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Account

Acyclic and heterocyclic tellurathianitrogen compounds: a review on recent publications

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Dedicated to Professor Dr L.M. Yagupolskii, Kiev, on the occasion of his 80th birthday

Abstract

Intensive and broad studies of chemical reactions concerning $X(NSO)_2$ ($X = Se$, Te), $X_2Te(NSO)_2$ ($X = F$, Cl, Br) and $X'_2Te(NSC)_2X'_2$ ($X' = F$, Cl) provides besides new interesting compounds also valuable intermediates for a better understanding of reaction pathways in chalcogen–nitrogen chemistry. Based on the mechanism elucidated for the formation of $[\overline{SeSeNSN}^+]_2$-$[MF_6^-]_2$ or $[Cl\overline{SeSeNSN}][SbCl_6^-]$ from $Se(NSO)_2$ and MF_5 ($M = As$, Sb, Nb) or $Se(NSO)_2$ and $SbCl_5$ respectively an interpretation of the reaction sequences of other procedure such as $Te(NSO)_2 + SbCl_5$ or e.g. $Cl_2Te(NSO)_2$ with MCl_3 ($M = Ga$, Al, Fe) could be provided. It was proved that a desulfurisation process is responsible for transforming $Cl_2Te(NSO)_2$ and derivated products in the presence of MCl_3 into $[(Cl_2Te)_2N^+][MCl_4^-]$ and $[Cl\overline{TeSNSN}^+][MCl_4^-]$. The results gained in these studies led directly to the synthesis of $[\overline{SSNNN}^+][TeCl_5^-]$, the first ring with three cummulated nitrogen atoms. In order to learn more about the possible structures of $Cl_2Te(NSN)_2TeCl_2$, careful and intensive investigations proved the formation of the cage $N[Te(Cl)NSN]_3$. A thorough reinvestigation of the original synthesis of the cage yielded S_4N_4 as an additional product and by varying the stoichiometry between the educts $TeCl_4$ and $(CH_3)_3SiNSNSi(CH_3)_3$ important intermediates could be detected and isolated. They provided the base for understanding the consecutive steps during the procedure between educts and to yield products. Fluorine substituted acyclic, cyclic, neutral and ionic chalcogen–nitrogen compounds are described as well as relationship among themselves and related compounds. Interesting and valuable correlations are presented and evaluated. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Acyclic; Heterocyclic; Thiatelluranitrogen-chemistry; Reaction steps; Intermediates; 1,2-Dithia-3,4,5-triazolium; Fluoro; Chloro; Tellurate; Gallanate; Aluminate; Ferrate; Bis(sulfinylamido); Trifluoroacetate; Trifluoromethylsulfonate; TelluriumIV; Fluoride; Chloride; Bromide; Sulfurdiimidato; Ditellurium; $N[Te(X)NSN)_3$, $X = F$, Cl; Interpretation; Multistep reactions; Desulfurisation

1. Introduction

The origin of S–N chemistry has been determined since 1835 by synthesizing and characterizing new compounds, clearing their formulas and the arrangement of atoms by studying their chemical and physical properties. Later on, research was extended to determinations of molecular and electronic structures by extensive spectroscopical investigations. Electron rich S–N heterocycles were classified as Hückel aromatic systems and MO calculations were carried out based on structural parameters and spectroscopical data [1].

Discussions on possible intermediates, reaction steps and sequences including targeted synthesis confirming postulates were largely omitted.

Therefore, one should not be surprised, when Oakley [2] in his review article in 1988 pointed to this gap and came to the following conclusion:

> "Even now many fundamental issues remain unresolved. The observation that iodine oxidizes $S_3N_3^-$ to S_4N_4, for example, still represents a veritable Pandora's box for those who would venture a mechanistic interpretation."

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An interpretation of the mentioned reaction is given in comparison with transformation of S_6 into S_8 [3] in Scheme 1.

The fragmentation of the almost planar, zick zack SN-Chain [3c] may also occur in solution via radical fragments to S_2N_2 which dimerize to S_4N_4. Chalcogen–nitrogen chemistry especially of selenium and tellurium was highly stimulated by the synthesis of the rather small molecules $Se(NSO)_2$ [4], $Te(NSO)_2$ [5,6] and $X_2Te(NSO)_2$ (X = F, [7,11] Cl, [7,8,11] Br) [11]. They proved to be very important educts for interpreting complex multistep reactions [20].

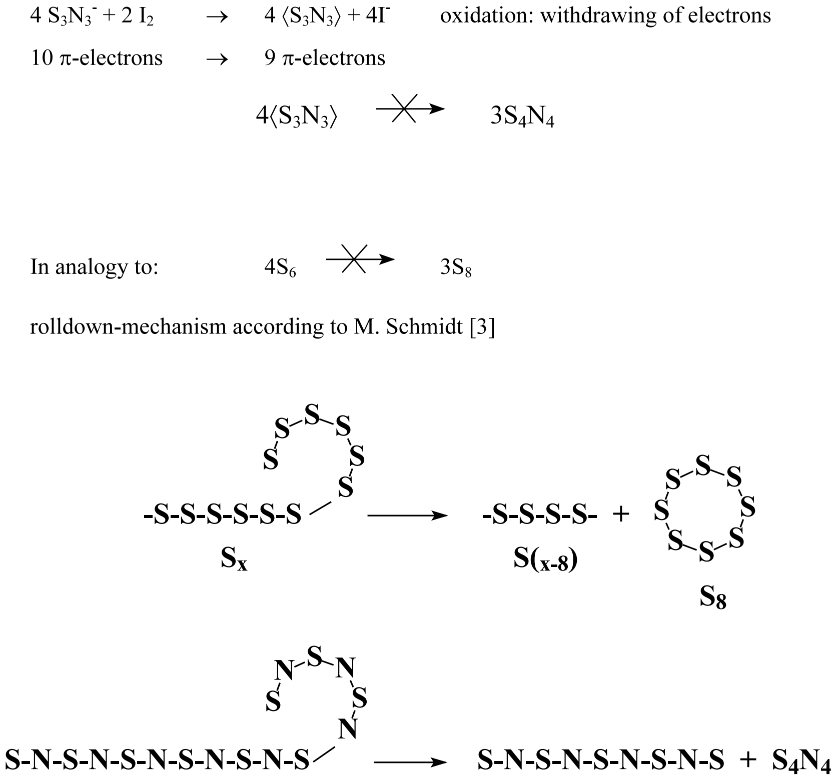
1.1. Reactions of $X(NSO)_2$ (X = Se, Te) with fluorinated and chlorinating Lewis-acids and interpretation of their pathways

Bis(sulfinylamido)selenium was prepared in good yields and preparative amounts from Se_2Cl_2 and $(CH_3)_3SiNSO$ and formed with strong, fluorinated Lewis-acids such as MF_5 the dication $[\overline{SeSeNSN}^+]_2$-$[MF_6^-]_2$ (M = As, Sb, Nb), which reacted with Cl_2 or Br_2 to the corresponding halogenated five membered monocations $[X\overline{SeSNSN}^+][MF_6^-]$ [4]. Chlorinating Lewis-acids such as $SbCl_5$ yielded as the final product $[Cl\overline{SeSeNSN}^+][SbCl_6^-]$. This result strongly suggests that the chlorination-process proceeds via the mentioned dication and is the final step as demonstrated in Scheme 2. All attempts to isolate a chlorinated intermediate e.g. $Cl_2Se(NSO)_2$ or synthesizing it failed. Postulated reaction steps and intermediates could be proved by:

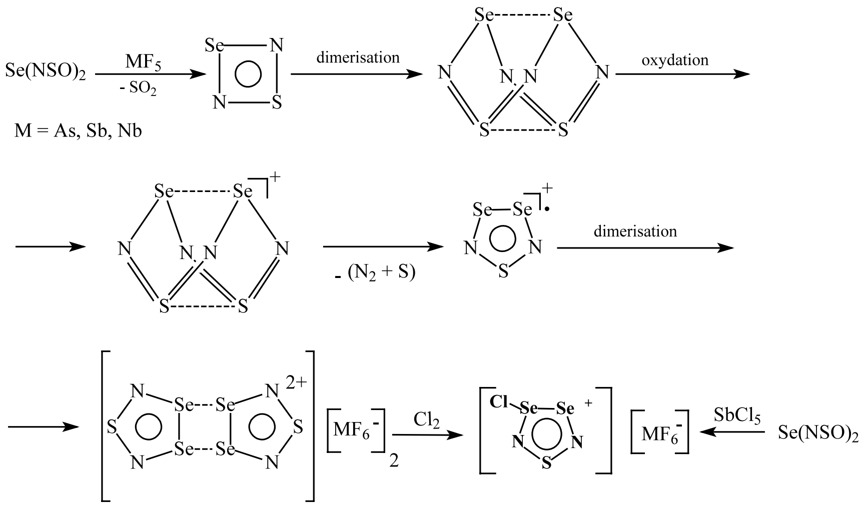
1. Isolating $(\overline{SeNSN}\cdot TiCl_4)_n$ and estimating SO_2 quantitatively [4].
2. Synthesis and X-ray structure of $Se_2S_2N_4$ by Laitinen and coworkers [10].
3. Synthesis and X-ray structure of $[FTeSe\overline{S_2N_4^+}]$ [7].
4. Prove of $[\overline{SeSeNSN}^{+\bullet}]$ by ESR spectroscopy [4].

The reaction with chlorinating reagents such as $SbCl_5$, $SeCl_4$, $POCl_3$, PCl_5 followed the same procedure. The process $Se(NSO)_2$ plus $MF_5 \rightarrow [\overline{SeSeNSN}^+]_2[MF_6^-]_2$ is the first in chalcogen–nitrogen chemistry where all postulated intermediates could either be isolated or detected (see Scheme 2). It serves as a base for explaining similar reactions. The corresponding $Te(NSO)_2$ [5,8] is best made by a metathetical process between para-halogens from $Te(SCF_3)_2$ and $Hg(NSO)_2$. It is very sensitive to moisture and thermically less stable than $Se(NSO)_2$, but it formed with $SbCl_5$ the polymer $[Cl_3Sb\cdots Cl\cdots Te(Cl)SNSN]_n$ as shown in Scheme 3. Its polymeric structure has been published elsewhere [6].

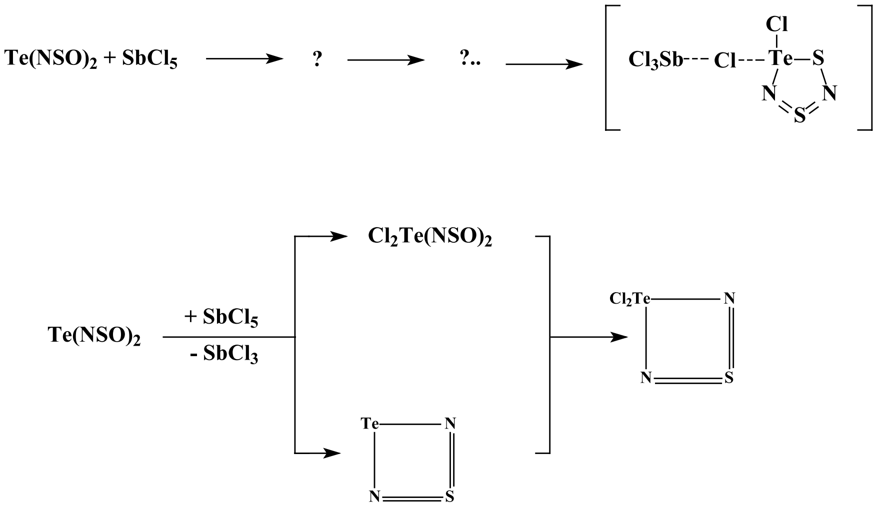
Once again one has to answer the question about its formation. Chlorination has to occur at an earlier step, as no tellurium containing dication $[\overline{TeTeNSN}^+]_2$ has been detected up to now and also attempts to synthesize it failed. Based upon the mechanism elucidated for



Scheme 1.



Scheme 2.



Scheme 3.

the reaction of $Se(NSO)_2$ and MF_5 or $SbCl_5$ (see Scheme 2), the chlorination has to take place either as a first or a second step as shown in Scheme 3.

1.2. The dominating role of $Cl_2Te(NSO)_2$ and $Cl_6Te_2N_2S$ in tellurathianitrogen chemistry

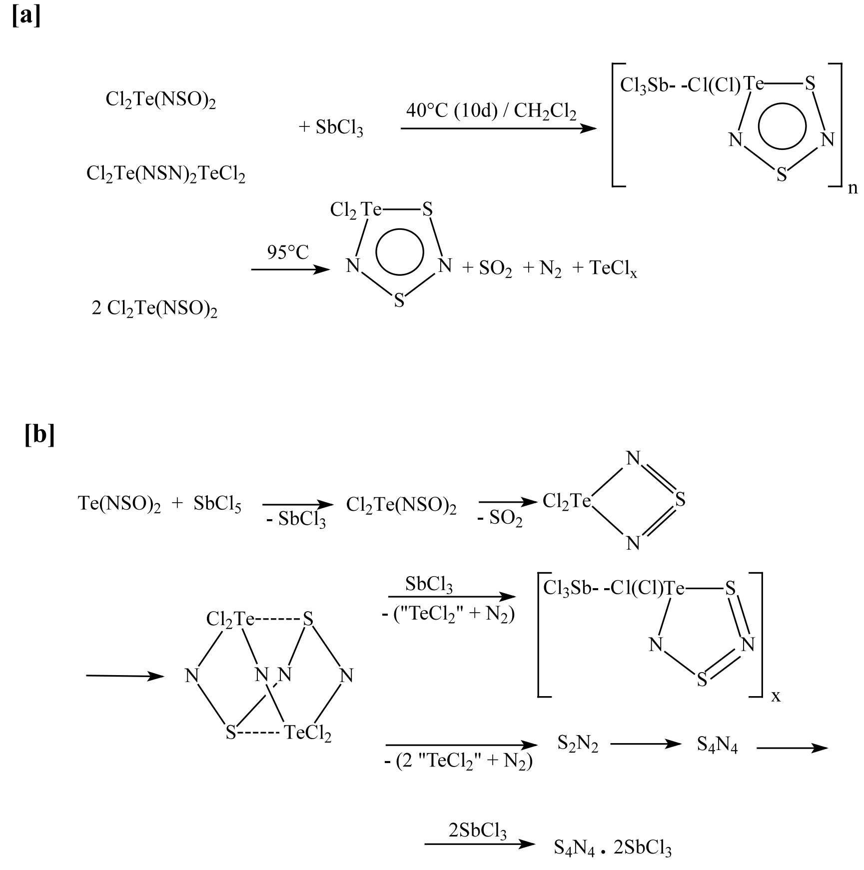
An answer was provided by synthesizing $Cl_2Te(NSO)_2$ [7,8,11,12] and studying its chemical reactivity including $Cl_2Te(NSN)_2TeCl_2$. Accordingly, the process should run through the intermediate $Cl_2\overline{TeNSN}$ provided in Scheme 4b. Particularly because $Cl_2Te(NSO)_2$ formed with $SbCl_3$ the polymer and its pyrolysis yielded $Cl_2\overline{TeSNSN}$ the non-coordinated ring which did not react with $SbCl_3$ to the polymer. From all this one can deduce that adduct formation is not the last step and $Cl_2\overline{TeSNSN}$ [8] is not an intermediate. Coordination of $SbCl_3$ takes place at an earlier stage (see Scheme 4a). In this Scheme 4, the existence of the four membered ring and its dimer, important intermediates, have not been proved yet.

The eight membered ring was prepared by several methods [7] which are demonstrated in Scheme 5. The bicyclus [7,8,11,12], which appears here for the first time, is an important synthon in Te–N heterocyclic chemistry and is formed by metathetical Cl–NSO change, chlorination of $Te(NSO)_2$, $Cl_2Te(NSO)_2$, $Cl_2Te(NSN)_2TeCl_2$, $F_2Te(NSO)_2$ and from $TeCl_4$ and $F_2Te(NSO)_2$.

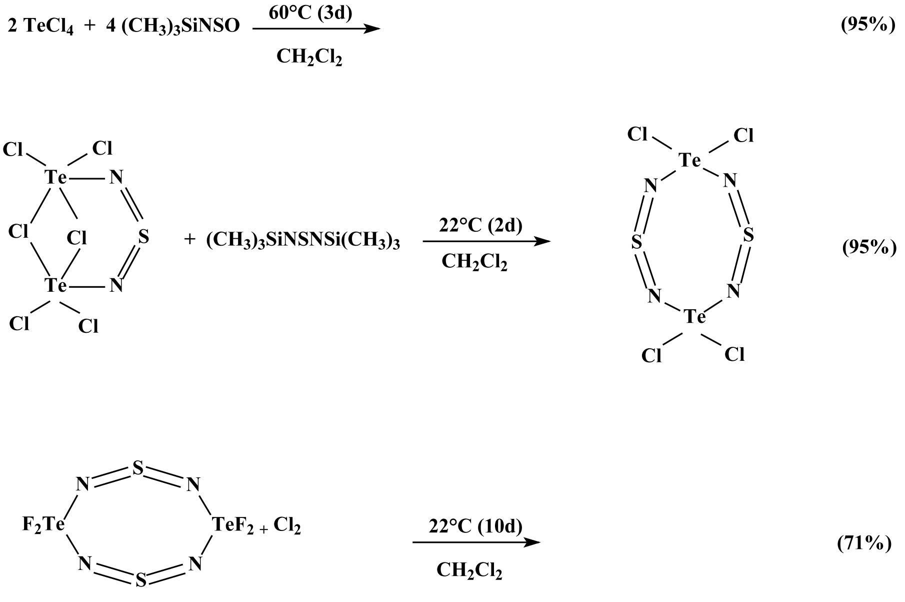
The formation of $Cl_6Te_2N_2S$ takes place via Cl_3TeNSO, which condenses intermolecularly with SO_2 elimination to unstable $Cl_3TeNSNTeCl_3$ rearranging to the bicyclus. The Cl–NSO metathesis was proved by treating $Cl_2Te(NSO)_2$ with CF_3SCl giving at −20 °C (3 days) quantitatively CF_3SNSO and the bicyclus [18]. These reactions are summarized in Scheme 6.

The structure of the eight membered ring is still an unsolved problem as an X-ray structure analysis could not be accomplished because of lack of suitable crystals. According to known synthesis and chemical reactivity all structures presented in Fig. 1 have to be considered. For each form good argumentation will be provided.

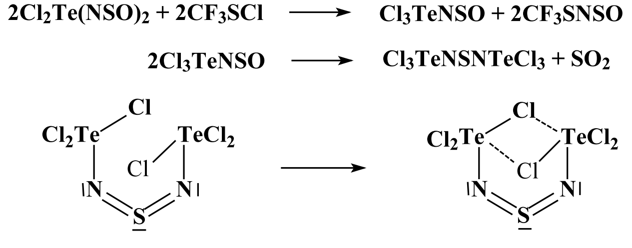
The existence of $Cl_2Te(NSN)_2TeCl_2$ was proved by



Scheme 4.



Scheme 5.



$$2Cl_2Te(NSO)_2 + 2CF_3SCl \longrightarrow Cl_3TeNSO + 2CF_3SNSO$$

$$2Cl_3TeNSO \longrightarrow Cl_3TeNSNTeCl_3 + SO_2$$

Scheme 6.

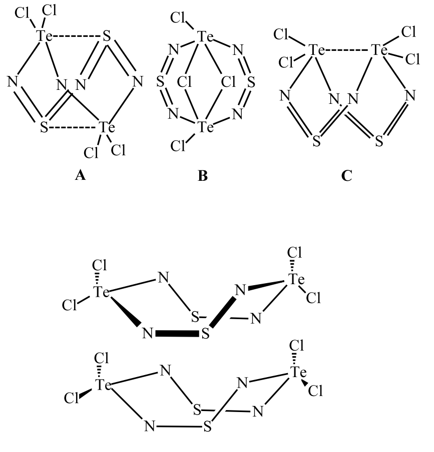


Fig. 1. Possible structures of $Cl_2Te(NSN)_2TeCl_2$.

several synthesis, analytical and spectroscopical data, but without structural proof. Evidence for the postulated intermediate $Cl_2\overline{TeNSN}$ is still missing.

1.3. Attempts to detect $Cl_2\overline{TeNSN}$

While $Se(NSO)_2$ formed with $TiCl_4$, the polymer $(\overline{SeNSN}\cdot TiCl_4)_n$ [4] which is isostructural with $S_2N_2\cdot TiCl_4$ [13], neither $Te(NSO)_2$ nor $Cl_2Te(NSO)_2$ yielded with $TiCl_4$ a comparable substance, but only insoluble mixtures which could not be characterized. Therefore, other non-chlorinating Lewis-acids such as MCl_3 (M = Ga, Al, Fe) were reacted with $Cl_2Te(NSO)_2$. In all cases, the adduct $Cl_5Te_2N\cdot MCl_3$ was isolated and characterized. With traces of $GeCl_4$ or CF_3SCl the basic compound Cl_5TeN was obtained, which is known in the literature and was made from $TeCl_4$ and $[(CH_3)_3Si]_3N$ [14].

Spectroscopical investigations and elemental analysis proved that the adduct was ionic and has the formula $[(Cl_2Te)_2N^+][GaCl_4^-]$. The cation might have in accordance with the corresponding selenium derivative $[(Cl_2Se)_2N^+][AsF_6^-]$ [15] a sickle like structure.

On stoichiometrical terms a desulfurisation process should take place with ClSN elimination. But neither ClSN nor its trimer $(ClSN)_3$ could be detected in the reaction mixture. When $AlCl_3$ or $FeCl_3$, respectively was employed besides $[(Cl_2Te)_2N^+][MCl_4^-]$ a sulfur containing product could be isolated. For M = Fe red–brown crystals became available. The X-ray structure analysis proved a five membered ring form [18] for the cation with structural parameters being in good agreement with literature data [16].

In all reactions with MCl_3, after isolating the insoluble $[(Cl_2Te)_2N^+][MCl_4^-]$, in the red coloured filtrate $[Cl\overline{TeSNSN}^+][MCl_4^-]$ could be detected. For the formation of both cations $[(Cl_2Te)_2N^+]$ and $[Cl\overline{TeSNSN}^+]$ explanations are needed.

1.4. Reaction steps leading to the formation of $[(Cl_2Te)_2N^+]$ and $[Cl\overline{TeNSNS}^+]$

The desulfurisation of the educts takes place via the central molecule $Cl_6Te_2N_2S$ as an intermediate which is formed by metathetical reactions. When $Cl_2Te(NSN)_2$-$TeCl_2$ or $Cl_2Te(NSO)_2$ are used, then MCl_3 yields via 2Cl–NSN- or Cl–NSO-metatheses $Cl_3TeNSNTeCl_3$ or Cl_3TeNSO and unstable $Cl_2MNSNMCl_2$ or Cl_2MNSO as intermediates. Each single step and an understandable desulfurisation processes using $GaCl_3$ are summarized in Scheme 7. This problem becomes even more complex, if results of Passmore et al. [17] are also considered. They obtained a dimeric form of $[(Cl_2Te)N^+][AsF_6^-]$ when reacting Cl_5Te_2N and AsF_5 in SO_2. This dimeric structure was proved by an X-ray structural investigation. According to these informations, the central four membered ring of the cation contains four exocyclic bonded and four bridging chlorine atoms (see Fig. 2). A dimeric form for the cation with $[MCl_4^-]$ (M = Ga, Al, Fe) as counterions can be excluded on the base of IR- and Raman investigations. While the monomeric cation including Cl_5Te_2N shows ν(Te–N) in the range of 900–600 cm^{-1}, the dimer exhibits absorptions only at 518 and 395 cm^{-1}, which were assigned to ν(Te–N) [18].

The question 'how was the sulfur containing cation generated?' also has to be answered. As ClSN or $Cl_3S_3N_3$ could not be isolated they must be educts for the formation of $[Cl\overline{TeNSNS}^+]$. Under the reaction conditions (70 °C in CH_2Cl_2) an equilibrium between $Cl_3S_3N_3$ and ClSN exists, and as also shown in Scheme 8, the chain like dimer starts the formation of the five membered ring via $Cl_2\overline{TeN{=}S{=}N}$ which dimerizes and decomposes according to Scheme 4b. The amounts of $TeCl_4$, necessary to start the reaction, can be provided by decomposition of $Cl_6Te_2N_2S$ into $TeCl_4$ and $Cl_2\overline{TeNSN}$. The latter joins the described procedure. Additionally $TeCl_4$ is also formed from the decomposition products $TeCl_2$ and Cl_2 (see also Scheme 4b).

1.5. Preparation of [SSNNN$^+$]: the first ring with three cummulated nitrogens

These results provoke the question 'how does $Cl_3S_3N_3$ react with $TeCl_4$ at 70 °C in CH_2Cl_2?'. The outcome of this experiment was a completely unexpected result. A crystal mixture was obtained and bright yellow as well as red crystals could be isolated mechanically. Elemental analysis, IR-, Raman-, mass-spectra and X-ray structural determinations showed that the bright yellow crystals were $[S_4N_3^+][Te_2Cl_9^-]$ [19] and the red ones consisted of a positive charged five membered ring with three consecutive linked nitrogen atoms [9,20]. In more than 150-year-old SN-chemistry this is the first example and in addition it is stable at 20 °C. The reaction is shown in Scheme 9 and structures in Fig. 3. Meanwhile, the $S_2N_3^+$-cation was also made and fully characterized by reacting $Cl_3S_3N_3$ with $HgCl_2$ in CH_2Cl_2 [24].

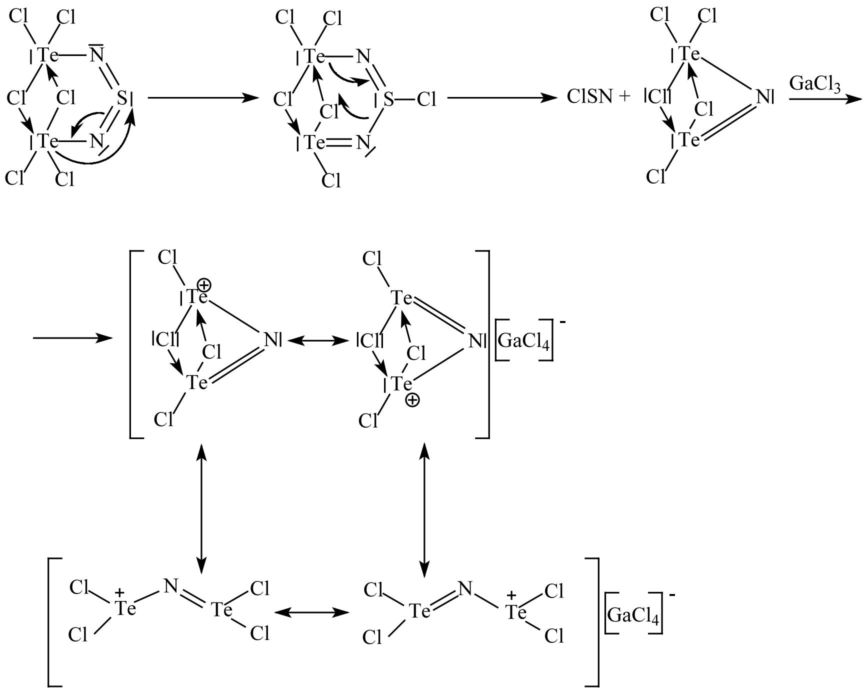
This surprising and sensational result proves how complicated chalcogen–nitrogen chemistry can be. Such results are encouraging but have to be explained as well. It must be made plausible how a six membered ring with an alternated arrangement of sulfur and nitrogen atoms is converted into a cationic five membered ring with three cummulated nitrogen atoms. The answer is finally rather simple.

Coordination of $TeCl_4$ to the planar three Cl-atoms of $Cl_3S_3N_3$ distorts the almost planar S_3N_3-ring to an unsymmetrical $(Cl_3S)_3{\equiv}N_3$ prism, which eliminates SCl_2 providing ionic $[S_2N_3^+][TeCl_5^-]$ as illustrated in Scheme 10. The cation is stabilized by two resonance structures. As SCl_2 remains in equilibrium with S_2Cl_2 and chlorine, the formation of $[S_4N_3^+][Te_2Cl_9^-]$ can be explained by partial ring opening of $Cl_3S_3N_3$ forming the linear trimer which is trapped in a cyclo addition process by S_2Cl_2, eliminating SCl_4 and yielding tetrathiatriazenium chloride [1]. The final product $[S_4N_3^+][Te_2Cl_9^-]$ is obtained by reaction between S_4N_3Cl and 2 mols $TeCl_4$ [20].

With reference to the reaction of Cl_5Te_2N with AsF_5 in SO_2 yielding $[(Cl_2Te)_2N^+]_2[AsF_6^-]_2$ as carried out by Passmore et al. [17] also $[(Cl_2Te)_2N^+][GaCl_4^-]$ was treated in liquid SO_2 with AsF_5. Instead of the expected dimeric cation, a completely new compound was synthesized. On the base of total elemental analysis, IR-, Raman-, mass-, ^{19}F- and ^{125}Te-NMR spectra, the formula $[(Cl_2Te)_2AsF^{2+}][GaCl_4^-][AsF_6^-]{\bullet}AsF_5$ was assigned to the colourless, amorphous compound. Additional proof for the cation formation is the evolution of NF_3, which was detected by IR-spectroscopy as a volatile reaction product [18].

1.6. Comparison of the reaction courses between $Te(NSO)_2$ plus $SbCl_5$ and $Cl_2Te(NSO)_2$ plus MCl_3 (M = Ga, Al, Fe)

At first sight, these two reactions might have nothing in common. But knowing that $SbCl_5$ chlorinates $Te(NSO)_2$ to $Cl_2Te(NSO)_2$ being reduced to $SbCl_3$, one has to consider a 1:1 reaction between $Cl_2Te(NSO)_2$ with non-chlorinating Lewis-acids e.g. MCl_3 and $SbCl_3$.



Scheme 7.

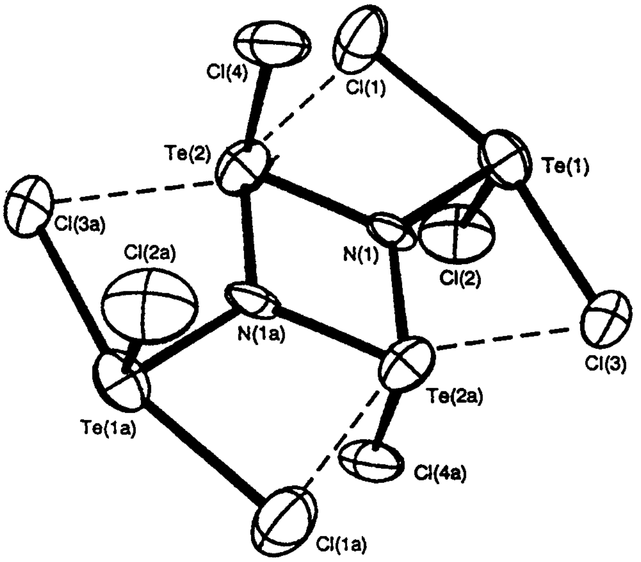


Fig. 2. Structure of the $Te_4N_2Cl_8^{2+}$ cation showing intracationic contacts (a indicates symmetry equivalent atoms at $1.0-x$, $-y$, $-z$). Bond distances (Å) and angles (°): Cl(1)–Te(1) 2.51(2), Cl(2)–Te(1) 2.27(2), Cl(3)–Te(1) 2.50(2), Te(1)–N(1) 2.05(4),Te(2)–N(1) 2.04(4), Te(2)–N(1a) 1.98(4), Te(2)–Cl(4) 2.30(2), Cl(1)–Te(1)–Cl(3) 158.9(5), Cl(2)–Te(1)–Cl(3) 91.8(6), Cl(1)–Te(1)–Cl(2)88.7(6), Cl(4)–Te(2)–N(1) 95(1), Te(1)–N(1)–Te(2) 124(1), Te(2)–N(1)–Te(2a) 108(2), Te(1)–N(1)–Te(2a) 127(2), Cl(1)–Te(1)–N(1) 80(1), Cl(3)–Te(1)–N(1) 79(1), Te(2)–N(1)–Te(2)–N(1) 0.0. The transannular Te···Te separatioj is 3.252(2) Å. Shortest intracationic contacts (< 3.81 Å): Te(2)···Cl(1) 2.881(12), Te(2a)···Cl(3) 2.905(10). Shortest intercation–anion and intercation–SO_2 contacts (< 3.6 Å): Te(1)···Fe(1) 2.65(5), Te(1)···Fe(3) 3.16(5), Te(1)···Fe(7) 3.41(9), Te(1)···Fe(8) 3.18(8), Te(1)···Fe(10) 3.22(9), Te(1)···Fe(11) 3.46(6), Te(2)···Fe(5) 3.00(6), Te(2)···Fe(9) 3.12(8), Te(1)···O(2) 3.24(6), Te(2)···O(1) 2.88(4).

In both cases, the five membered ring $Cl_2\overline{TeSNSN}$ is part of final product, forming with MCl_3 ionic $[Cl\overline{TeSNSN}^+][MCl_4^-]$ and with $SbCl_3$ polymeric $Cl_3Sb\cdots Cl\text{–}\overline{Te(Cl)SNSN}$.

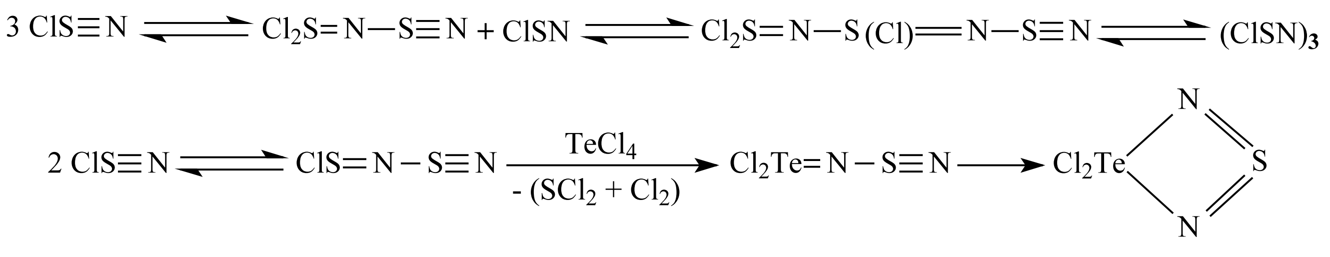
Until the formation of the postulated intermediate $Cl_2\overline{TeNSN}$ the reaction courses are different (see Scheme 4) but later they are comparable with the exception that the final product $Cl_3Sb\cdots Cl\text{–}\overline{Te(Cl)SNSN}$ is not formed from $SbCl_3$ and $Cl_2\overline{TeSNSN}$. Another remarkable difference is the formation of S_4N_4 as the main product, which was isolated as $S_4N_4{\cdot}2SbCl_3$ and characterized by an X-ray structure analysis (see section 5) [25]. The formation of small amounts of an ionic or polymeric product $Cl_5Te_2N{\cdot}SbCl_3$ cannot be ruled out. These observations show once again how sensitive tellurium–chalcogen–nitrogen compounds act on educts and reaction conditions.

2. Intermediates on the way to the $N[Te(Cl)NSN]_3$ cage

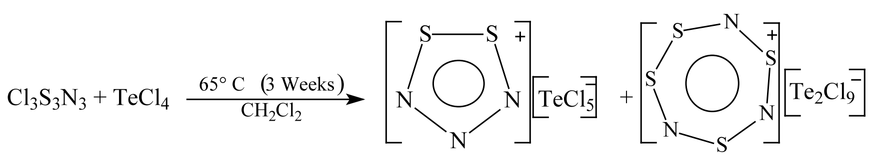
Special attention was dedicated to possible structures for the eight membered ring $Cl_2Te(NSN)_2TeCl_2$. The orange compound dissolves in (tetrahydrofuran) THF and freshly prepared solutions are green-coloured. After 2 days, the colour changes to orange and a yellow precipitate is deposited. Pursuing this phenomenon by ^{125}Te-spectroscopy showed a δ(Te) signal for the freshly prepared green solution at 1200 ppm. After 2 days, two signals at 1200 and 1281 ppm are observed. After 5 days, the solution turns red and the amount of precipitate increases.

The signal at 1281 ppm disappears and a new one is observed at 1736 ppm, which was assigned to $TeCl_4$ ($\delta = 1736$ [21]). The yellow, crystalline precipitate was proved to be, according to spectroscopical investigations and an X-ray structure determination, the already known cage $(ClTeNSN)_3N$ [22] coordinated by 2 mols of THF (see Fig. 4). All data were in good agreement with published results.

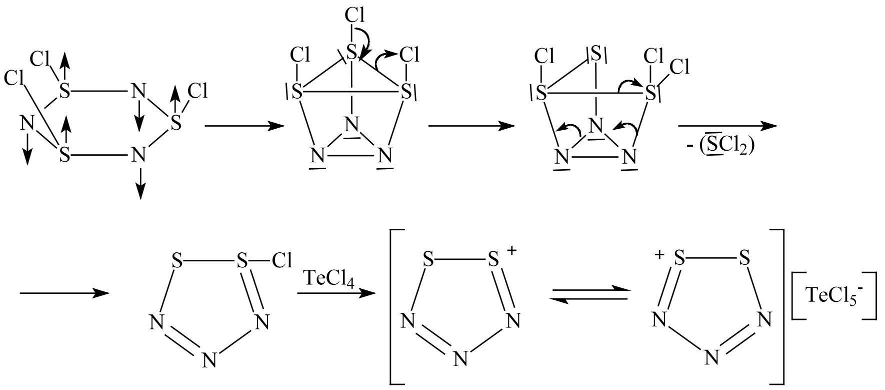
In order to prove the formation of $TeCl_4$ besides a ^{125}Te-NMR evidence, additional chemical reactions are



Scheme 8.



Scheme 9.



Scheme 10.

carried out. The decomposition of $Cl_2Te(NSN)_2TeCl_2$ in THF was studied on a preparative scale in the presence of MCl_3 (M = Ga, Al, Fe). Therefore, solutions of $Cl_2Te(NSN)_2TeCl_2$ and MCl_3 in THF were stored at room temperature. After 24 h, the formation of yellow crystals is observed in all cases and additionally red crystals ($AlCl_3$), as well as dark green ($FeCl_3$) and orange ($GaCl_3$) highly viscous oils are obtained, respectively. Besides spectroscopical and analytical data, the X-ray structure determination with red single crystals provided the structure shown in Fig. 5 for $[AlCl_2^+][TeCl_5^-]$. The cation is coordinated by four molecules of THF and the anion by one.

Elucidating this homogeneous decomposition of $Cl_2Te(NSN)_2TeCl_2$ in THF, it was necessary to reproduce the original synthesis for $(ClTeNSN)_3N$ [22] and to pay attention to intermediates and additional products. Reacting $TeCl_4$ with $(CH_3)_3SiNSNSi(CH_3)_3$ in THF, it was possible to isolate S_4N_4 for the first time as a side product. When 2 mols of $TeCl_4$ were treated in CH_2Cl_2 at − 50 °C with $(CH_3)_3SiNSNSi(CH_3)_3$ an almost quantitative amount of $Cl_6Te_2N_2S$ was yielded. In a reaction carried out separately the bicyclus formed with 1 mol $(CH_3)_3SiNSNSi(CH_3)_3$ at 20 °C (2 days) 90% $Cl_2Te(NSN)_2TeCl_2$.

Moreover, it could be demonstrated that $Cl_2Te(NSN)_2TeCl_2$ in CH_2Cl_2 decomposed in the presence of $(CH_3)_3SiNSNSi(CH_3)_3$ at 60 °C (10 days) to $(ClTeNSN)_3N$. A precise stoichiometrical consideration of the last step pointed to the fact, that a substitution of 2Cl-atoms in $Cl_2Te(NSN)_2TeCl_4$ by the divalent-NSN-moiety with elimination of $(CH_3)_3SiCl$ is not possible, despite the proof of its formation by IR-spectroscopy among the volatile products.

Similarly to the decomposition in pure THF, $Cl_2Te(NSN)_2TeCl_2$ separates as shown in Scheme 11 ClSN and $TeCl_4$. The latter forms, according to the steps $2TeCl_4 + (CH_3)_3SiNSNSi(CH_3)_3 \rightarrow Cl_3TeNSNTeCl_3 \rightarrow Cl_6Te_2N_2S$, the starting material $Cl_2Te(NSN)_2TeCl_2$ with elimination of $(CH_3)_3SiCl$. The formation of $(ClTeNSN)_3N$ may take place as illustrated in Scheme 11. The overall reaction is: $2Cl_2Te(NSN)_2TeCl_2 \rightarrow N[Te(Cl)NSN]_3 + ClSN + TeCl_4$.

The migration of a nitrogen atom into the centre of the cage molecule still remains obscure. An answer to this problem might help also to learn more about the possible structures of $Cl_2Te(NSN)_2TeCl_2$, which are pictured in Fig. 1. Form **A** is a most suitable structure whereby the already discussed ClSN-elimination yields an unsaturated fragment, which adds a second mol

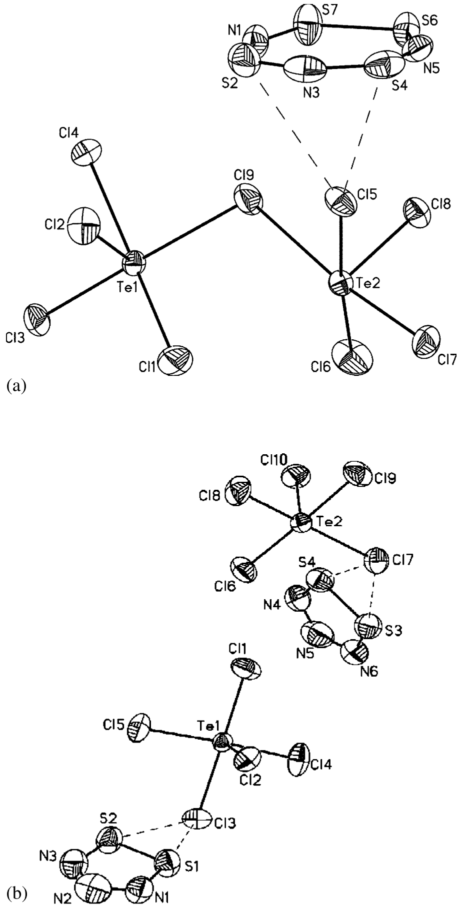


Fig. 3. Molecular structure of: (a) $[S_4N_3^+][Te_2Cl_9^-]$; (b) $[S_2N_3^+][TeCl_5^-]$.

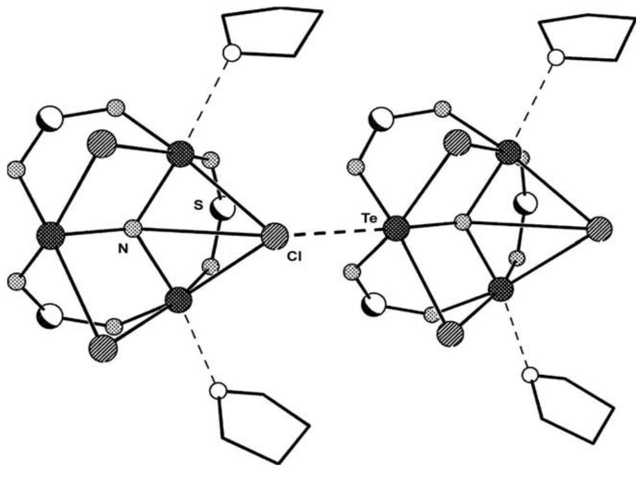


Fig. 4. Molecular structure of N[Te(Cl)NSN]$_3$·2THF.

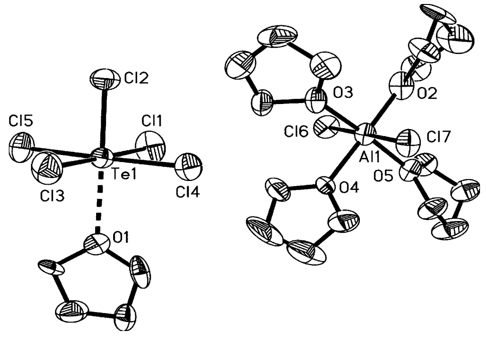


Fig. 5. Molecular structure of [AlCl$_2$·4THF$^+$][TeCl$_5$·THF$^-$].

educt to an additional intermediate and decomposes into TeCl$_4$ and the final product as delivered in Scheme 11.

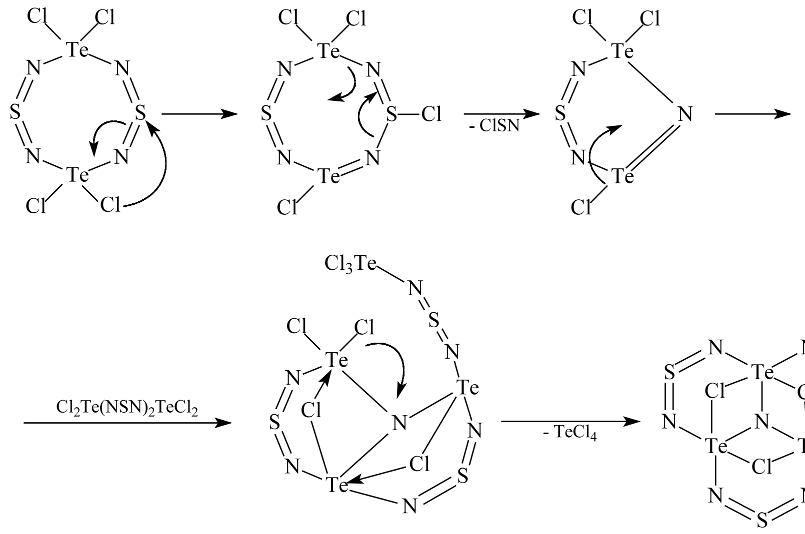
Starting from structure **B** the reaction runs through all intermediates mentioned before providing the product, but bridging chlorine atoms are already present. In the case that two molecules of **B** are linked by additional intramolecular chlorine bonds forming a dimer its indifferent to whether ClSN or TeCl$_4$ is eliminated first.

It was also shown [18] that the bicyclus Cl$_6$Te$_2$N$_2$S especially in the presence of chlorinated Lewis-acids eliminates ClSN yielding Cl$_5$Te$_2$N [14]. In a blank reaction it was found that Cl$_5$Te$_2$N forms with (CH$_3$)$_3$SiNSNSi(CH$_3$)$_3$ N[Te(Cl)NSN]$_3$, characterized by an X-ray structure analysis. This proves that intermediate **2** can also be formed by a second reaction path from Cl$_5$Te$_2$N and (CH$_3$)$_3$SiNSNSi(CH$_3$)$_3$. Both routes are presented in Scheme 12.

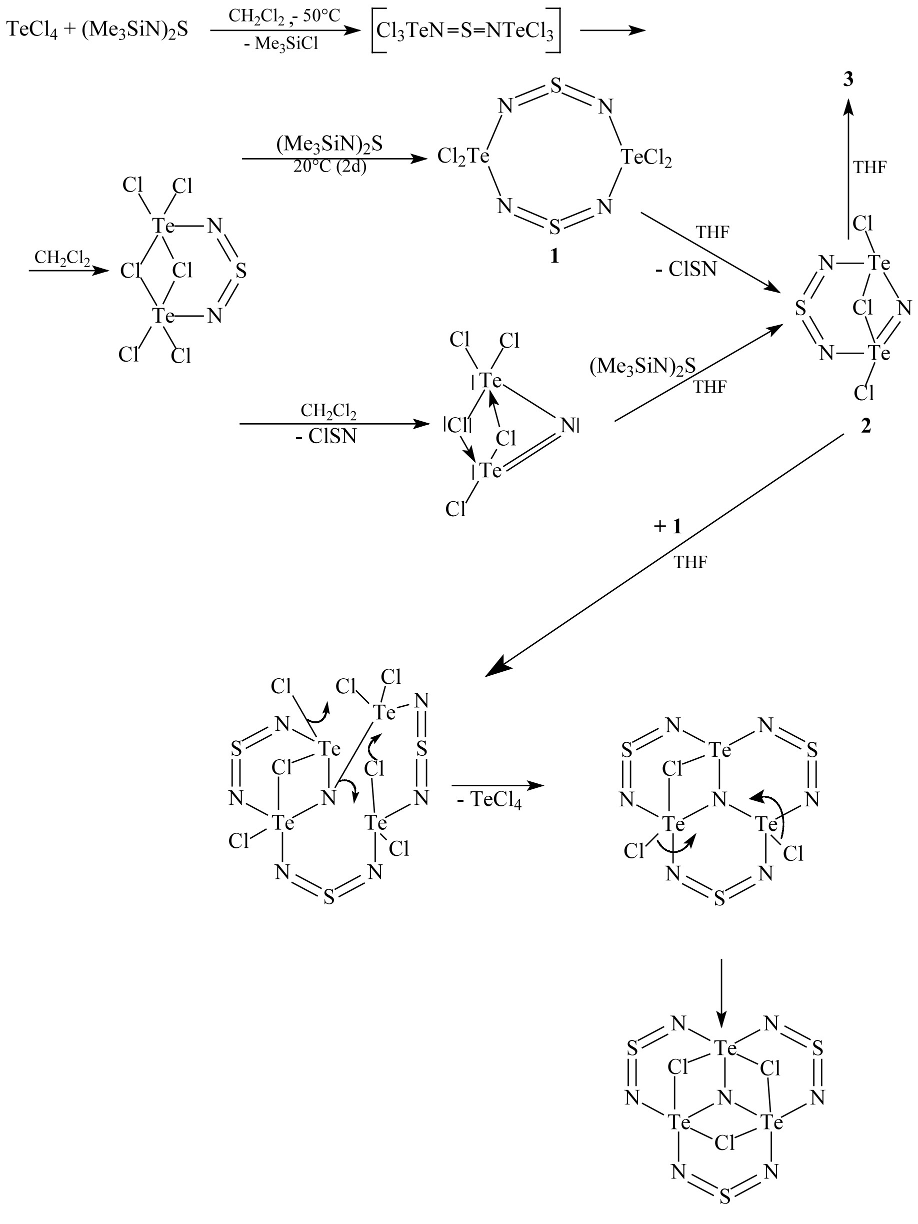
It was also attempted to find out if fluorine substituted tellurachalcogen–nitrogen compounds with ^{19}F as an NMR-label can contribute to elucidate reaction sequences.

3. Fluorine substituted acyclic and cyclic TeSN-compounds

First of all it had to be said that all attempts to prepare corresponding fluorine substituted compounds by metathesis failed. Different procedures had to be applied. A first ray of hope was the preparation of F$_2$Te(NSO)$_2$ [7,11] from TeF$_4$ and a mixture of (CH$_3$)$_3$SiNSO and (CH$_3$)$_3$SiOSi(CH$_3$)$_3$, although some fluorinated heterocycles became available before. So pyrolysis [11] of F$_2$Te(NSO)$_2$ yielded a difluorinated five membered ring, which formed with fluorinated Lewis-acids such as AsF$_5$ and SbF$_5$ the corresponding monofluorinated salts. In THF solution F$_2$Te(NSO)$_2$ rearranges at 20 °C (10 days) with SO$_2$ elimination to the tetrafluorinated eight membered ring



Scheme 11.



Scheme 12.

$F_2Te(NSN)_2TeF_2$. These procedures are summarized in Scheme 13. In analogy to $Cl_2Te(NSN)_2TeCl_2$ it decomposes with TeF_4 elimination, which reacts with $(CH_3)_3SiNSNSi(CH_3)_3$ to $(CH_3)_3SiF$ and producing $(FTeNSN)_3N$ [23]. Physical data of the fluorinated cage are in good agreement with literature results [23]. By explaining the reaction sequences it has to be considered that **no** fluorinated bicyclus $F_6Te_2N_2S$ is known so far. It is obvious that the intermediate $F_3TeNSNTeF_3$ did not stabilize as bicyclus but reacts further with $(CH_3)_3SiNSNSi(CH_3)_3$ to give $F_2Te(NSN)_2TeF_2$, which, as shown in Scheme 11, eliminates accordingly FSN and TeF_4 at 60 °C (10 days) in CH_2Cl_2 yielding $(FTeNSN)_3N$.

By metathetical substitution $F_2Te(NSO)_2$ and also $F_2Te(NSN)_2TeF_2$ provide with $(CH_3)_3SiR$ the compounds given in Scheme 14. Partly different products are obtained by reacting $TeCl_4$ with $R_2Te(NSO)_2$. Besides analogous Cl_3TeR no substituted eight membered rings are yielded but instead $Cl_6Te_2N_2S$ and SO_2.

The X-ray structure of the so prepared $[CF_3C(O)O]_2Te(NSO)_2$ is pictured in Fig. 6. The parameters obtained allows comparison with e.g. $Te(NSO)_2$.

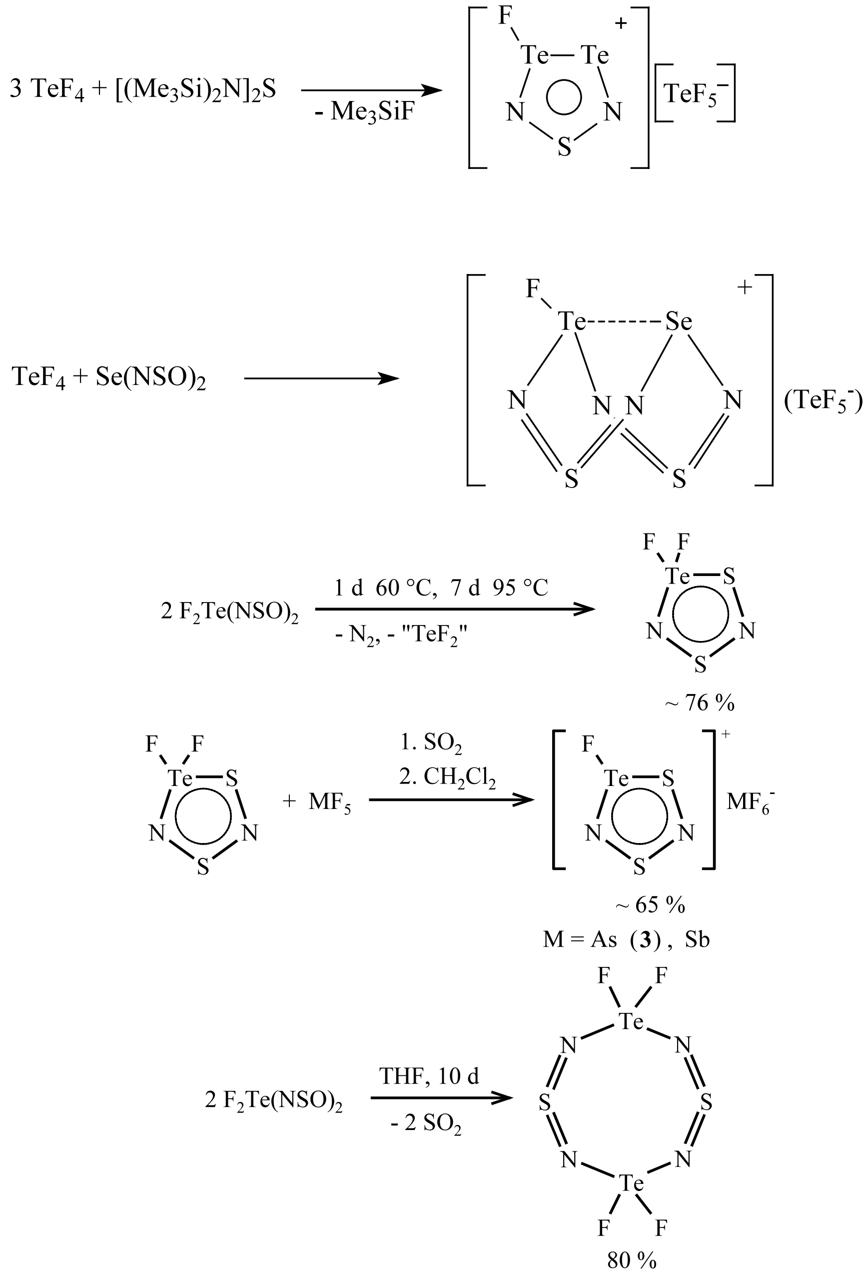
Remarkable progress was made in regard to possible structures of $F_2Te(NSN)_2TeF_2$ by reacting $F_2Te(NSO)_2$ with MF_5 (molar ratio 1:1) in SO_2 at 22 °C (5 days) providing directly $[FTe(NSN)_2TeF^{2+}][MF_6^-]_2$ (M = As, Sb). Both salts could be also made analogously from $F_2Te(NSN)_2TeF_2$ and MF_5 (molar ratio 1:2) [11]. If on the contrary AlF_3 is used in CH_2Cl_2 or THF at 60 °C (10 days) then 90% $[F_2Te(NSN)_2TeF^+][AlF_4^-]$ are formed. A fourfolded positive cation could be made not only from $F_2Te(NSN)_2TeF_2$ but also from $[FTe(NSN)_2TeF^{2+}][AsF_6^-]_2$ [18] with a large excess of AsF_5 in SO_2. In this connection it was also interested to know something about the reactivity of $F_2Te(NSO)_2$ with MF_5 in CH_2Cl_2. When $F_2Te(NSO)_2$ is treated with MF_5 (molar ratio 1:1) in CH_2Cl_2 at −20 °C (12 days) then 90% of the intermediate $[FTe(NSO)_2^+][MF_6^-]$ are formed. A temptative interpretation of these results, especially the transformation of acyclic $F_2Te(NSO)_2$ to cyclic $[FTe(NSN)_2TeF^{2+}]$ in the presence of MF_5 via the intermediate $[FTe(NSO)_2^+]$, which was synthesized and characterized, allow to formulate the equations given in Scheme 15.

Hereby the step $2[FTe(NSO)_2^+]$ to $[FTe(NSN)_2TeF^{2+}]$ is without proof. Dimerisation could take place either by intramolecular condensation via the intermediate cyclic $[F\overline{TeNSN}{}^+]$ or by intermolecular condensation of two molecules $[FTe(NSO)_2^+]$ with SO_2 elimination [11].

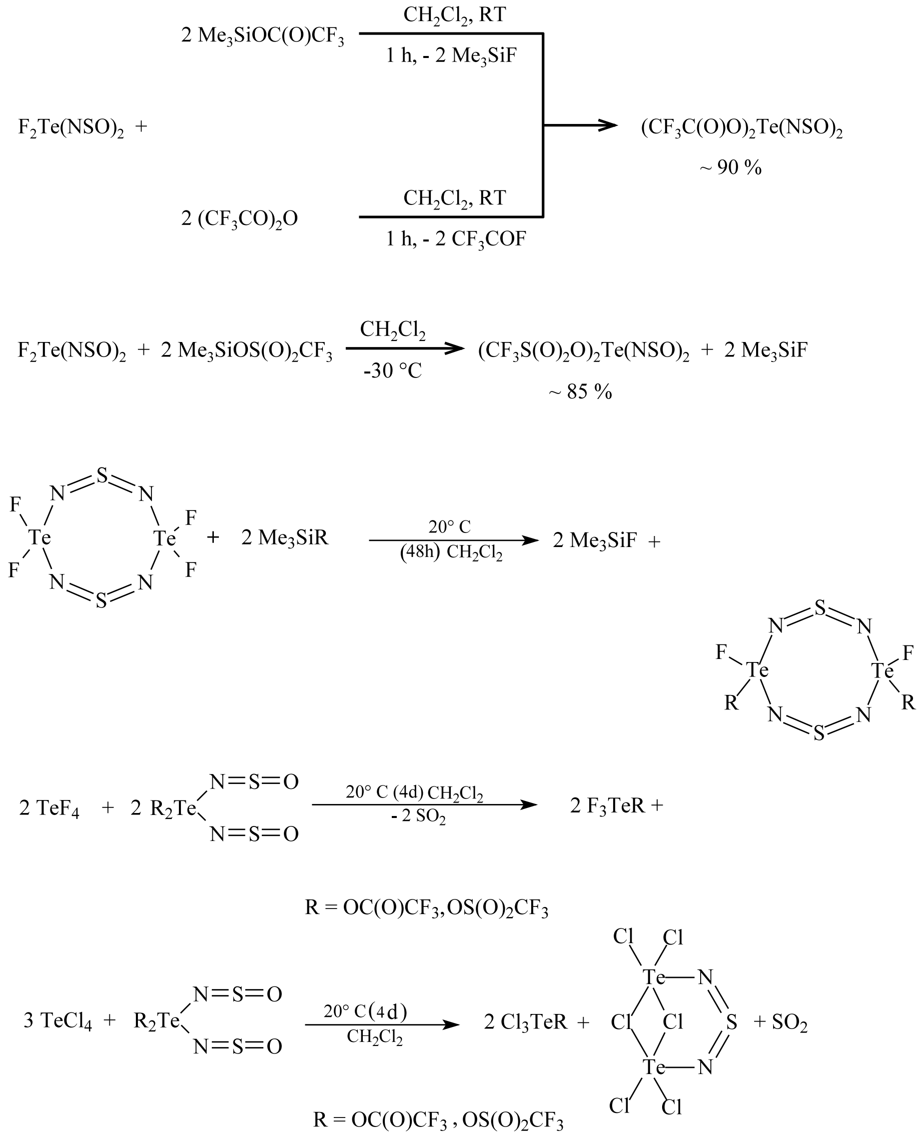
Changing the solvent to SO_2 and applying AsF_5 (molar ratio 1:2) at 22 °C (24 days) then 90% $[Te(NSO)_2^{++}][AsF_6^-]_2$ [11] were yielded.

In this connection a possible relation between $[Te(NSO)_2^{++}]$ and $[Te(NSN)_2Te^{4+}]$ should also be considered.

Pyrolyses of $[FTe(NSN)_2TeF^{2+}][AsF_6^-]_2$ form



Scheme 13.



Scheme 14.

$[\overline{FTeSNSN}^+][AsF_6^-]$ [11]. An overall view of these reactions is shown in Scheme 16. So the structure problem for $X_2Te(NSN)_2TeX_2$ (X = F, Cl) and correspondingly $F_2Te(NSN)_2TeF_2$ deviated cations remains an open question.

4. Conclusions

Intensive experimental studies with $E(NSO)_2$ (E = Se, Te), $X_2Te(NSO)_2$ (X = F, Cl, Br), $Cl_6Te_2N_2S$ and $X_2Te(NSN)_2TeX'_2$ (X′ = F, Cl) yielded new but also known compounds which proved to be very important for a better understanding of reaction pathways and interpreting mechanisms. These studies allowed to explain the formation of cyclic from acyclic structures and for the first time to understand how the cage $N[Te(Cl)NSN]_3$ is made up from $(CH_3)_3SiNSNSi(CH_3)_3$ and $TeCl_4$. At the same time, intermediates are isolated and their part in this synthesis elucidated. A better understanding of these topics inspires new ideas which for example led to the first $\overline{SSNNN}$-cation with three cumulated nitrogens, made for the first time in more than 150 years of SN-chemistry.

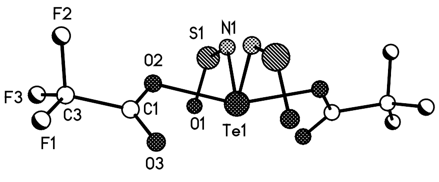
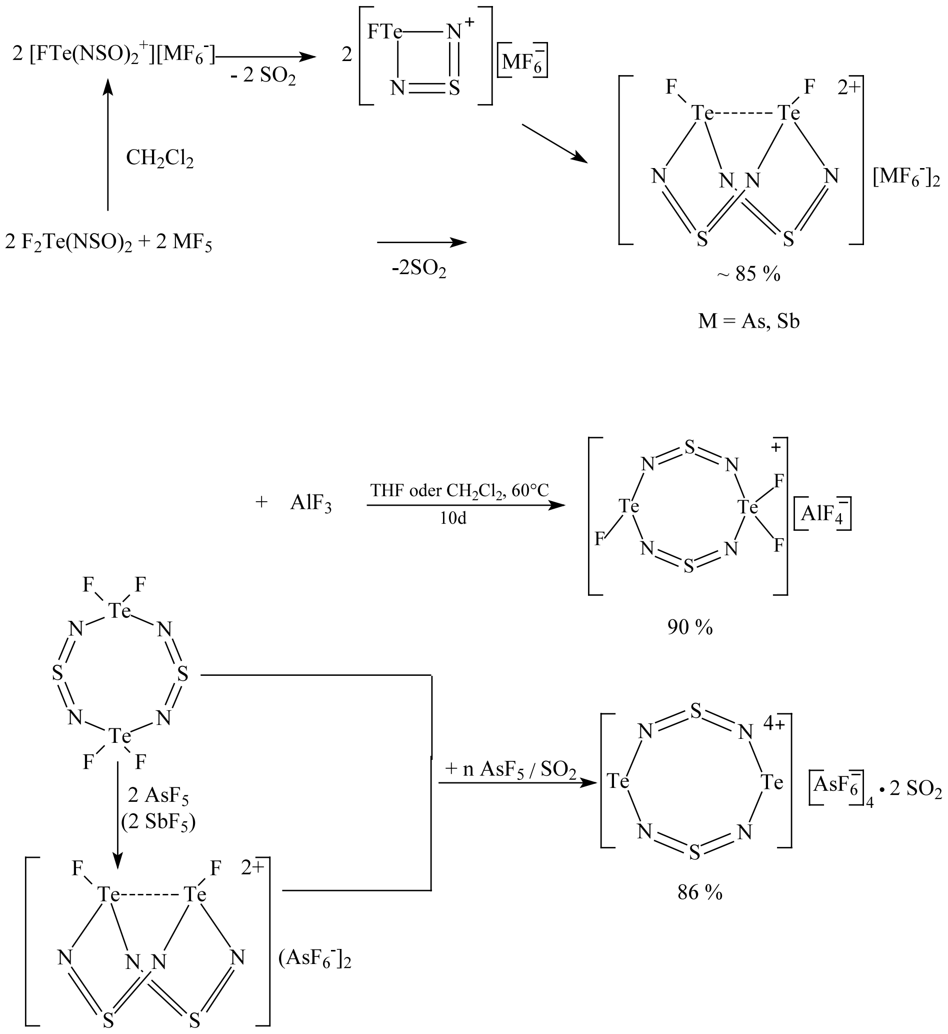
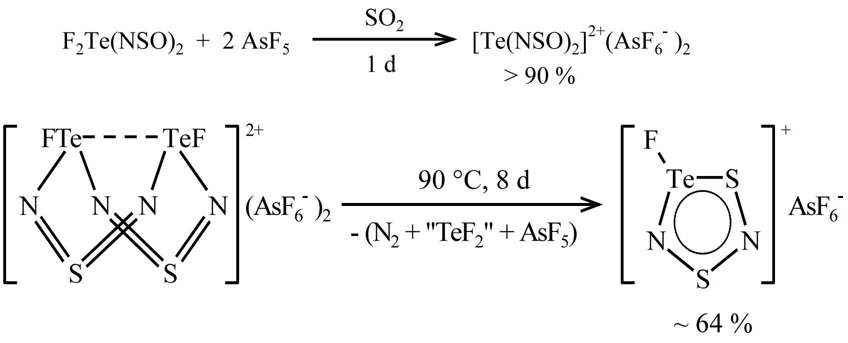


Fig. 6. Molecular structure of $[CF_3C(O)O]_2Te(NSO)_2$.



Scheme 15.



Scheme 16.

The more one understands this field of chemistry, the more it becomes obvious that there are strong relations between chalcogen–nitrogen and heterorganic chemistry. Precise answers to intelligent and appropriate questions based on experimental work are a good approach for further development and a better understanding of this topic.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited as supplementary publication no. CSD 412367 with the Crystal Structure Deposition (CSD) at FIZ Karlsruhe. Copies of this information may be obtained free of charge from crysdata@fiz-karlsruhe.de.

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