

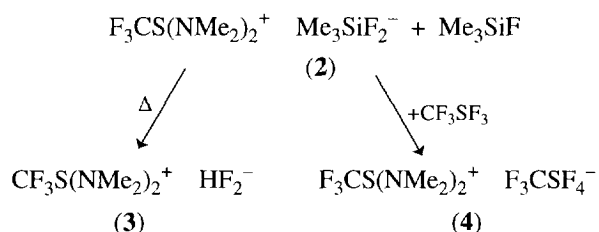
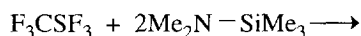
Syntheses and structures of fluorosulfur–nitrogen anions

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TAS-fluoride, $(\text{Me}_2\text{N})_3\text{S}^+ \text{Me}_3\text{SiF}_2^-$ (**1**) [1], and tri-fluoromethyl-DAS-fluoride, $\text{F}_3\text{CS}(\text{NMe}_2)^+ \text{Me}_3\text{SiF}_2^-$ (**2**), obtained according to:



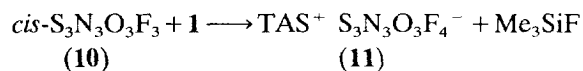
are useful fluoride donors. The HF_2^- salt **3** was isolated from the thermal decomposition while **4** is the ionic isomer to $\text{CF}_3\text{SF}_2(\text{NMe}_2)$ [2].

Cleavage of the Si–N bond in $\text{Me}_3\text{SiNS}(\text{O})\text{F}_2$ gives the $\text{NS}(\text{O})\text{F}_2^-$ ion [3], i.e.

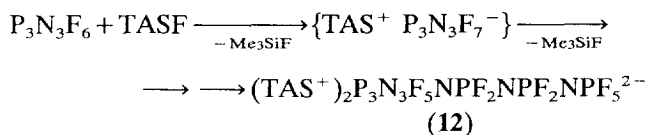


Like its isoelectronic counterpart NSF_3 , the anion of **5** exhibits a rather short S–N bond distance $\{d(\text{SN}) = 142.0(5) \text{ pm at } -160^\circ\text{C}$. Similar short bonds are found in $\text{Hg}[\text{NS}(\text{O})\text{F}_2]_2$ (**6**), $\text{ClHgNS}(\text{O})\text{F}_2$ (**7**), $[-\text{CH}_2-\text{N}(\text{CH}_3)\text{SF}_2 \equiv \text{N}]_2$ (**8**) and $(\text{CF}_3)_3\text{CSF}_2 \equiv \text{N} \cdot \text{AsF}_5$ (**9**).

The trimer $[\text{NS}(\text{O})\text{F}]_3$ exists in two isomeric forms, the *cis/trans* isomerization being catalyzed by the F^- anion [4]. On addition of F^- via **1**, the intermediate involved in this isomerization may be isolated:



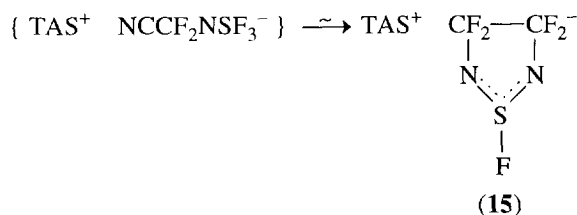
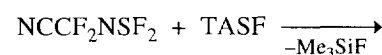
The primary product of F^- addition to $\text{P}_3\text{N}_3\text{F}_6$, which is isoelectronic with **10**, is not stable:



and might be considered as one of the first steps in the anion-catalyzed formation of polyphosphazenes from cyclic oligomers. The TAS salt of the cyclic acyclic phosphazene dianion **12** may be isolated in almost quantitative yield.

The F^- anion adds exclusively to the sulfur centres in the bifunctional systems $\text{NC}-\text{NSF}_2$ and $\text{NC}-\text{NS}(\text{O})\text{F}_2$ with $\text{TAS}^+ \text{NC}-\text{NSF}_3^-$ and $\text{TAS}^+ \text{NC}-\text{NSOF}_3^-$ (**13**) being formed respectively. Similar reactions are possible with CsF slow hydrolysis of $\text{Cs}^+ \text{NC}-\text{NS}(\text{O})\text{F}_3^-$ giving $\text{Cs}^+ \text{NC}-\text{NSO}_2\text{F}^-$ (**14**).

Attack by the F^- anion also occurs at the sulfur atom in $\text{NC}-\text{CF}_2-\text{NSF}_2$, the primary product rearranging quantitatively to the cyclic bis(imino)fluorosulfinate **15**.



The X-ray structures of compounds **2–15** are reported and the bonding properties of the compounds discussed.

References

- [1] W.J. Middleton, US Patent 3 940 402, 1976; *Org. Synth.*, **64** (1985) 221.
- [2] G.H. Sprenger and A.H. Cowley, *J. Fluorine Chem.*, **7** (1976) 333.
- [3] S.J. Chen and E. Cutin, manuscript in preparation.
- [4] O. Glemser, cited in G. Wagner, *Dissertation*, University of Göttingen, 1976.

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