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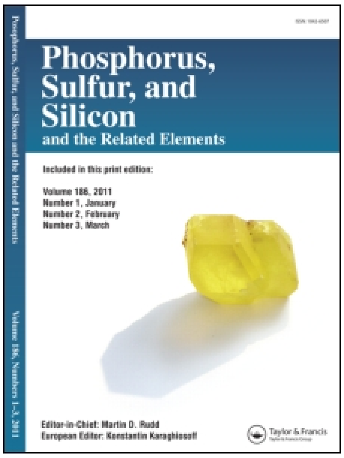

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Fluoride Ion Attack Towards Triazines

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FLUORIDE ION ATTACK TOWARDS TRIAZINES

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Abstract: From the reaction of TAS-fluoride $(Me_2N)_3S^+Me_3SiF_2^-$(1) and fluorotriazines $(FCN)_n(FSN)_{3-n}$ ($n = 1$-3) and sulfanuric fluoride $(FS(O)N)_3$ stable salts with the anions $[(F_2CN)(FCN)_{n-1}(FSN)_{3-n}]^-$ and $[(NS(O)F)_3F]^-$ are isolated. Interaction with $P_3N_3F_6$ gives $(TAS^+)_2$ $P_3N_3F_5NPF_2NPF_2NPF_5^{2-}$, a cyclic-acyclic dianion. From the addition of F^- to $\overline{CF_2-CF_2-N=S=N}$ cyclic bis(imino)fluorosulfinate is formed, from S_4N_4 and 1 TAS^+ $S_3N_3^-$ is obtained.

The generation and chemistry of the "naked" or nearly naked fluoride ion is currently investigated in several groups in inorganic and organic chemistry [1,2]. The classical fluoride ion donor is CsF, but more recently organic salts like "TAS-Fluoride" $(Me_2N)_3S^+Me_3SiF_2^-$ [3], $Me_4N^+F^-$ [4] and $[(Me_2N)_3PNP(NMe_2)_3]^+F^-$ (5) have attracted much interest.

TAS-Fluoride and its trifluoromethyl-derivative CF_3-TAS-Fluoride are readily prepared by the interaction of Me_2NSiMe_3 and SF_4 or CF_3SF_3, respectively:

$$SF_4 + 3\ Me_2NSiMe_3 \longrightarrow \underset{\mathbf{1}}{(Me_2N)_3S^+Me_3SiF_2^-} + 2\ Me_3SiF$$

$$CF_3SF_3 + 2\ Me_2NSiMe_3 \longrightarrow \underset{\mathbf{2}}{CF_3S(NMe_2)_2{}^+Me_3SiF_2^-} + Me_3SiF$$

Interaction of 1 and 2 with fluorotriazines gives cyclic anions, fluoride ion attack exclusively occurs at carbon centres.

$$1 + (FCN)_3 \longrightarrow TAS^+ [(F_2CN)(FCN)_2]^-$$

3

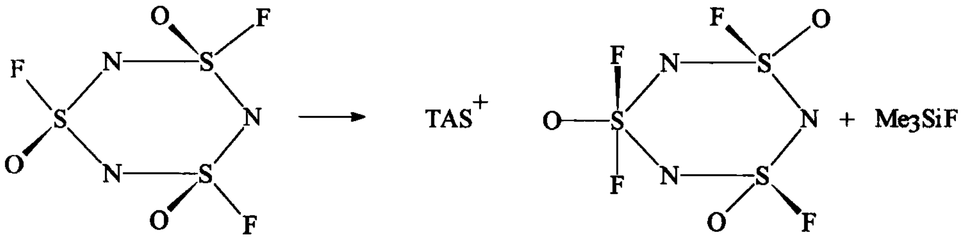
$$1 + (FCN)_2(FSN) \longrightarrow TAS^+ [(F_2CN)(FCN)(FSN)]^-$$

4

$$1 + (FCN)(FSN)_2 \longrightarrow TAS^+ [(F_2CN)(FSN)]^-$$

5

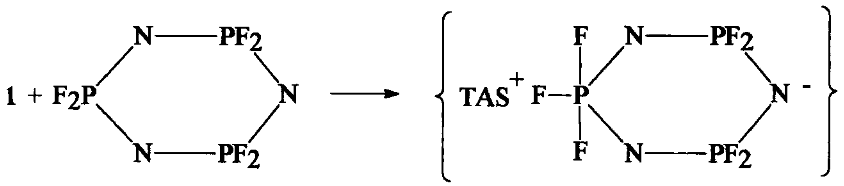
Salts **3** - **5** are readily characterized by ^{19}F- nmr-spectroscopy. The primary product of the interaction with $(NSF)_3$ decomposes, $TAS^+NSF_2^-$ (**6**) is formed. Contrary to this, with $(NS(O)F)_3$ stable $TAS^+ [(NS(O)F)_3F)]^-$ (**8**) is isolated.



7 **8**

In solution, ready exchange of the trans-bonded fluorine between the sulfur centres leads to equivalent cis-bonded fluorines.

A different behaviour is found for $(F_2PN)_3$, isoelectronic with **7**. The primary product is unstable, possibly ring opening occurs and the acyclic anion attacks unreacted starting material.



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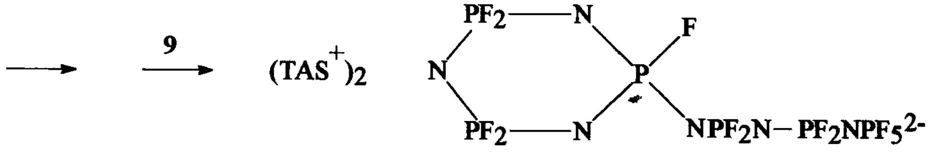
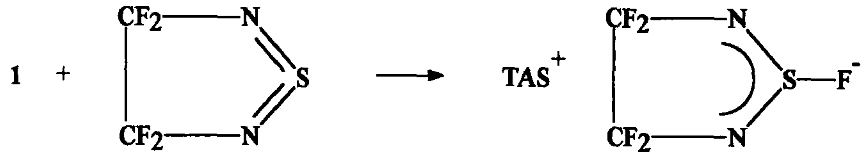


10

With $P_4N_4F_8$ (11) and $P_5N_5F_{10}$ (12) the expected monoanions are formed.

Fluorine ion addition can be extended to other ring-sizes in sulfur-nitrogen chemistry. From the cyclic five membered sulfur diimide 13 the stable bis (imino)fluorosulfinate 14 is formed.



13 **14**

S_4N_4 is decomposed by 1, TAS^+ $S_3N_3^-$ (15) is isolated.

X-ray structures of 2, 4, 6, 8, 10, 11, 14 and 15 are reported, bonding properties and spectroscopic behaviour is discussed.

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