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Recent Investigations on Cyclic Sulfur-Nitrogen-Halogen Compounds*

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Halocyclothiazenes, Oxycyclothiazenes, Ionic Halocyclothiazenes

Cyclic sulfur-nitrogen-halogen compounds constitute a traditional field of inorganic chemistry. Established as long ago as the close of the previous century by DEMARCAY’S preparation of (NSCl)₃, S₄N₃Cl₂, S₃N₂Cl₄, S₃N₂Br-compounds whose SN cyclic structures were only recognized much later - the study of halocyclothiazenes, as these species are now called, has gained considerable impetus during the past quarter of a century.

We divide the halocyclothiazenes into two categories:
1. Cyclothiazenes having the halogen covalently bonded to atoms of the SN ring;
2. Cyclothiazenes with ionic bonding of the halogen to the SN ring.

Of the two possibilities of bonding the halogen, only SX bonds are formed in case 1); cyclothiazenes having an NX bond have not yet been detected. While only fluorine an chlorine derivatives have hitherto been discovered in case 1), bromine and iodine compounds also occur in case 2).

Furthermore, class 1) contains only representatives with an eight-membered ring and various six-membered rings, while class 2) includes a ten-, a seven-, and a five-membered ring. Compared to the halocyclophosphazenes, the variability of ring size is only modest in halocyclothiazenes. An attempt will therefore be given later on to offer an explanation of this difference in behavior.

1. Cyclothiazenes Having Covalently Bonded Halogen

1.1. Compounds containing sulfur with oxidation number +4; coordination number 3

Both types of compound containing chlorine and fluorine can be prepared by chlorination and fluorination, respectively, of S₄N₄. As has long been known, chlorination of S₄N₄ affords (NSCl)₃. On performing the chlorination in CS₂ at 30 °C, an unstable intermediate was detected, presumably...
(NSCl)$_4$, by infrared spectroscopy: this intermediate is readily transformed into (NSCl)$_3$ according to:

\[
\text{CS}_2/30 \, ^\circ\text{C} \quad \xrightarrow{\sim \text{min}} \quad \text{Intermediate "A" [(NSCl)$_4$]}
\]

\[
\xrightarrow{\text{hours}} \quad (\text{NSCl}_3) + \text{NSCl}
\]

\[
\xrightarrow{3 \, \text{NSCl}} \quad (\text{NSCl})_3
\]

The fluorine (NSF)$_3$ analogous to (NSCl)$_3$ is formed from (NSCl)$_3$ by fluorination with AgF$_2$ in CCl$_4$ or by polymerization of NSF. Attempts to build up (NSF)$_4$ from smaller units, e.g. from NSF, were unsuccessful. It appears essential to perform the eight-membered ring, i.e. to start from the eight-membered ring of S$_4$N$_4$ and to fluorinate it with AgF$_2$. During this reaction we observed both (NSF)$_4$ and (NSF)$_3$. Recent confirmation of this result has been provided by low-temperature fluorination of S$_4$N$_4$ (−78 °C, F$_2$ + He) in a nickel tube. The residue in the nickel tube contained 12% of (NSF)$_4$, and the condensation trap contained 81% of volatile (NSF)$_3$. Hence, (NSF)$_4$ is very probably an intermediate in the synthesis of (NSF)$_3$ from S$_4$N$_4$ and fluorine, in line with the above assumptions pertaining to formation of (NSCl)$_3$ on chlorination of S$_4$N$_4$. If the above-mentioned intermediate "A" is (NSCl)$_4$, then it would have arisen, like (NSF)$_4$, directly from the eight-membered ring of S$_4$N$_4$, i.e. by topogenic reaction.

**Structures of (NSCl)$_3$ and (NSF)$_3$:** The structures of (NSCl)$_3$ and (NSF)$_3$ are shown alongside those of NSCl($g$) and NSF($g$) in Fig. 1.

The molecular structures of (NSCl)$_3$ and (NSF)$_3$ are very similar. The halogen atoms are in axial positions and nonbonding electron pairs on the nitrogen and sulfur in equatorial positions. Both rings have a chair conformation (deviations of the planes passing through the N and S atoms 0.18 and 0.23 Å). The SN bond lengths of 1.605 and 1.593 Å are practically equal (SN bond order 1.4). This is interpreted by Dewar’s theory, which has recently gained considerable support from Faraday effect measurements performed by Labarre. The interpretation assumes three islands of delocalized SNS $\pi$-bonds (d $\pi$-$p\pi$ overlapping) arising by way of three-center two electron bonds between one N and two S atoms. Considering the spatial distribution and repulsive action of the nonbonding electron pairs of nitrogen and sulfur, especially on the $\pi$-bonds, then their influence is seen to be a minimum in this arrangement. This might possibly explain the chairtype conformation of the ring and the fact that only the present cis-form and no isomers are found. If this assumption is correct, then we also understand why the polymerization of NSCl and NSF to the trimeric species (NSCl)$_3$ and (NSF)$_3$ is so slow: the (NSX) units have to adopt a mutual arrangement conducive to formation of this cis-ring structure.

Fig. 2 shows the structure of (NSF)$_4$. The puckered, compact structure of the molecule is a consequence of the almost identical bond angles at the nitrogen and sulfur (very similar orbital hybridization) compared to the chair-shaped six-membered ring of (NSF)$_3$. But only two F-atoms have axial positions. The (NSF)$_4$ ring does not
possess an appreciable amount of delocalized \( \pi \)-bonds: two different SN bond lengths of 1.54 Å (bond order 1.7) and 1.66 Å (SN bond order 1.1) are present. This must be due mainly to steric constraints. Let us consider the sequence F\(_1\) F\(_2\) S\(_1\)-N\(_1\)-S\(_2\)-N\(_2\) in the structure. The S\(_1\)-N\(_1\) and N\(_1\)-S\(_2\) bonds are stereochemically different (see Fig. 2c). Hence the S\(_1\)-N\(_1\) bond length will be increased by the repulsive action of the nonbonding electron pair of the atom F\(_1\) on the nonbonding electron pair of the atom N\(_1\), while the N\(_1\)-S\(_2\) bond length will be shorter in the absence of any significant electron repulsion.

Comparison of the cyclic structures of (NSF\(_3\))\(_3\) and (NSF\(_4\)) suggests that the six-membered ring should be the more stable owing to electron delocalization.

This conclusion is confirmed by the chemical properties. Thus (NSF\(_3\))\(_3\) reacts, e.g. with AsF\(_5\) and SbF\(_5\), according to

\[
(\text{NSF})_3 + \text{MF}_5 \rightarrow \text{N}_3\text{S}_3\text{F}_2^+\text{MF}_6^-; [\text{M} = \text{As, Sb}]
\]

forming the salts N\(_3\)S\(_3\)F\(_2\)^+MF\(_6\)^-. The salts are stable in the solid state. Under the same conditions, (NSF\(_4\))\(_4\) yields a mixture of N\(_3\)S\(_3\)F\(_2\)^+MF\(_6\)^- and NS\(^+\)MF\(_6\)^- according to

\[
(\text{NSF})_4 + \text{MF}_5 \rightarrow \text{N}_3\text{S}_3\text{F}_2^+\text{MS}^+\text{MF}_6^-
\]

Chemical properties: A number of interesting chemical properties of (NSCl\(_3\)), (NSF\(_3\)), and (NSF\(_4\)) deserve mention. While (NSCl\(_3\))\(_3\) reacts with SO\(_3\) to give (NSOCl\(_3\))\(_3\) via an addition product, and thus opens a pathway from cyclothiazenes to the oxocyclothiazenes, (NSF\(_4\)) and SO\(_3\) afford the oxide S\(_3\)N\(_2\)O\(_5\), which was first obtained from S\(_4\)N\(_4\) and SO\(_3\).

On reaction with BCl\(_3\) and SCl\(_2\), (NSCl\(_3\)) furnishes pale yellow hygroscopic crystals of the salt N(SCl\(_2\))^+BCl\(_6^-\). The interesting horseshoe-shaped cation N(SCl\(_2\))^+ is planar and has a cis-configuration, see Fig. 3. The SN distance corresponds to a bond order of 1.7–1.8. The large SNS angle of 149.2° strongly suggests participation of the nonbonding electron pair on nitrogen in the SN-\( \pi \)-bond.

Ring expansion is observed when (NSCl\(_3\)) reacts with the radical (CF\(_3\))^+NO or with Hg[(CF\(_3\))^+NO] to give N\(_4\)S\(_4\)[ON(CF\(_3\))^+NO], whose SN ring structure can be compared with that of (NSF\(_4\)). As in the latter, two different SN bond lengths (1.56 Å; N = 1.6 and 1.62 Å; N = 1.3) and similar angles are found in the ring (Fig. 4).

We now come to structural types having sulfur.
with oxidation number $+4$, $+6$ and coordination number 3, 4.

1.2. Compounds containing sulfur with oxidation number $+4$, $+6$; coordination number 3, 4

The structural types occurring in this category form only six-membered rings. Ready interconversion of the three types, as already demonstrated by the reaction of $(NSCl)_3$ with $SO_3$ and substantiated below, becomes understandable on comparison of the angles at the N and S atoms and of the SN bond lengths (Fig. 5). The angles at the N atoms are practically identical, ranging between 123.2 and 123.8°. The same applies to the angles at the S atoms which vary between 112.6 and 113.4°. The SN bond lengths differ by only 0.045 Å. Hence, similar orbital hybridization, mainly $sp^2$ and $sp^3$, can be assumed at the N and at the S atoms in order to rationalize the possible exchange of an SX for an SOX group.

Compounds having mixed oxidation numbers of sulfur ($+4$, +6) and differing coordination numbers (3, 4) are obtained by reaction of $S_3N_2O_2$ and liquid chlorine according to

$$S_3N_2O_2 + Cl_2 \rightarrow (NSCl)(NSCl)_2 \rightarrow (NSCl)_3$$

The corresponding partly and per-fluorinated compounds are accessible from species 1 and 2 by treatment with suitable fluorinating agents such as $AgF_2$ or $SbF_3$. Only a low yield of 2 is obtained by the method just described. However, derivatives of 2 are obtainable in good yield by the follow route.

$$\text{(NSOF)}_2 + 2CH_3SH + 2N(CH_3)_3 \rightarrow \text{(NSOF)}_2(\text{NSO}) \cdot [\text{HN(CH_3)_3}]$$

5 can also be prepared by an alternative route, viz. reaction of $N_3S_3O_2F_2NH_2$, whose synthesis will be considered later, with $SOCl_2$ according to

While no stereoisomers have been found for the ring systems $(NSX)_3$ and $(NSOX)(NSX)_2$, the NMR spectrum of the compounds $(NSOF)(NSX)$ indicates the presence of isomers.
Table I. Compounds of type
(NSOX)(NSX)2, (NSOX)2(NSX)32–35.

<table>
<thead>
<tr>
<th>Isomers</th>
<th>Mp. or bp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NSOCl)(NCS)2</td>
<td>m.p. 110 °C</td>
</tr>
<tr>
<td>(NSOCl)(NFS)2</td>
<td>colorless cryst.</td>
</tr>
<tr>
<td>(NSOF)(NCS)2</td>
<td>XMR mass sp.</td>
</tr>
<tr>
<td>(NSOF)(NFS)2</td>
<td>b.p. 34°/0.01 T</td>
</tr>
<tr>
<td>(NSOCl)(NSCI)</td>
<td>mass.-spect.</td>
</tr>
<tr>
<td>(NSOCl)(NSF)3</td>
<td>mass.-spect.</td>
</tr>
<tr>
<td>(NSOF)(NCS)2</td>
<td>b.p. 30–32°/0.1 T</td>
</tr>
<tr>
<td>(NSOF)3(NSF)</td>
<td>b.p. 21–23°/0.1 T</td>
</tr>
</tbody>
</table>

As will be seen a little later, the so-called cis-trans isomers are also present in (NSOF)3. We understand why isomers are found in (NSOF)3 but not in (NSF)3 if we assume a weaker repulsive action of the S = 0 nonbonding electron pairs of nitrogen and sulfur in (NSOF)3, but not in (NSOF)(NSF)3. Therefore other isomers than the cis-form are also favorable. This property is efficient in (NSOX)3(NSX) but not in (NSOX)(NSX)2.

It is certain that no rings larger than the hexacycles have yet been found in (NSOX)3, despite numerous attempts to prepare larger ones. This is a remarkable result in view of very large mass–spect. (e.g. (NSOCl)3, (NPX)3 species isoelectronic to the (NSOX)3 compounds. Let us consider the structural formulae (NPX)3 and (NSOX)3.

The s-bonds are shown in the two formulae (approximate sp3 hybridization of the orbitals on P and S, nearly sp2 hybridization of the orbitals on N). Each ring atom then possesses one further electron. These are utilized to form three three-center two-electron π-bonds; see also MO schemes. Three islands of delocalized π-bonds result, two different orbitals (dxy and dz2) being required at each P and S atom for the π-bonds oriented in different directions (Fig. 6).

In the (NSOX)3 ring, however, sulfur forms an exocyclic π-bond with oxygen, utilizing either the dxy or dz2 orbital. According to the MO model this electron pair resides in the nonbonding orbital and thus has some perturbing effect on the SN π-bond. Furthermore in the larger NPX3 species the PNP angle exceeds 120°, which is explained by participation of the nitrogen nonbonding electron pair in the PN π-bond, i.e. with an overlapping of this Np-orbital and the empty dπ*-orbital of the phosphorus. Obviously a similar overlapping which leads to an additional stabilization of the ring does not occur in higher (NSX)- or (NSOX)-rings as may be deduced from the structure of (NSF)3 with an SNS-angle of 123.9°.36

**Preparation of (NSOCl)3 and (NSOF)3:** (NSOCl)3 is best prepared according to Kirsanov37 by thermolysis of ClSO2NPCl3. Both α- and β- (NSOCl)3 are isolated from the reaction product. The former has been shown by X-ray structural analysis38 to have all the chlorine atoms axial and the oxygen atoms equatorial (Fig. 7). The uniform SN bond length of 1.571 Å (SN bond order 1.5) can be interpreted by the model with three islands of delocalized π-bonds which we have just considered. The structure of β-(NSOCl)3 is unknown.

So far (NSOF)3 can only be obtained from α-(NSOCl)3 by fluorination39–41 (preferably with SbF5) as a so-called cis-trans isomeric mixture in 80% yield. The desired compound is accompanied by 10% of (NSOF)3(NSOCl) and (NSOF)(NSOF)3 as colorless liquids. Both substances are formed as a
mixture of three isomers each, which can be completely separated by analytical gas chromatography and characterized by their $^{19}$F-NMR spectra. Assuming these partially fluorinated rings to have a chair shape, such as occurs in the structure of the starting material, solid a-(NSOCl)$_3$, then other conformations are also conceivable. However, they can be ruled out with a high degree of certainty on the basis of the experimental results – sharp bands corresponding to the three isomers in the gas chromatography, only three signals in the NMR spectrum. Nevertheless it is possible, that other conformations are only existent at lower temperatures and/or that the transformation energy to the more stable conformations is low.

The three isomers of (NSOCl)$_2$(NSOF)$_2$ are depicted in Fig. 9, assuming the ring to be planar.

Moreover, numerous sulfur oxide difluorides such as CsNSOF$_2$, Hg(NSOF)$_2$)$_2$, (CH$_3$)$_3$Sn-NSOF$_2$, B(NSOF)$_3$, have been found to decompose with liberation of (NSOF)$_3$ and/or polymeric (NSOF)$_2$, in some cases even at room temperature. It has not been established whether the product (NSOF)$_3$, obtained in very small amounts and detected by mass spectrometry is an eight-membered ring.

Reactions and derivatives of (NSOCl)$_3$ and (NSOF)$_3$: In contrast to the cyclotriphosphazenes, (NSOCl)$_3$ generally undergoes ring opening rather than substitution on reaction with nucleophilic reagents. (NSOF)$_3$ is more stable than (NSOCl)$_3$. This difference in stability is clearly seen in the behavior of the two compounds towards water. The latter is hydrolyzed as far as imidosulfamide HN(SO$_2$NH$_2$)$_2$; the intermediacy of trisulfimide has recently been established by formation of Ag$_3$(NSO$_2$)$_3$ with silver ions.

(NSOF)$_3$ is very resistant to attack by water. It is hydrolyzed to amidosulfonate and NH$_3$ by boiling sodium hydroxide solution. On heating of (NSOF)$_3$ with water in the presence of Ph$_4$PCl, the salt 9 is precipitated, in accord with

$$\text{(NSOF)}_3 + \text{H}_2\text{O} + \text{Ph}_4\text{PCl} \xrightarrow{100 \ ^\circ \text{C}} \text{Ph}_4\text{P}^+[(\text{NSO)}_3\text{F}_2\text{O}]^- + \text{HF} + \text{HCl}$$

The species 1, which occurs in the cis- and trans-form, is the first anion of an oxohalocyclotriazene ring. Remarkably, no such anion has yet been observed for the isoelectronic halocyclophosphazenes.

Among the derivatives, we can distinguish triply, doubly, and singly substituted species having the general formula N$_3$S$_3$O$_3$R$_3$, N$_3$S$_3$O$_3$X$_2$R, and N$_3$S$_3$O$_3$X$_2$R. Only two derivatives of (NSOCl)$_3$, namely N$_3$S$_3$O$_3$Cl$_5$CH$_3$ and N$_3$S$_3$O$_3$Cl(C$_6$H$_5$)$_2$, have been described. There is one example of the trisubstituted species with R = morpholino and one with R = C$_6$H$_5$. The latter is accessible both directly from PhSOCl azide and from (NSOF)$_3$ and benzene in the presence of aluminium chloride according to

$$\text{PhSOCl} + \text{N}_3 \xrightarrow{-30 ^\circ \text{C, CH}_3\text{CN}} \text{PhSOn}_3$$

$$\text{(NSOF)}_3 + 3\text{C}_6\text{H}_5 \xrightarrow{\text{ACl, mp.} 177 ^\circ \text{C}} \text{N}_3\text{S}_3\text{O}_3(\text{C}_6\text{H}_5)_3$$
Two substances having different melting points were obtained, which were interpreted as isomeric compounds. Further derivatives containing C₆H₅ and amines such as morpholine, 2,6-dimethylmorpholine, piperidine, and pyrrolidine have already been described in several reviews.

Starting from [NSOF]₃ and NH₃ in ether, we prepared a series of derivatives shown in Table II.

We have studied the reactions of (NSOF)₃ with primary and secondary amines in some detail. Literature reports that only disubstitution products are formed could not be confirmed. Instead, tri-, di-, and mono-substitution products were obtained with secondary amines. In the following, no attempt will be made to discuss all the compounds we have synthesized, but merely to describe the principles we have found to govern substitution with the aid of selected examples.

We found that secondary amines only exchange the disubstituted derivatives occurring only in R = CH₃, C₂H₅. In the same solvent diethylamine affords 3 in 85% yield.

Primary and secondary amines give trisubstituted compounds on heating to 60 °C with (NSOF)₃ in a glass bomb.

At lower temperatures primary amines and (NSOF)₃ lead to 1:1 mixtures of the amino products and the corresponding hydrofluorides. These adducts, which have not yet been found with the isoelectronic cyclophosphazenes, can be formulated on the basis of their IR spectra as:

![Cyclophosphazene structure]

The free amines are liberated from the adducts by reaction of an ethereal suspension with hydrogen chloride. In the structural formulae, the formula of the free amines is shown separated from the addend [H₂NR]. The amines are more acidic than the corresponding amines of cyclotriphosphazenes (from NMR data). In contrast to the reaction of (NSOF)₃ with secondary amines, no disubstituted products with primary amines as H₂NCH₃, H₂NC₂H₅ were observed.

The anion [NSOF]⁻: Reaction of (NSOF)₃ with methyl alcohol in the presence of trimethylamine does not afford the methanol derivative but a tetramethylammonium salt, according to

\[(NSOF)₃ + CH₃OH + 2 N(CH₃)₂ → -20 °C \rightarrow (NSOF)₃ + CH₃₂OH + [N(CH₃)₂H]F \quad (17)\]

which contains the anion described in connection with the hydrolysis of (NSOF)₃, i.e. [NSOF]⁻. The free acid can be isolated in water by the action of a cation exchanger, and evaporation yields the mono-hydrate [NSOF]·H₂O, which exhibits a pKₐ value of +1.7 aqueous solution. Addition of silver carbonate to the aqueous solution precipitates the silver salt [NSOF]Ag⁺. Reaction with alkyl iodides proceeds according to

\[N₃S₃O₃F₂ + RI \rightarrow CH₂Cl₂\]

Table II. Derivatives of [NSOF]₃

<table>
<thead>
<tr>
<th>Compound</th>
<th>Property</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NSOF]₃</td>
<td>b.p. 65 °C/15 T</td>
<td>47, 48, 55</td>
</tr>
<tr>
<td>[NSOF]₃ + 2 NHR₂</td>
<td>ether</td>
<td>40 °C</td>
</tr>
<tr>
<td>[NSOF]₃ + 2 HN(C₃H₅)₂</td>
<td>heptane</td>
<td>60 °C</td>
</tr>
<tr>
<td>[NSOF]₃ + C₂H₅NH</td>
<td>CH₂CN</td>
<td>40 °C</td>
</tr>
<tr>
<td>[NSOF]₃ + C₆H₁₀NH</td>
<td>CH₂CN</td>
<td>44 °C</td>
</tr>
</tbody>
</table>

At higher temperatures, too, only monosubstitution products were obtained in non-polar solvents, the disubstituted derivatives occuring only in traces. When acetonitrile is used as solvent, partial dissubstitution takes place even in the presence of an excess of (NSOF)₃. In the same solvent diethylamine affords 3 in 85% yield.

Primary and secondary amines give trisubstituted compounds on heating to 60 °C with (NSOF)₃ in a glass bomb.

At lower temperatures primary amines and (NSOF)₃ lead to 1:1 mixtures of the amino products and the corresponding hydrofluorides. These adducts, which have not yet been found with the isoelectronic cyclophosphazenes, can be formulated on the basis of their IR spectra as:

![Cyclophosphazene structure]
On the basis of the $^{19}$F-NMR spectrum ($F_\beta$ doublet; $\delta_{FS} = -64.2$ ppm; $F_a$ doublet of quartets $\delta_{SF} = -62.7$ ppm; $J_{FF} = 3.75$ Hz) the following structure is proposed:

\[
\begin{array}{c}
\text{F} \quad \text{S} \quad \text{N} \quad \text{CH}_3 \\
\beta \quad \alpha \\
\end{array}
\]

(\(\text{NSOF}_2\))$_2$(\(\text{RNSO}_2\)) has two asymmetric sulfur-atoms (which are marked by * in the Eq. below) and two enantiomeric pairs are expected. But as the fluorine-atoms in (\(\text{NSOF}_2\))$_2$(\(\text{RNSO}_2\)) are in a cis-position, only the two enantiomers, 3R, 5R- and 3S, 5S-3,5-difluoro-1,1,3,5-tetraoxo-1,3,5,2,4,6-cyclotrithiatriazene, can be formed by alkylation.

We could demonstrate the optical activity of (\(\text{NSOF}_2\))$_2$(\(\text{RNSO}_2\)) by $^{19}$F-NMR spectroscopy in the presence of butanol-2. When (\(\text{NSOF}_2\))$_2$(\(\text{RNSO}_2\)) is reacted with butanol-2 in a nonpolar and inert solvent, the alcohol first coordinates to the sulfur adjacent to the $\alpha$-fluorine-atom thus forming a diastereomeric pair (equation). As a result all resonance signals for $F_\alpha$ and $F_\beta$ are doubled.

Also for the resulting substituted product two singulett instead of one is observed for the left-over $F_\beta$.

This is to our opinion the second proof of optically active inorganic ring compounds, where the origin of optical activity is an atom of the ring.

A reaction analogous to the one we have considered takes place on treatment of \(\text{N}_3\text{S}_3\text{O}_3\text{F}_2\text{N}(\text{CH}_3)_2\) with $\text{CH}_3\text{OH}$ to form a salt.

\[
\text{N}_3\text{S}_3\text{O}_3\text{F}_2\text{N}(\text{CH}_3)_2 + \text{CH}_3\text{OH} + 2 \text{N}(\text{CH}_3)_2 \xrightarrow{\text{CH}_3\text{CN} \text{, } 60 \degree \text{C}} \text{[N}_3\text{S}_3\text{O}_3\text{FN}(\text{CH}_3)_2]\text{O}^\text{+}[\text{N}(\text{CH}_3)_3]\text{H}\text{F} \quad (19)
\]

The two N atoms adjacent to the $\text{SO}_2$ group of this anion are no longer equivalent. Its silver salt was prepared as described above and reacted with $\text{CH}_3\text{I}$ according to

Since no coupling is observed in the $^{19}$F-NMR spectrum of 1, the $\text{CH}_3$ group cannot be adjacent to the $\text{S(O)F}$ group. In this case the dimethylamino group exerts an electron-releasing effect and thus strengthens the $\text{N-C}$ bond of the $=\text{N-CH}_3$ group. This behavior should be generally valid for mono-substituted derivatives of $\text{N}_3\text{S}_3\text{O}_3\text{F}_2\text{O}^\text{+}$.

If $\text{N}_3\text{S}_3\text{O}_3\text{F}_2\text{O}^\text{+}\text{Ag}^\text{+}$ is subjected to reaction with organometallic halides, such as (\(\text{CH}_3\))$_2\text{MCl}$ (M = Si, Sn), then the organometallic cation adds to an O atom of the anion.

\[
\begin{array}{c}
\text{Ag}^\text{+} \quad \text{CH}_3\text{I} \\
\text{CH}_2\text{Cl}_2 \quad \text{AgI} \\
\text{Ag}^\text{+} \quad \text{CH}_3\text{Cl}_2 \\
\text{CH}_2\text{Cl}_2 \quad \text{AgCl} \\
\text{M} = \text{Si, Sn}
\end{array}
\]
The structure given is supported by NMR spectra. The F atoms are chemically equivalent, and no coupling with fluorine is seen in the Si-NMR spectrum. Moreover, the chemical shift lies in the range characteristic of Si-O bonds. The behavior observed for the organometallic halides is due to the favorable energetics of the Si-O and Sn-O bond.

1.3. Compounds with sulfur having oxidation number +6, +4; coordination number 4, 2

On irradiation of CISO2NSO

\[
2\text{CISO}_2\text{NSO} \rightarrow \text{CISO}_2\text{NSO} + \text{Cl}_2
\]

mp. 105-108°C

\[
\begin{array}{c}
\text{N} \\
\text{S} \\
\text{O} \\
\text{N}
\end{array}
\]

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array}
\]

a new type of halocyclotriazene was recently synthesized which is very sensitive to hydrolysis.

2. Cyclothiazenes with Ionic Halogen Bonding

So far four types of such compounds have been found, viz. S$_3$N$_2$Cl$^+$ X$^-$ [X = Cl, Br], S$_3$N$_2^{2-}$ (X)$_2$O$^-$, S$_4$N$_3^-$ X$^-$ (X = F, Cl, Br), and S$_6$N$_4^-$ 2X$^-$ (X = Cl, Br). All the cations have an S-S bond in the ring.

2.1. S$_3$N$_2$Cl$^+$ Cl$^-$, obtained as orange-red crystals, e.g. from S$_3$N$_4$ and S$_2$Cl$_2$$_{11}$, or (NSCl)$_2$ and S$_2$Cl$_3$$_{57}$, is shown by X-ray structure analysis to contain a five-membered chair-shaped ring bearing one covalently bonded and one ionically bonded Cl atom.

It is certainly inappropriate to deduce a delocalized $\pi$-bonding system in the ring from the widely differing SN bond lengths, which range between 1.543 and 1.615 Å, as has recently been attempted by various authors. The bromide S$_3$N$_2$Br$_2$ having the same composition as the chloride has recently been isolated from S$_3$N$_4$ and bromide. Whether it has the same structure as the chloride remains to be established.

Reactions of S$_3$N$_2$Cl$_2$. It has long been known that, on heating to 80–90 °C in a vacuum, S$_3$N$_2$Cl$_2$ is converted into greenish-black S$_3$N$_2$Cl, which in turn yields S$_3$N$_3$Cl at 150 °C. The variously bonded Cl atoms in S$_3$N$_2$Cl$_2$ can be consecutively replaced. For instance, treatment with halosulfonic acids furnishes the derivatives S$_3$N$_2$Cl$^+$ (SO$_2$F)$^-$, (S$_3$N$_2$Cl)$^+$ (SO$_2$Cl)$^-$, (S$_3$N$_2$F)$^-$ (SO$_2$F)$_2$ and (S$_3$N$_2$F)$^+$ (SO$_2$Cl)$_2$.$^{24}$

2.2. S$_4$N$_3^-$ X$^-$: The most important compound is S$_4$N$_3$Cl, which is accessible in various ways. The classical method starts from S$_3$N$_4$ and sulfur halides$^{11,63}$ such as S$_2$Cl$_2$ or SOCl$_2$, but direct approaches also lead to the desired product.$^{64}$

\[
3 \text{S}_2\text{Cl}_2 + 2 \text{LiN}_3 \xrightarrow{\text{CCl}_4} 4 \text{S}_3\text{N}_3\text{Cl}
\]

Ice-cold solutions of S$_4$N$_3$Cl furnish orange-yellow S$_4$N$_3$Br on reaction with KBr, and brick-red S$_3$N$_3$I with KI.$^{65}$ S$_4$N$_3$F · 1.5 HF can be prepared from the chloride and HF.$^{66}$

Although the structure of the S$_4$N$_3^-$ cation has been known for a long time, it will now be briefly described.$^{67}$ The molecular cation is planar, and the relatively short and equal SN bond lengths (1.55 Å, bond order 1.7), the unusually large bond angle at the nitrogen, and the UV/visible spectra suggests a delocalized $\pi$-electron system, which does not include the S-S bonds. However, some authors do assume that the $\pi$-electron bond system also extends over the S-S bridge.
Properties of S$_4$N$_3$X: Both S$_4$N$_3$Cl and S$_4$N$_3$Br undergo ring expansion to give S$_4$N$_4$ and the gaseous monomers NSCl and NSBr, respectively, on thermal decomposition. This technique has led to the first detection of monomeric NSBr according to

$$2 \text{S}_4\text{N}_3\text{Cl} \xrightarrow{120 \degree \text{C}} \text{S}_4\text{N}_4 + 2 \text{NSCl} + 2 \text{S} \quad (24)$$

$$2 \text{S}_4\text{N}_3\text{Br} \xrightarrow{90 \degree \text{C}} \text{S}_4\text{N}_4 + 2 \text{NSBr} + 2 \text{S} \quad (25)$$

$$4 \text{S}_4\text{N}_3\text{I} \xrightarrow{0-30 \degree \text{C}} 3 \text{S}_4\text{N}_4 + 2 \text{I}_2 + 4 \text{S} \quad (26)$$

No monomeric NSI is formed on decomposition of S$_4$N$_3$I. A remarkable reaction of S$_4$N$_3$Cl with triphenylphosphine affords, inter alia, the following interesting substance:

$$\left[\text{C}_6\text{H}_5\text{P} - \text{N-S=N-P(C}_6\text{H}_5\text{)}\right]^6 \quad \text{mp. 101-104\degree C (decomp.)}$$

2.3. $S_4N_2X$ ($X = Cl, Br$): The greenish-black crystals of S$_4$N$_3$Cl are formed in 80% yield from S$_4$N$_4$Cl and dry formic acid. A recent structural determination of the chlorosulfonic acid derivative of S$_4$N$_3$Cl surprisingly revealed that S$_3$N$_2$Cl is a salt-like compound S$_6$N$_4$Cl$^-$2Cl$^-$.

The cation S$_6$N$_4$Cl$^-$ consists of two planar S$_2$N$_2$ rings. The S-S bonds in the ring are somewhat longer than an S-S single bond; the S-S contacts between the rings are shorter than the van der Waals distances, but longer than the SS contacts in S$_4$N$_4$. The bicyclic cation S$_4$N$_4$Cl$^-$ is special kind of structural type, having a four-center interaction between pairs of S atoms in two identical rings with delocalized $\pi$-bonding. If S$_4$N$_4$ is regarded as a 6 $\pi$-Hückel ring, then the S$_4$N$_4$Cl$^-$ ring should comprise two aromatic 1,2-dithiolium cations linked via pairs of S atoms in a four-center two-electron bond.

**Reaction:** On reaction of S$_6$N$_4$Cl with AlCl$_3$ or FeCl$_3$, the SS bonds of the two S$_2$N$_2^+$ rings are ruptured to give [S$_2$N$_2$Cl]$^+$MCl$_3^-$ (M = Al, Fe).

Littie is known about S$_4$N$_3$Br. Since no recent studies are available, it remains an open question whether the bromide bears a structural resemblance to the chloride.

2.4. Compounds with sulfur having oxidation number $+4$, $+2$; coordination number 3, 2

The brick-red compound S$_6$N$_3$Cl was already obtained by Demarcay on chlorination of S$_4$N$_4$, and its preparation has recently been reproduced (mp. 165 °C, dec.). It can be formulated as a cyclic compound containing covalently bonded chlorine; however, ionic bonding cannot be entirely ruled out.

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12. A. Meuwesen, Ber. dtsch. chem. Ges. 64, 2311 [1881].


T. P. LIN and O. Glemser, to be published.


An experience similar to this one was first applied for organic substances by RABAN and MISLOW, Tetrahedron Letters 1965, 4249.


D. L. WAGNER, H. WAGNER, and O. GLEMser, to be published.


Added in proof: Via-trans isomerisation occurs to give an equilibrium where (NSO)₃ is or its derivatives are treated with Fe₃⁺ ions as catalyst. The catalytic effect can easily be explained by an S₃N₄-attack of Fe₃⁺ ions with inversion of the sulfur atom. This reaction also provides references that the different structure of these isomers is due to a different arrangement of the substituents rather than to a different shape of the (SN)₄-ring. This result would be in good agreement to a proposed structure of β-(NSO)₃, which was derived by comparing the experimental dipole moment of β-(NSO)₃ with calculated moments.