

# Tris(dimethylamino)sulfonium, TAS,–1,1,3,5-tetrafluoro-1,3,5-trioxo-1 $\lambda$ 6,3 $\lambda$ 6,5 $\lambda$ 6,2,4,6-trithiatriazine–Synthesis and Crystal Structure

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From the reaction of  $(\text{Me}_2\text{N})_3\text{S}^+\text{Me}_3\text{SiF}_2^-$  and  $[\text{NS}(\text{O})\text{F}]_3$ ,  $(\text{Me}_2\text{N})_3\text{S}^+ \{[\text{NS}(\text{O})\text{F}]_2[\text{NS}(\text{O})\text{F}_2]\}^-$  **2** is prepared and its X-ray crystal structure determined.

The structures of the two isomers of sulfanuric chloride  $[\text{NS}(\text{O})\text{Cl}]_3$  (1,3,5-trichloro-1,3,5-trioxo-1 $\lambda$ 6,3 $\lambda$ 6,5 $\lambda$ 6,2,4,6-trithiatriazine)<sup>1</sup> are well established. The oxygen atoms are always in equatorial positions; in the  $\alpha$ -form a chair conformation with all chlorine atoms in an axial *cis*-position,<sup>2</sup> in the  $\beta$ -isomer a boat conformation with one of the chlorine atoms in a *trans*-position were found.<sup>3</sup> Sulfanuric fluoride,  $[\text{NS}(\text{O})\text{F}]_3$ ,<sup>4</sup> also exists in two isomeric forms; the structure of the *cis*-fluoride, recently confirmed by X-ray diffraction in the solid state and by electron diffraction in the gas phase,<sup>5</sup> is very similar to that of  $\alpha$ - $[\text{NS}(\text{O})\text{Cl}]_3$ . The structure of the *trans*-form should be closely related to that of  $\beta$ - $[\text{NS}(\text{O})\text{Cl}]_3$ . Both isomers can be isolated in a pure state. In MeCN solution at room temp.,  $\text{F}^-$  catalyses the formation of an equilibrium with *cis*:*trans* in a ratio of 3:1.<sup>6</sup> Glemser and Wagner suggested for this isomerisation an  $\text{S}_\text{N}2$  reaction with inversion at the sulfur,<sup>6</sup> Scheme 1.

**1** is a plausible transition state for this reaction. From *cis*- $[\text{NS}(\text{O})\text{F}]_3$  and stoichiometric amounts of TAS-fluoride,  $(\text{Me}_2\text{N})_3\text{S}^+\text{Me}_3\text{SiF}_2^-$  salt **2** was isolated in quantitative yield, Scheme 2.

From the reaction mixture, **2** is precipitated by the addition of diethyl ether below  $-30^\circ\text{C}$ . **2** is a moisture sensitive colourless solid.

The structure of the anion of **2** is presented in Fig. 1.† The anion  $\text{S}_3\text{N}_3\text{O}_3\text{F}_4^-$  is closely related to the proposed transition state **1**; due to the attack of  $\text{F}^-$  one of the tetracoordinated sulfur centres [S(1)] is transformed to pentacoordination. The fluorine substituents at S(1) are found, as expected, to form the axial 3-centre-4e<sup>-</sup> FSF bond with rather long SF-distances S(1)–F(1) = 171.8(2) pm, S(1)–F(2) = 166.3(2) pm. N(1), N(3) and O(1) form the equatorial plane surrounding S(1). In **2** the S(1)F-bonds are not equal. This may be explained as an anomeric effect, interaction of the non-bonding electron pairs at N(1) and N(3) with  $\sigma^*[\text{S}(1)\text{F}(1)]$  is much more effective than with  $\sigma^*[\text{S}(1)\text{F}(2)]$ . Interaction between F(1) and S(2) ( $d = 279.0$  pm) and F(1) and S(3) ( $d = 276.8$  pm) (the sum of the van der Waals radii of S and F is 320 pm) might also cause a lengthening of the S(1)F(1) distance. The deviation of the F(1)S(1)F(2) angle from  $180^\circ$  by  $4.3^\circ$  can also be explained by this interaction.

The bonding situation in the anion is shown in Fig. 2.

Anion formation has almost no influence on the S–O, S–F, and S–N bonds at the tetracoordinated centres [140.4(3), 155.5(2), and 155.1(3) pm] compared with 139.6(2), 153.8(2),

and 155.3(2) in  $[\text{NS}(\text{O})\text{F}]_3$ , respectively.<sup>5</sup> The intramolecular S–N bonds to the pentacoordinated S(1) are stretched by about 6–7 pm [N(1)S(1) 162.4(3), N(3)S(1) 161.4(3) pm]; S(1)O(1) [142.0(2) pm] is only slightly influenced.

The  $^{19}\text{F}$  NMR spectrum of **2** in solution‡ shows only two broad singlets at  $\delta$  89.0 and 120.9 in the intensity ratio of 3:1. This is readily explained by a rapid exchange of F(2) between the three sulfur centres. Migration of F(2) must be connected to a strong change in the conformation of **2**; Fig. 3(a–d) show a possible pathway.

The interaction of  $\text{F}^-$  with  $[\text{NS}(\text{O})\text{F}]_3$  is not only a model reaction for the attack of a nucleophile at a tetracoordinated sulfur centre, this reaction might also be regarded a step toward fluoride ion complexation by inorganic heterocycles.

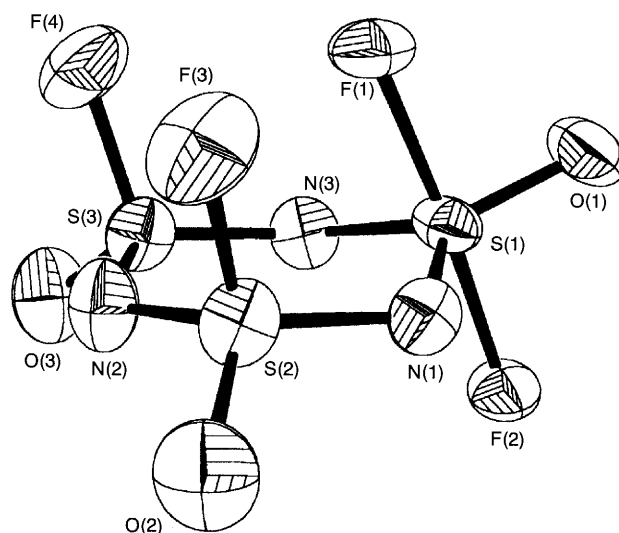
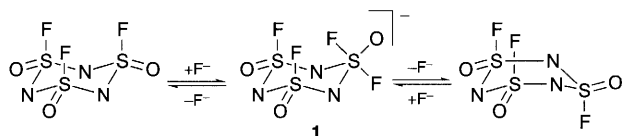
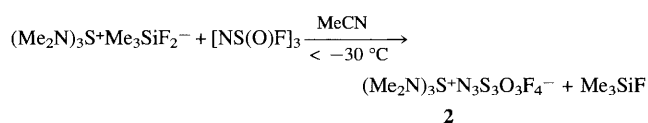


Fig. 1 Structure of the anion with 50% thermal ellipsoids; bond distances (pm) and the bond angles ( $^\circ$ ): S(1)–F(1) 171.8(2), S(1)–F(2) 166.3(2), S(1)–O(1) 142.0(2), S(1)–N(1) 162.4(3), S(1)–N(3) 161.4(3); N(1)–S(2) 152.8(3), S(2)–F(3) 155.8(2), S(2)–O(2) 140.6(3), S(2)–N(2) 155.1(3), N(2)–S(3) 155.1(3), S(3)–F(4) 155.2(2), S(3)–O(3) 140.1(3), S(3)–N(3) 152.9(3), F(1)–S(1)–F(2) 175.7(1), F(1)–S(1)–O(1) 91.9(1), F(1)–S(1)–N(1) 89.8(1), F(1)–S(1)–N(3) 89.5(1), F(2)–S(1)–O(1) 92.4(1), F(2)–S(1)–N(1) 87.5(1), F(2)–S(1)–N(3) 88.7(1), O(1)–S(1)–N(1) 123.2(2), O(1)–S(1)–N(3) 121.5(2), N(1)–S(1)–N(3) 115.2(1), S(1)–N(1)–S(2) 118.7(2), F(3)–S(2)–O(2) 104.2(2), F(3)–S(2)–N(1) 108.7(1), F(3)–S(2)–N(2) 102.5(2), O(2)–S(2)–N(1) 112.5(2), O(2)–S(2)–N(2) 112.4(2), N(1)–S(2)–N(2) 115.4(1), S(2)–N(2)–S(3) 124.9(2), F(4)–S(3)–O(3) 104.8(2), F(4)–S(3)–N(2) 103.1(2), F(4)–S(3)–N(3) 108.2(1), O(3)–S(3)–N(2) 111.8(2), O(3)–S(3)–N(3) 112.3(2), N(2)–S(3)–N(3) 115.7(1), S(3)–N(3)–S(1) 118.4(2).



Scheme 1



Scheme 2

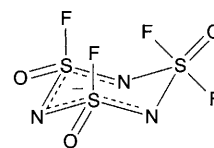


Fig. 2 Bonding situation in  $\text{S}_3\text{N}_3\text{O}_3\text{F}_4^-$

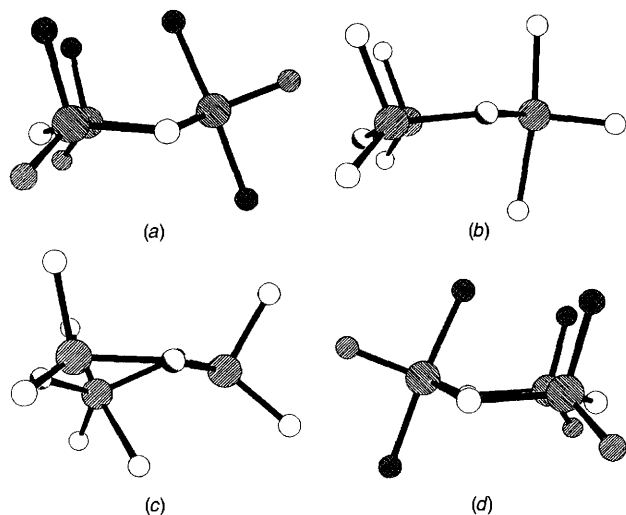


Fig. 3 (a)–(d) Fluoride ion migration in  $S_3N_3O_3F_4^-$

We are grateful to the Fonds der Chemischen Industrie for financial support. We thank Professor Dr U. Behrens and Dr P. G. Watson for helpful discussions.

Received, 27th February 1995; Com. 5101190F

### Footnotes

† Crystal data for TAS<sup>+</sup>  $[[NS(O)F]_2[NS(O)F_2]]^-$ : monoclinic, space group  $P2_1/c$ ,  $a = 1298.7(6)$ ,  $b = 831.1(2)$ ,  $c = 1590.9(5)$  pm,  $\beta = 99.95(3)^\circ$ ,  $U = 1.6913$  nm<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.675$  g cm<sup>-3</sup>,  $\mu = 0.622$  mm<sup>-1</sup>,  $F(000) = 880$ , crystal dimensions  $0.5 \times 0.3 \times 0.15$  mm. 4094 reflections collected with  $2.77 < \theta < 27.6^\circ$ , 3869 unique ( $R_{int} = 0.0283$ ) used in the structural analysis. The data set was collected on a Siemens P4 diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 71.073$  pm) at 153 K. The structure was solved by direct methods. All non-H-Atoms were refined anisotropically. The refinement (215 parameters) converged with  $wR2 = 0.0986$  ( $R1 = 0.0428$ ) and final difference electron density maxima of  $457$  e nm<sup>-3</sup> and minima of  $-395$  e nm<sup>-3</sup>. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ NMR standards: all NMR shifts are reported as positive to high frequency of CCl<sub>3</sub>F.

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