
123 (2)	123 (15)	123 (7)	$CN_2S_2F^+$
113 (13)	113 (41)	113 (43)	AsF_2^+
	105 (2)	104 (6)	$CN_2S_2^+$
96 (10)	96 (15)	96 (14)	$CNSF_2^+$
94 (7)	94 (5)	94 (2)	AsF^+
89 (38)	89 (7)	89 (71)	SF_3^+
78 (46)	78 (100)	78 (100)	S_2N^+
	75 (7)	75 (< 1)	As^+
70 (18)		70 (7)	SF_2^+
	64 (6)	64 (2)	S_2^+
		58 (2)	CNS^+
51 (6)		51 (< 1)	SF^+

* A few crystals of $F_5SCNSNSAsF_6$ were mixed with CsF (excess) in a melting point tube and the mixture was immediately introduced into the mass spectrometer.



Scheme 2

conditions in the presence of CsF. At energies necessary for fluoride-ion transfer directly from AsF_6^-, the cleavage of the C(1)–S(3) bond and rearrangement may occur as in Scheme 2. The sums of the bond energies of the species **1** and **2** are about equal (2400 and 2373 kJ mol^{-1}, respectively), therefore both species are possible.†

Crystal structure of $F_5SCNSNSAsF_6$

The crystal data show that the unit cell consists of discrete $F_5SCNSNS^+$ cations and AsF_6^- anions (Fig. 2) with some cation–anion interaction (Fig. 3). The bond distances and angles of the 6π $F_5SCNSNS^+$ ring are similar to those in some related $CNSNS^+$ containing cations (see Tables 6 and 7) within the (rather low) accuracy of the data, i.e. there seems to be no marked change in intercationic geometry of the ring with the nature of the substituent. The N–S–N and S–N–S bond angles [102.5(8) and 113.2(9)°] are smaller than those predicted (112 and 130°) on the basis of the S–N bond lengths, implying the presence of some ring strain in the structure.‡ The geometry of the SF_5 group [S–F_{ax} 1.58(2), S–F_{eq} (average) 1.56(1) Å, F_{ax}–S–F_{eq} (average) 90.2(8)°] is similar to that in $SF_5(CN)$ [S–F (average) 1.564(6) Å, F_{ax}–S–F_{eq} (average) 90.1(2)°, see ref. 2]. However, the C–S(3) bond distance in $F_5SCNSNS^+$ [1.82(2) Å] is greater than that in $SF_5(CN)$ [1.765(5) Å, see ref. 2]. This may arise from electrostatic repulsion between the partially positively charged sulfur and carbon atoms. A similar effect is observed in SF_5Me (r_{SC} = 1.793 Å) and $SF_5(CF_3)$ (r_{SC} = 1.887 Å).[33,34] The approximate equivalence of the F_{ax}–S(3)–F_{eq} and C–S(3)–F_{eq} angles ($\approx$ 90°) suggests that the electronegativity of the $CNSNS^+$ ring is similar to that of fluorine. Although the carbon in the ring is likely partially positively charged, most of the charge resides on the sulfur atoms S(1) and S(2), as is reflected by the number and strength of the anionic fluorine contacts to the cation (Fig. 3, Table 6). The strength of these contacts§ is reflected in the sum of the S ··· F valency units S(1) ··· F (0.32 v.u.) and S(2) ··· F (0.28 v.u.) which are similar to those found in $MeCNSNS^+$ [S(1) ··· F (0.34 v.u.) and S(2) ··· F (0.23 v.u.); ref. 10]. There are no C ··· F contacts and only one N(2) ··· F(9) interionic contact is observed at a distance of 2.93(2) Å, close to the related N(2) ··· F contact in $MeCNSNS^+$ [N(2) ··· F 2.99(2) Å]. The bond orders in the $CNSNS^+$ ring of the $F_5SCNSNS^+$ cation (Table 7) indicate that π bonding is strongest in the C–N bond, weaker in the N–S bonds, and weakest of all in the C–S(2) bond. In valence bond terms the resonance structures **3** and **4** are major contributors to the electronic structure of the cation. The average As–F distance of 1.67 Å in the AsF_6^- anion is slightly

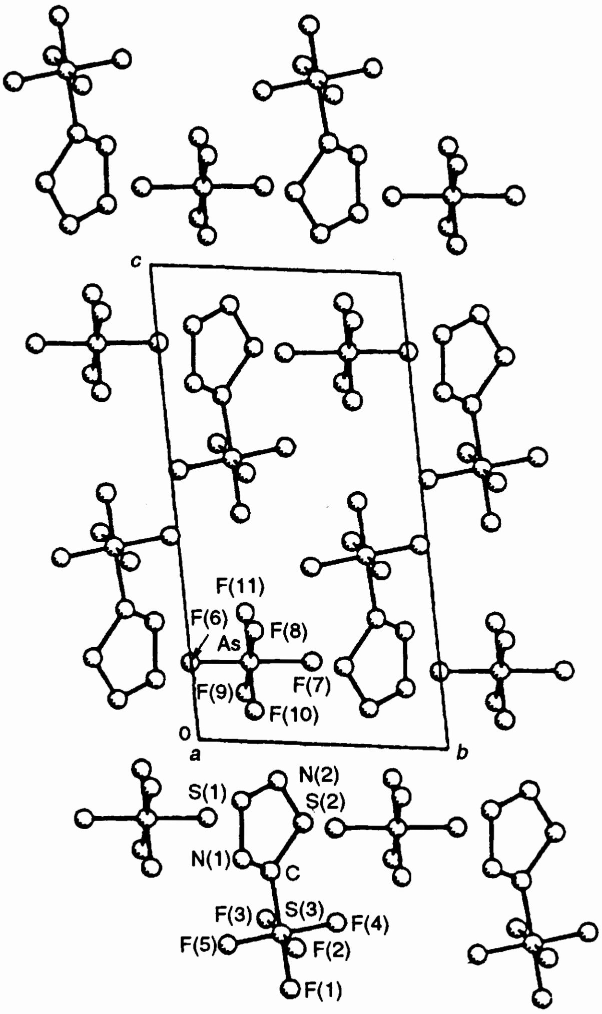


Fig. 2 Crystal packing of $F_5SCNSNSAsF_6$ projected down the *a* axis

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† Bond energies (kJ mol^{-1}): C–F, 485; S–F, 284; S–N, 248; S=N, 335; C–N, 305; C=N, 615; C–S, 272 (see ref. 29).

‡ In compounds of S^{II} and S^{IV} the S–N bond length [*d*(S–N)/pm] is related to the N–S–N angle (in °) by *d*(S–N) = 213.00 – 0.4861 (N–S–N). For cationic SNS moieties the angle at the N atom is given by *d*(S–N) = 187.03 – 0.2263 (S–N–S) (see ref.25).

§ It has been shown that the strength of the S^{IV} ··· F contacts can be assessed by the relative magnitude of the bond valences (*S*) and is directly correlated to the localization of positive charge. An increase of positive charge on an atom leads to an increase in the sum of bond valences around the atom and this is accompanied by the formation of additional bonds and contacts (inter- and/or intra-cationic) equal to the charge on the atom. The bond valence *S* in valence units (v.u.) is given by: $S = (R/R_0)^{-N}$, where *R* is the observed bond distance (Å), R_0 = 1.55 Å and *N* = 3.8 for S^{IV} ··· F (see ref. 35).

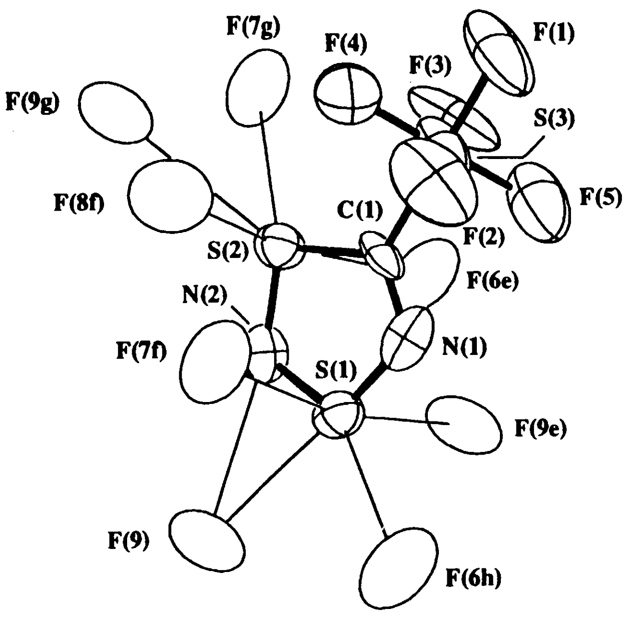


Fig. 3 Structure of the $F_5S\overline{CNSNS}^+$ cation and the cation–anion contacts (all contacts included for S $\cdots$ F $\leqslant$ 3.27, C $\cdots$ F $\leqslant$ 3.17). The symmetry relations denoted by letters e–h are defined as in Table 6

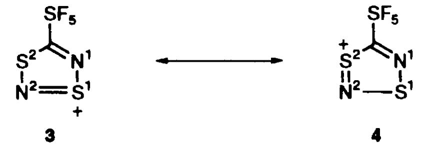


Table 4 Crystal data for $F_5S\overline{CNSNS}AsF_6$

Formula	$AsCF_{11}N_2S_3$
M	420.11
No. reflections for unit-cell determination (2θ range/°)	20 (20–30)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	6.252(5)
b/Å	7.070(6)
c/Å	13.116(8)
α/°	95.71(8)
β/°	96.64(3)
γ/°	104.35(6)
U/Å^3	553(2)
Z (molecules per cell)	2
D_c/Mg m^{-3}	2.523
F(000)	400
λ(Mo-Kα)/Å	0.710 69
μ(Mo-Kα)/cm^{-1}	37.40
No. reflections measured	3263
No. unique reflections	3067
No. observed reflections [$I_0 > 3.00\sigma(I_0)$]	1090
No. variables	164
$R = \Sigma(F_o - F_c)/\Sigma(F_o)$	0.0842
$R' = [\Sigma w(F_o - F_c)^2/\Sigma(wF_o)^2]^{\frac{1}{2}}$	0.0836
Goodness of fit *	2.082

* Standard deviation of an observation of unit weight: $[\Sigma w(F_o - F_c)^2/(n_d - n_p)]^{\frac{1}{2}}$, where n_d = number of data (reflections) and n_p = number of parameters.

shorter than that in $KAsF_6$ [1.719(3) Å, 90.0(2)°]^{36} likely reflecting greater cation–anion contacts in the potassium salt .

Identification of the radical $F_5S\overline{CNSNS}^{\bullet}$

The radical $F_5S\overline{CNSNS}^{\bullet}$ was prepared in dilute SO_2 solution from the reduction of $F_5S\overline{CNSNS}AsF_6$ with NMe_4Cl and $SbPh_3$ [equation (7)] and identified by its ESR spectrum (see Fig. 4). The ESR spectrum consists of a 1 : 1 : 1 triplet with g = 2.0065, a^{N^2} = 11.44 G typical for $R\overline{CNSNS}^{\bullet}$ derivatives (ranges: a^{N^2}, 10.8–11.2 G; g, 2.0048–2.0065, see refs. 8 and 37). The triplet shows some fine structure and is more complex than expected from coupling with only N(2). The ESR spectrum of the related radical $F_3C\overline{CN(1)SN(2)S}^{\bullet}$ showed only a coupling to N(2) (11.2 G), with none to N(1) or to the fluorine atoms, even though the spectra of other derivatives show small a^{N^1} values of 0.5–1.5 G.^{38}

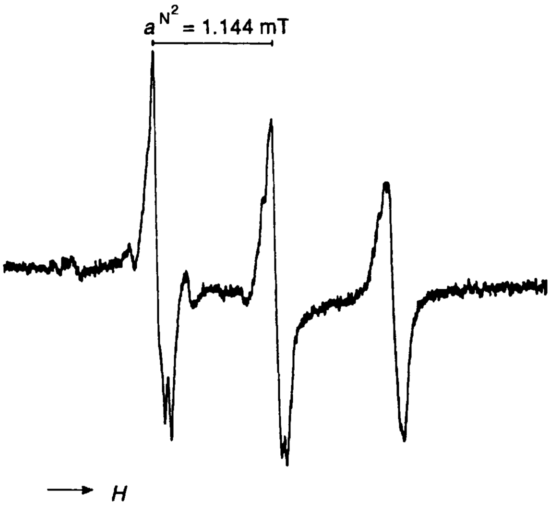


Fig. 4 The ESR spectrum of $F_5S\overline{CNSNS}^{\bullet}$ in SO_2 at room temperature. Microwave frequency, 9.197 GHz; microwave power, 10 dB

Table 5 Fractional atomic positional parameters for $F_5S\overline{CNSNS}AsF_6$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
As	−0.4844(3)	0.2420(3)	−0.8308(2)
S(1)	−0.8706(8)	0.1469(7)	−1.1253(4)
S(2)	−1.1215(8)	0.3869(8)	−1.1665(4)
S(3)	−1.187(1)	0.254(1)	−1.4031(4)
F(1)	−1.286(3)	0.265(2)	−1.518(1)
F(2)	−0.946(2)	0.305(2)	−1.432(1)
F(3)	−1.431(2)	0.197(3)	−1.373(1)
F(4)	−1.170(3)	0.474(2)	−1.375(1)
F(5)	−1.210(3)	0.030(2)	−1.431(1)
F(6)	−0.530(2)	−0.002(2)	−0.837(1)
F(7)	−0.436(2)	0.491(2)	−0.825(1)
F(8)	−0.232(2)	0.274(2)	−0.765(1)
F(9)	−0.738(2)	0.211(2)	−0.897(1)
F(10)	−0.353(3)	0.241(2)	−0.934(2)
F(11)	−0.619(3)	0.244(2)	−0.728(1)
N(1)	−0.950(3)	0.127(2)	−1.247(1)
N(2)	−0.986(2)	0.305(2)	−1.080(1)
C	−1.071(3)	0.237(3)	−1.271(1)

$$F_5S\overline{CNSNS}AsF_6 + NMe_4Cl + \tfrac{1}{2}SbPh_3 \xrightarrow{SO_2,CFCl_3} F_5S\overline{CNSNS}^{\bullet} + NMe_4AsF_6 + \tfrac{1}{2}Sb_3Ph_3Cl_2 \quad (7)$$

Radicals $R\overline{CNSNS}^{\bullet}$ in which R is an electron withdrawing group (or atom) rearrange rapidly at room temperature to $R\overline{CNSSN}^{\bullet}$ radicals (a^{N^1}, 5.0–5.3 G, g 2.0106–2.0119; see refs. 8 and 27). However, the rearranged radical $F_5S\overline{CNSNS}^{\bullet}$ was not observed on standing for 10 d at −10 °C in the dark.

Conclusion

The low-temperature fluorination of $SF_3(CN)$ provides an improved route to $SF_5(CN)$ and allows us to determine its

Table 6 Bond distances (Å) and angles (°) for $F_5SCNSNSAsF_6$ including interionic contacts, with e.s.d.s in parentheses (see Fig. 3 for labelling of the atoms)

As–F(6)	1.67(1)	As(1)–F(11)	1.67(1)	S(2)–C	1.76(2)	S(3)–F(4)	1.54(2)
As–F(7)	1.70(1)	S(1)–N(1)	1.60(2)	S(3)–F(1)	1.58(1)	S(3)–F(5)	1.55(2)
As–F(8)	1.66(1)	S(1)–N(2)	1.57(2)	S(3)–F(2)	1.56(1)	S(3)–C	1.82(2)
As–F(9)	1.67(1)	S(2)–N(2)	1.58(2)	S(3)–F(3)	1.58(1)	N(1)–C	1.25(2)
As–F(10)	1.67(2)						

F(6)–As(1)–F(7)	179.4(6)	F(8)–As–F(10)	84(1)	F(1)–S(3)–F(4)	89.6(8)	F(3)–S(3)–C	90.1(8)
F(6)–As(1)–F(8)	90.5(7)	F(8)–As–F(11)	96(1)	F(1)–S(3)–F(5)	90.4(8)	F(4)–S(3)–F(5)	179(1)
F(6)–As(1)–F(9)	89.8(7)	F(9)–As–F(10)	96(1)	F(1)–S(3)–C	179(1)	F(4)–S(3)–C	91.3(8)
F(6)–As(1)–F(10)	90.5(7)	F(9)–As–F(11)	83.6(9)	F(2)–S(3)–F(3)	179(1)	F(5)–S(3)–C	88.7(8)
F(6)–As(1)–F(11)	89.7(7)	F(10)–As–F11)	179(1)	F(2)–S(3)–F(4)	90.4(9)	S(1)–N(1)–C	114(1)
F(7)–As(1)–F(8)	89.1(7)	N(1)–S(1)–N(2)	102.5(8)	F(2)–S(3)–F(5)	91(1)	S(1)–N(2)–S(2)	113.2(2)
F(7)–As(1)–F(9)	90.6(7)	N(2)–S(2)–C	95.6(8)	F(2)–S(3)–C	89.2(8)	S(2)–C–S(3)	120(1)
F(7)–As(1)–F(10)	89.0(7)	F(1)–S(3)–F(2)	90.5(8)	F(3)–S(3)–F(4)	91(1)	S(2)–C–N(1)	115(1)
F(7)–As(1)–F(11)	90.9(8)	F(1)–S(3)–F(3)	90.2(8)	F(3)–S(3)–F(5)	87.9(9)	S(3)–C–N(1)	125(2)
F(8)–As(1)–F(9)	179.7(8)						

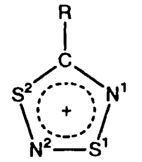
S(1)–N(1)–C–S(2)	1(2)	N(2)–S(1)–N(1)–C	1(2)	S(1)–N(2)–S(2)–C	2(1)
S(1)–N(1)–C–S(3)	179.2(9)	S(3)–C–S(2)–N(2)	180(1)	N(1)–C–S(2)–N(2)	−2(2)
S(2)–N(2)–S(1)–N(1)	−2(1)				

Interionic contacts *

S(1) ··· F(6h)	3.00(1)	N(1) ··· S(1) ··· F(6h)	91.0(8)	N(2) ··· S(2) ··· F(7g)	132.2(6)
S(1) ··· F(7f)	2.97(1)	N(1) ··· S(1) ··· F(7f)	80.0(6)	N(2) ··· S(2) ··· F(8f)	104.7(5)
S(1) ··· F(9)	2.97(2)	N(1) ··· S(1) ··· F(9)	175.5(7)	N(2) ··· S(2) ··· F(9g)	118.1(6)
S(1) ··· F(9e)	3.12(1)	N(1) ··· S(1) ··· F(9e)	91.4(6)	C ··· S(2) ··· F(6e)	78.5(7)
S(2) ··· F(6e)	3.04(1)	N(2) ··· S(1) ··· F(6h)	152.9(5)	C ··· S(2) ··· F(7g)	120.6(7)
S(2) ··· F(7g)	3.09(1)	N(2) ··· S(1) ··· F(7f)	80.8(6)	C ··· S(2) ··· F(8f)	85.8(7)
S(2) ··· F(8f)	3.12(2)	N(2) ··· S(1) ··· F(9)	73.0(6)	C ··· S(2) ··· F(9g)	143.7(7)
S(2) ··· F(9g)	3.24(2)	N(2) ··· S(1) ··· F(9e)	94.1(6)	S(1) ··· N(2) ··· F(9)	76.0(6)
N(2) ··· F(9)	2.93(2)	N(2) ··· S(2) ··· F(6e)	82.4(5)	S(2) ··· N(2) ··· F(9)	170.5(8)

* All contacts included for S ··· F $\leqslant$ 3.27, C ··· F $\leqslant$ 3.17 and N ··· F $\leqslant$ 3.27 (sum of the isotropic van der Waals radii, i.e. C 1.70, F 1.47, N 1.55, S 1.80 Å).[30] Selected interionic contact angles are given. Symmetry relationships: e $-2-x, -y, -2-z$; f $-1-x, 1-y, -2-z$; g $-2-x, 1-y, -2-z$; h $-1-x, -y, -2-z$.

Table 7 Comparison of bond distances and angles, and bond orders (in square brackets) in $RCNSNS^+$ cations (R = Me,[10] SBr[26] or SF_5)



Compound	C–N(1)	S(1)–N(1)	S(1)–N(2)	N(2)–S(2)	S(2)–C	C–R
$MeCNSNS^+AsF_6^-$	1.32(3)	1.57(2)	1.59(2)	1.63(2)	1.77(2)	1.46(3)
	[1.6]	[1.7]	[1.5]	[1.4]	[1.1]	[1.3]
$BrSCNSNS^+Br_3^-$	1.37(2)	1.60(2)	1.56(2)	1.67(1)	1.76(1)	1.72(1)
	[1.4]	[1.6]	[1.8]	[1.2]	[1.2]	[1.3]
$F_5SCNSNS^+AsF_6^-$	1.25(2)	1.60(2)	1.57(2)	1.58(2)	1.76(2)	1.82(2)
	[2.0]	[1.6]	[1.7]	[1.7]	[1.2]	[1.0]

	S(2)–C–N(1)	N(2)–S(2)–C	S(1)–N(2)–S(2)	N(1)–S(1)–N(2)	S(1)–N(1)–C
$MeCNSNS^+AsF_6^-$	110.6(15)	98.4(9)	110.4(10)	104.6(9)	115.7(16)
$BrSCNSNS^+Br_3^-$	114(1)	96.3(7)	112.0(9)	106.0(8)	112(1)
$F_5SCNSNS^+AsF_6$	115(1)	95.6(8)	113.2(9)	102.5(8)	114(1)

S(1)–C–S(3) in $BrSCNSNS^+Br_3^-$, 123.1(8)°; $F_5SCNSNS^+AsF_6^-$, 120(1)°

[a] The bond orders for the C–C, C–S and C–N bonds were estimated using Pauling's bond distance–bond order relationship, $D(n') = D_1 - 0.71 \log n'$, where n' is the bond order, $D(n')$ is the observed bond length in Å and D_1 the single bond distance (= sum of the covalent radii: C–C 1.54, C–N 1.47, C–S, 1.81 Å).[31] The bond orders for the S–N bonds were calculated using Nyberg's equation, b.o.(NS) = 0.429 + 6.850 d(NS) −3.825 $d(NS)^2$, where b.o.(NS) is the bond order and d(NS) the observed bond length in Å.[32]

physical properties more accurately and to explore its chemistry. The compound $SF_5(CN)$ undergoes a *reverse-electron-demand cycloaddition* with $SNSAsF_6$ in SO_2 at 60 °C within 3 d to give $F_5SCNSNSAsF_6$. The reduction of this salt leads to the unstable radical $F_5SCNSNS^{\bullet}$. The mass spectrum of $F_5SCNSNSAsF_6$ is consistent with the loss of AsF_5 and fluoride-ion transfer to give $F_5SCNSNSF$ which dissociates to SF_4 and F_2CNSNS.

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