

Chelation of Fluoride Ion by $F_2C(SF_3)_2$: Formation of a Four-membered CS_2F Heterocycle with a Symmetrically Bridging Fluoride

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In the solid state $CF_2(SF_3)_2$ adds F^- with formation of a stable symmetrically bridged anion $F_2C(\mu-SF_3\cdots)_2F^-$, the structure of the caesium salt of which has been determined by X-ray crystallography.

Sulfur tetrafluoride and *S*-perfluoroalkylsulfur trifluorides, R_fSF_3 [$R_f = CF_3$ or $(CF_3)_2CF$], may act as F^- donors^{1,2} as well as F^- acceptors.^{3,4} This ambivalence is reflected in the gas phase structure of $F_2C(SF_3)_2$.^{5,6} One of the axial fluorine atoms of each of the pseudo-trigonal-bipyramidal coordinated sulfur centres interacts with the other. This nonbonding SF distance (266 ppm) is distinctly shorter than the sum of the van der Waals radii (330 pm).

With AsF_5 , bis(trifluorosulfur)difluoromethane forms a thermally unstable salt⁷ $F_2C(SF_3)SF_2^+AsF_6^-$ of unknown

structure; a dication is not formed even with a large excess of Lewis acid. With strong fluoride-ion donors, *e.g.* CsF or TAS fluoride [TAS = $(Me_2N)_3S^+Me_3SiF_2^-$],⁸ stable salts of the monoanion are formed; attempts to add a second F^- were not successful⁹ [reactions (1) and (2)].⁹ Salts **2** and **4** are formed in almost quantitative yield when **1** is added to the appropriate fluoride in small excess at -40 to -30 °C in MeCN solution.

At room temperature the ^{19}F NMR spectrum of **2** exhibits only two broad signals [CF: $\delta -77.3$ (rel. int. 2) and SF: $\delta 23.0$ (rel. int. 7)], while those of **4** are further split into a triplet [SF:

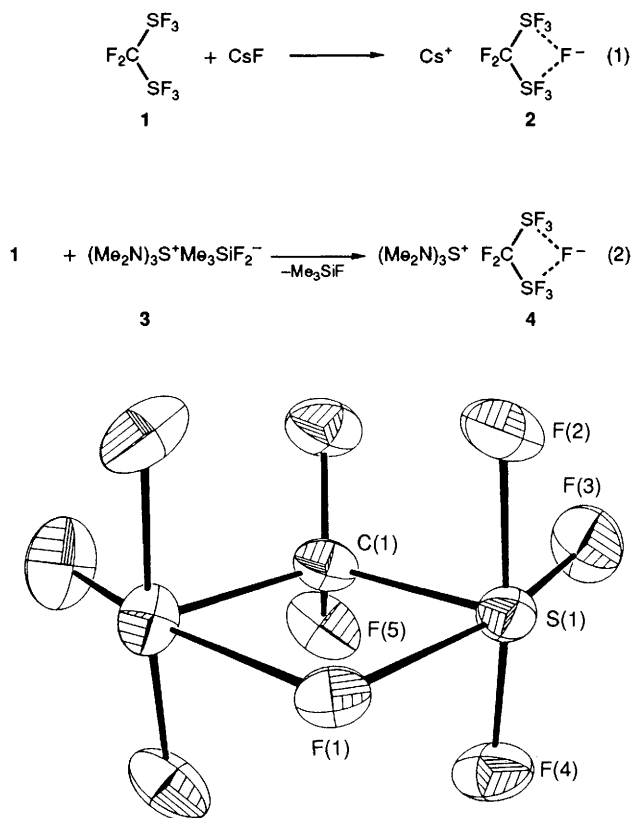


Fig. 1 Structure of the anion with 50% thermal ellipsoids; bond distances (pm) and bond angles ($^\circ$): S(1)–F(1) 211.7(1), S(1)–F(2) 172.9(2), S(1)–F(3) 160.7(2), S(1)–F(4) 170.0(2), S(1)–C(1) 189.9(2), C(1)–F(5) 133.2(3), F(1)–S(1)–F(2) 87.8(1), F(1)–S(1)–F(3) 166.7(1), F(2)–S(1)–F(3) 89.3(1), F(1)–S(1)–F(4) 91.6(1), F(2)–S(1)–F(4) 173.6(1), F(3)–S(1)–F(4) 89.8(1), F(1)–S(1)–C(1) 76.4(1), F(2)–S(1)–C(1) 86.5(1), F(3)–S(1)–C(1) 90.4(1), F(4)–S(1)–C(1) 87.1(1), S(1)–F(1)–S(1A) 95.7(1), S(1)–C(1)–F(5) 109.9(1), S(1)–C(1)–S(1A) 111.4(2), F(5)–C(1)–F(5A) 105.6(3)

δ 20.3, 3J 12.7 Hz (rel. int. 7)] and an octet [CF_2 : δ –77.2 ppm, 3J 12.7 Hz (rel. int. 2)]. Because of rapid intramolecular F^- exchange all fluorine atoms bonded to sulfur are equivalent. At low temperatures (-55°C), the SF signal of **4** becomes poorly resolved and unsymmetrical. This could be due either to an open-chain ground-state structure [similar to the system $\text{FC(O)}-(\text{CF}_2)_n-\text{C(O)F}_2^-$ ($n = 0, 1, 2$)¹⁰] or to a slow intramolecular exchange process.

The molecular structure of the Cs salt **2** has been determined by X-ray diffraction (Fig. 1).[†] The SF_3 centres are symmetrically bridged by a fluoride ion with S–F(1) = 211.7 pm, compared to S–F(3) = 160.7 and S–F(2)/S–F(4) = 172.9/170.0 pm for the nonbridging SF distances.

[†] Crystal data for CsCF_9S_2 : orthorhombic, space group $Pnna$, $a = 944.8(1)$, $b = 1052.5(1)$, $c = 842.2(1)$ pm, $U = 0.838$ nm³, $Z = 4$, $D_c = 3.014$ g cm⁻³, $\mu = 5.02$ mm⁻¹, $F(000) = 696$, crystal dimensions $0.3 \times 0.3 \times 0.5$ mm. 1759 reflections collected with $8 < 2\theta < 55^\circ$, 960 unique and 892 with $F > 4\sigma(F)$ used in the structural analysis. The data set was collected on a Siemens-Stoe AED diffractometer using Mo-K α radiation ($\lambda = 71.073$ pm) at 153 K. Semiempirical absorption corrections were applied. The structure was solved by Patterson and Fourier methods. All atoms were refined anisotropically. An extinction correction with $\chi = 0.0011(1)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$, was applied. 62 parameters were refined with a weighting scheme $\{w^{-1} = \sigma^2(F) + 0.0001 F^2\}$. The refinement converged with $R = 0.018$, $R_w = 0.023$ and final difference electron density maxima of 0.97×10^{-6} e pm⁻³ and minima of -0.40×10^{-6} e pm⁻³. Atomic coordinates, bond lengths and angles, and anisotropic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

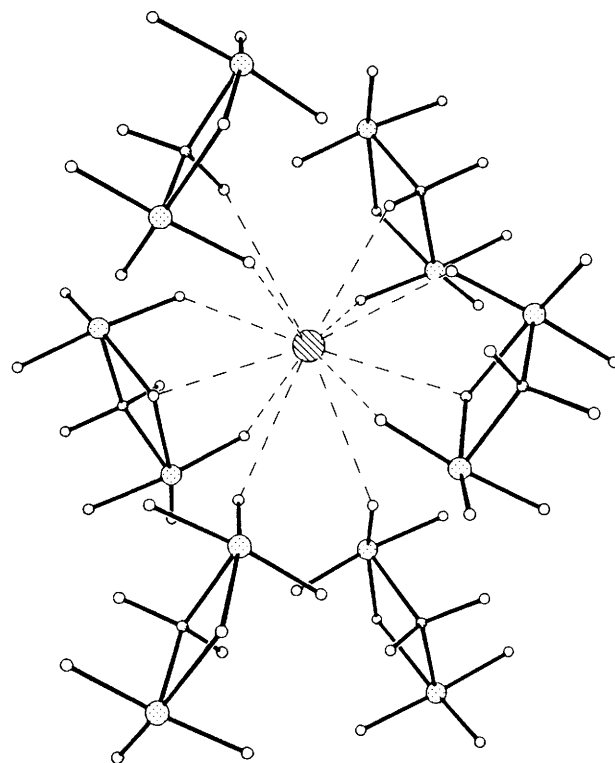


Fig. 2 Coordination of the Cs ion; the Cs–F distances are in the range 297.6(2)–339.1(2) pm

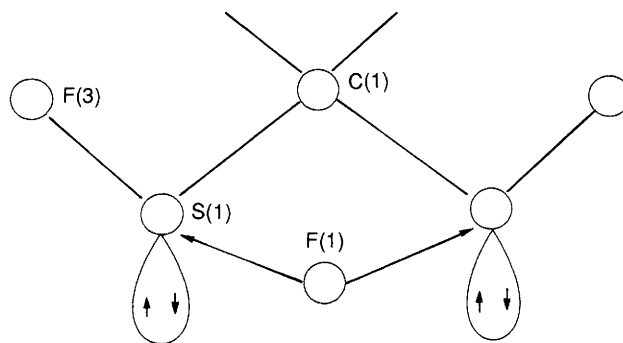


Fig. 3 Attack of the incoming F(1) on the sulfur centres in the equatorial plane

This experimentally determined bridged structure is also suggested by an *ab initio* structure optimization for the naked $[\text{F}_2\text{C}(\text{SF}_3)_2\text{F}]^-$ anion using the Gaussian 90 program package¹¹ at the HF/3-21G* level. According to this optimization the SF_3 centres are symmetrically bridged by a fluoride ion with S–F(1) = 201.4 pm; the nonbridging SF distances are S–F(3) = 160.5 pm and S–F(2)/S–F(4) = 166.5 pm, respectively. These deviations from the experimentally determined structure could be due to the interaction of the bridging fluoride with the Cs^+ counter ion in the crystal (Fig. 2).

Interestingly, these calculations also indicate a second minimum with an asymmetrically bridging F^- anion with appreciably different distances to the two S atoms (177.5 and 230.0 pm). The 50% probability ellipsoids shown in Fig. 1 give no indications of a possible dynamic disorder involving such a structure in the crystal. This second minimum is even more stable by 5.4 kJ mol⁻¹ at the HF/3-21G*//HF/3-21G* level, and by 5.7 kJ mol⁻¹ at the HF/6-31+G*//HF/3-21G* level, whereas the inclusion of correlation effects at the MP2/6-31+G*//HF/3-21G* level indicates the symmetrical minimum being more stable by 4.5 kJ mol⁻¹.

For anions $R_f-SF_4^-$, obtained from F^- addition to R_fSF_3 [$R_f = CF_3$ or $(CF_3)_2CF$], a pseudo-octahedral structure with four equivalent basal fluorine and an apical R_f group has been established by NMR spectroscopy.^{3,4} These anions might be regarded as transition states for S_N2 nucleophilic substitutions at pentacoordinated centres. The beginning of such an attack may be visualised in the gas phase structure of $CF_2(SF_3)_2$.⁵ The anion of **2** is a further step on the reaction coordinate towards the transition state. The attack occurs in the equatorial plane. The bond angle C(1)S(1)F(3) has changed from 120° in an ideal trigonal-bipyramidal structure to $97.2(11)^\circ$ in $CF_2(SF_3)_2$ and to the ideal angle of $90.4(1)^\circ$ for a pseudo-octahedral environment in **2**. The incoming F(1) approaches S(1) almost exactly between C(1) and a possibly sterically active lone pair (Fig. 3). The SF bond distances in the anion of **2** are ca. 5 pm longer than in the parent neutral molecule $F_2C(SF_3)_2$;⁵ the difference in the bond lengths $\Delta = d(SF_{ax}) - d(SF_{eq}) = 10$ pm has not changed. This comparison might be questioned because the structures were determined by different methods.

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