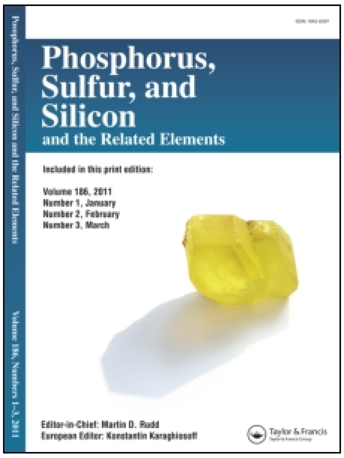

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CHALCOGENA-NITROGEN HETEROCYCLES: PREPARATION, STRUCTURES AND REACTION PATHWAYS

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The aim of this presentation is to demonstrate the unexpected properties of bis(sulfinylamino)chalcogenanes $E(NSO)_2$, E = S, Se, Te, as synthons for the preparation of chalcogen-nitrogen heterocycles. Their syntheses and structures are described and their chemical properties will be discussed. Under the influence of superacids they proved to be good precursors for the syntheses of new ionic and neutral chalcogen-nitrogen heterocycles and cages. The complicated pathway from e.g. $Te(NSO)_2$ to the heterocycle $Cl_3Sb\cdots Cl\cdots\overline{Te(Cl)SN=S=N}$ will be elucidated on the base of postulated intermediates in comparison with heterocycle formation using $Se(NSO)_2$ as a synthon.

Keywords: Sulfinylamino / Chalcogenanes / Thiaselenatelluradiazoles / Thiatelluratetrazocinium / Tellurium(IV) compounds / Tellurathiadiazete

Bis(sulfinylamino)chalcogenanes proved to be good and versatile synthons for the preparation of neutral and ionic chalcogena-nitrogen heterocycles. In 1952 Goehring and Schuster[1] published the preparation of $S(NSO)_2$, which is made today on a preparative scale either from $(CH_3)_3SiNSO$ and SCl_2[2] or from $(CH_3)_3SiN{=}S{=}NSi(CH_3)_3$[3],[4] and $SOCl_2$. The reactions between $S(NSO)_2$ and $TiCl_4$ or $SbCl_5$ yielded two key compounds, namely $(S_2N_2{\cdot}TiCl_4)_x$ and $S_4N_4{\cdot}SbCl_5$ showing that the first reaction step is intramolecular elimination of SO_2 providing S_2N_2 which is either precipitated as a polymeric 1:1 adduct with $TiCl_4$[4] or oligomerizes in solution to S_4N_4 and forming a 1:1 adduct with $SbCl_5$[5]. The structure of the latter compound consists of an S_4N_4 cage with $SbCl_5$ coordinated to nitrogen[6].

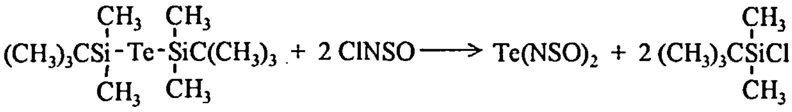
$$(CH_3)_3SiNSO + SCl_2 \xrightarrow{\text{reflux temp.}} \begin{array}{c} S(NSO)_2 \\ 68\% \end{array}$$

$$(CH_3)_3SiN{=}S{=}NSi(CH_3)_3 + SOCl_2 \xrightarrow[\text{benzene}]{60°C\ (3\ h)} \begin{array}{c} S(NSO)_2 \\ 83\% \end{array} \qquad (1)$$

$$S(NSO)_2 \begin{array}{l} + TiCl_4 \xrightarrow[CH_2Cl_2]{20°C} \begin{array}{l} S_2N_2{\cdot}TiCl_4 \\ \text{yellow precipitate} \end{array} \\ \\ + SbCl_5 \xrightarrow[CH_2Cl_2]{20°C} \begin{array}{l} S_4N_4{\cdot}SbCl_4 \\ \text{red crystals} \end{array} \end{array}$$

More than fourty years later $Se(NSO)_2$[7] was synthesized from $(CH_3)_3SiNSO$ and Se_2Cl_2 according to eq. (2).

$$2\,(CH_3)_3SiNSO + Se_2Cl_2 \xrightarrow[CH_2Cl_2]{22^\circ C\ (24\ h)} \underset{\sim 70\%}{Se(NSO)_2} + Se + 2\,(CH_3)_3SiCl$$



$$(CH_3)_3C\overset{CH_3}{\underset{CH_3}{Si}}\text{-}Te\text{-}\overset{CH_3}{\underset{CH_3}{Si}}C(CH_3)_3 + 2\,ClNSO \longrightarrow Te(NSO)_2 + 2\,(CH_3)_3C\overset{CH_3}{\underset{CH_3}{Si}}Cl \qquad (2)$$

New routes were needed for the synthesis of $Te(NSO)_2$[8] as analogous reactions failed to yield the tellurane derivative. It was found that it can be obtained as shown in scheme 2. Time consuming purification makes this procedure not very efficient and new ways were explored. It was proved that $Te(SCF_3)_2$ is a good starting material for the preparation of $Te(NSO)_2$, but it had only been obtained on a milligram scale by treating Te with CF_3S-radicals and was only poorly characterized[9]. New efficient reactions provide $Te(SCF_3)_2$ on a preparative scale in good yields and in a short time as shown in the following equations (3).

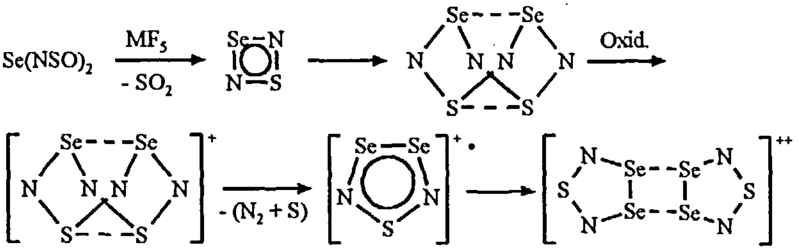
$$\begin{aligned}
&TeCl_4 + 4\,Hg(SCF_3)_2 \longrightarrow Te(SCF_3)_2 + CF_3SSCF_3 + 4\,CF_3SHgCl\\
&Na_2Te + 2\,CF_3SCl \longrightarrow Te(SCF_3)_2 + 2\,NaCl\\
&Na_2Te + 2\,Ph_3SnCl \longrightarrow Ph_3SnTeSnPh_3 + 2NaCl^{[10]}\\
&2\,(n\text{-}C_4H_9)_3SnH + Te \longrightarrow (n\text{-}C_4H_9)_3SnTeSn(n\text{-}C_4H_9)_3 + H_2^{[11]}\\
&R_3SnTeSnR_3 + 2\,CF_3SCl \longrightarrow Te(SCF_3)_2 + 2\,R_3SnCl,\ R = n_{C4}H_9, Ph^{[10]}\\
&Te(SCF_3)_2 + Hg(NSO)_2 \xrightarrow[(5\ d,\ dark)]{50^\circ C} \underset{60\%}{Te(NSO)_2} + Hg(SCF_3)_2
\end{aligned} \qquad (3)$$

When $Te(SCF_3)_2$ and $Hg(NSO)_2$ are reacted, a metathetical reaction between parahalogenes[11] takes place forming $Te(NSO)_2$ efficiently and in good yields.

According to X-ray structure determination Se- and Te$(NSO)_2$ are planar chainlike molecules.

Unexpectedly Se$(NSO)_2$ reacts with Lewis acids such as MF_5 (M = As, Sb, Nb) in liquid SO_2 at room temperature yielding bis(1,3,4,2,5-thiadiselenadiazolium) cations with the corresponding counter anions AsF_6^-, SbF_6^- and NbF_6^-[7]. The first two compounds were synthesized initially by Gillespie et al.[12] by reacting $[Se_n^{++}][AsF_6^-]_2$ (n = 4, 8) or $[Se_4^{++}][Sb_2F_{11}^-]$ with S_4N_4 in liquid SO_2 at 22°C. The structure of the dication consists of two planar Se_2N_2S five membered rings linked by two weak Se···Se interactions to a chair confirmation. It was proved that the samples obtained from Se$(NSO)_2$ are identical.

The cyclization of the chainlike molecule to a five membered ring unit is not understood at a first sight. But it was possible to prove that the first step in this reaction is the quantitative intramolecular elimination of SO_2 forming primary 1,3,2,4-thiaselenadiazete. This then dimerizes to an S_4N_4-type cage (see eq. 4) with replacement of two S- by two adjacent selenium atoms. However, the $S_2Se_2N_4$ cage containing the $\overline{\text{SeSeNSN}}$ ring frame is unstable and decomposes as shown below to the final products.

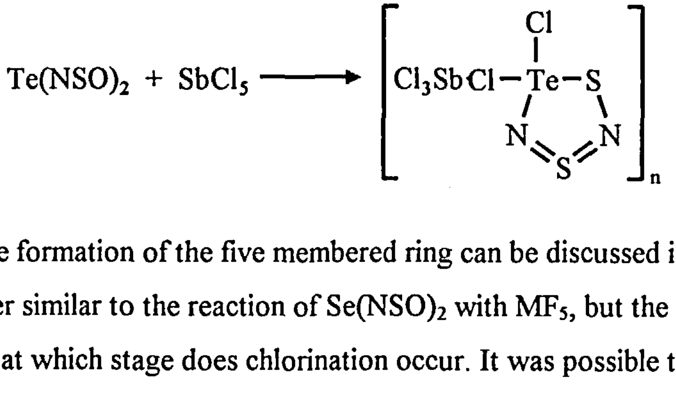


(4)

M = As, Sb, Nb

Among the postulated intermediates, two have been shown to exist, namely $\overline{\mathrm{SeNSN}}$ as an adduct with $TiCl_4$ and the radical cation by esr spectroscopy[7],[13] showing a quintet with $a_N = 3.006$[7] [Gauß] and $g = 2.01$[14]. Nothing can be said about the other postulated intermediates.

Transformation of $Te(NSO)_2$ into tellurium containing chalcogen nitrogen heterocycles may provide some additional information about possible pathways. Treatment of $Te(NSO)_2$ with $SbCl_5$ in SO_2 gives a polymeric product of the formula $[\overline{\mathrm{SNSNTe}}(Cl)Cl\cdot SbCl_3]_x$. Its structure has been established by X-ray cristallography showing a 3-chlorodithiatelluradiazole ring[15], see scheme 5.



(5)

The formation of the five membered ring can be discussed in a manner similar to the reaction of $Se(NSO)_2$ with MF_5, but the question arises at which stage does chlorination occur. It was possible to synthesize $Cl_2Te(NSO)_2$[10] by various methods, as shown below.

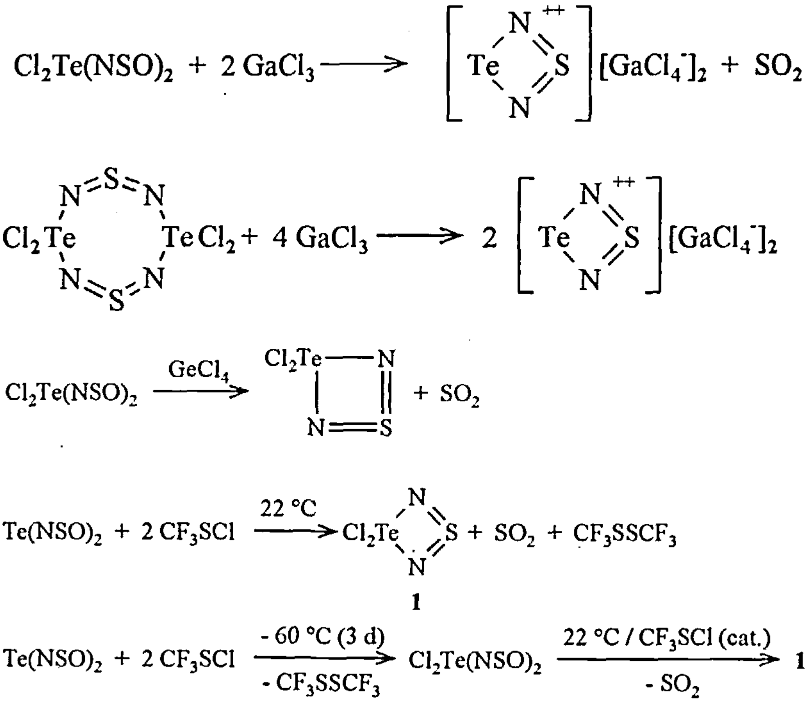
$$(CH_3)_3SiNSO\,/\,(CH_3)_3SiOSi(CH_3)_3 + TeCl_4 \xrightarrow{20°C\ (12\ h)} \underset{10\%}{Cl_2Te(NSO)_2}$$

$$Te(NSO)_2 + Cl_2 \xrightarrow[CS_2]{-196\ to\ 22°C} \underset{78\%}{Cl_2Te(NSO)_2}$$

$$Te(SCF_3)_2 + 2\,ClNSO \xrightarrow[CS_2]{0°C\ (3\ d)} \underset{98\%}{Cl_2Te(NSO)_2} + CF_3SSCF_3 \qquad (6)$$

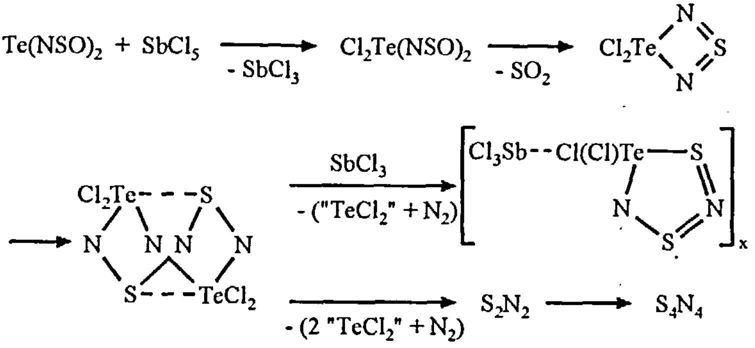
$$Te + 2\,ClNSO \xrightarrow[CS_2]{0°C\ (3\ d)} \underset{99\%}{Cl_2Te(NSO)_2}$$

It has been demonstrated that $Cl_2Te(NSO)_2$ undergoes intramolecular condensation yielding $Cl_2\overline{TeNSN}$[16] and SO_2. This four membered ring moiety can also be prepared according to scheme 7.

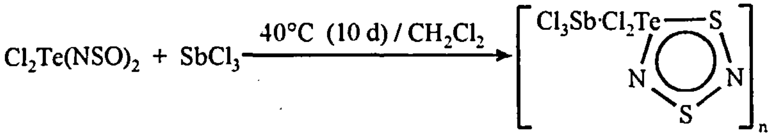


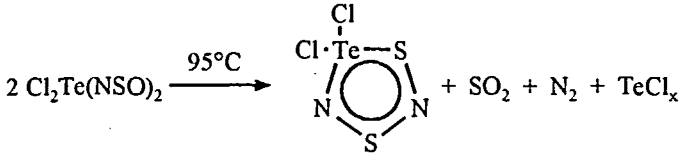
(7)

Thus in a second step the $Cl_2\overline{TeNSN}$ ring should be able to dimerize to an unstable cage like molecule analogous to $S_2Se_2N_4$. This cage then decomposes following two routes.



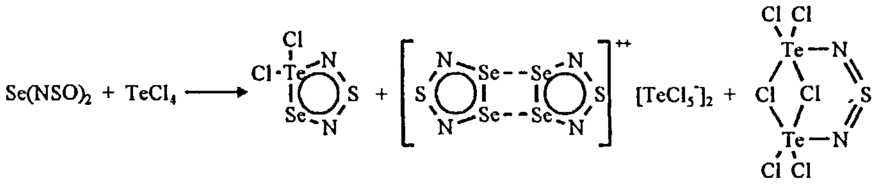
(8)

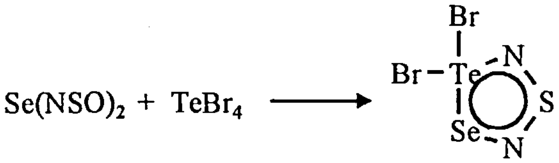




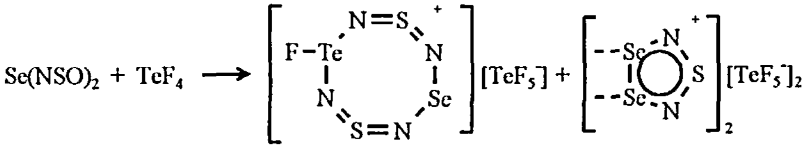
The main product in this reaction is, however, S_4N_4. The polymer can be made in much better yields directly from $Cl_2Te(NSO)_2$ and $SbCl_3$. The uncoordinated five membered ring can be prepared by heating $Cl_2Te(NSO)_2$ but no reaction takes place between the isolated hetercycle and $SbCl_3$. Adduct formation has to be accomplished at an earlier stage, e.g. with $Cl_2\overline{TeNSN}$. It was possible to demonstrate that the ring, made from $Te(NSO)_2$ and CF_3SCl, reacted with $SbCl_3$ at 40°C (10 d) in CH_2Cl_2 to the polymer. So far convincing evidence can be provided for the first two steps on the reaction of $Te(NSO)_2$ and $SbCl_5$. But is dimerisation of **1** to the cage and its decomposition realistic? An answer to this problem was found by studying reactions between $Se(NSO)_2$ with TeX_4 (X = F, Cl, Br).

$TeCl_4$ forms in a lengthy reaction in CH_2Cl_2 at 60°C (28 d) three compounds, as shown below.



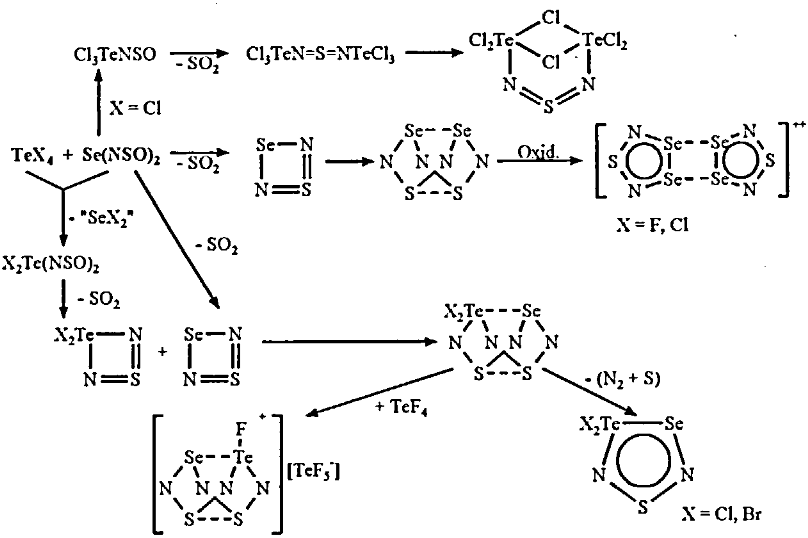


(9)



This procedure can be shortened to about three days by using $[TeCl_3]^+[AsF_6]^-$ in SO_2. The structures were confirmed by X-ray structure determinations. Less reactive $TeBr_4$ and $Se(NSO)_2$ give after six months in CH_2Cl_2 at 60 to 70°C 70% of the dibromotellurathiaselenadiazole and SO_2. No other product can be detected. A different course took the reaction between TeF_4 and $Se(NSO)_2$ at 60°C (7 days) in CH_2Cl_2. Almost quantitative yields of a fluoro-substituted dithiaselenatelluraazocinium cage besides $[Se_2N_2S^+]_2[TeF_5^-]_2$ and SO_2 are formed. The X-ray crystal structure determination proved the cage and ionic structure with fluorine being exocyclicly bonded to tellurium[17].

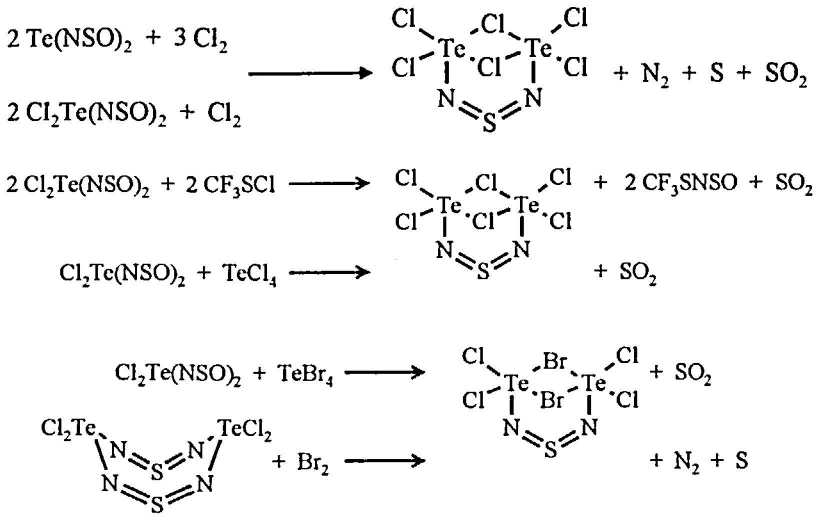
The formation of isolated and characterized tellurachalcogena-nitrogen heterocycles can be explained by the reaction pathways shown below.



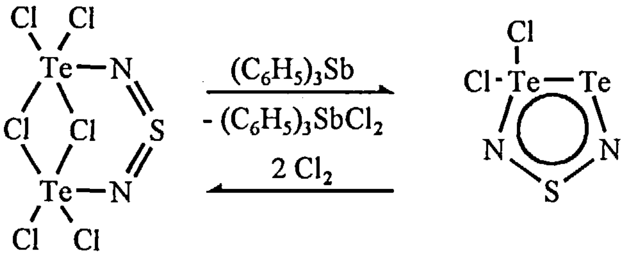
(10)

1. TeCl$_4$ reacts with Se(NSO)$_2$ primary to Cl$_3$TeNSO which condenses via intermolecular condensation to SO$_2$ and the TeCl$_3$ substituted sulfurdiimine followed by cyclization to Cl$_6$Te$_2$N$_2$S. This has been demonstrated by treating Cl$_2$Te(NSO)$_2$ with CF$_3$SCl at -10°C forming CF$_3$SNSO, SO$_2$ and Cl$_6$Te$_2$N$_2$S.
2. The Lewis acids TeF$_4$ and TeCl$_4$ form with Se(NSO)$_2$ analogously to MF$_5$ (M = As, Sb, Nb) $\overline{\text{SeNSN}}$ providing partly [Se$_2$N$_3$S$^+$]$_2$[TeX$_5^-$]$_2$ and in addition by metathesis Y$_2$Te(NSO)$_2$ with Y = F, Cl, Br.
3. Y$_2$Te(NSO)$_2$ eliminates SO$_2$ forming intramolecularly the corresponding four membered ring Y$_2\overline{\text{TeNSN}}$. Together with $\overline{\text{SeNSN}}$, formed as described just before, codimerisation may take place yielding the eight membered cage which for Y = Cl, Br decomposes with elimination of sulfur and nitrogen to the stable final products Y$_2\overline{\text{TeSeNSN}}$. If Y = F the cage is stabilized as a cation[17] with pentafluorotellurate(IV) as the counter anion.

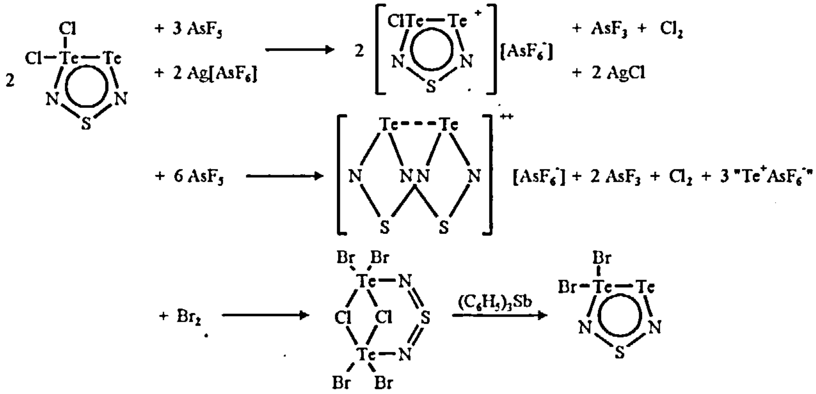
High yield synthesis of bicyclic $Cl_6Te_2N_2S$ is accomplished by the reactions described below.


(11)

These different types of chlorinations of $Cl_2Te(NSO)_2$ and a metathetical reaction with $TeCl_4$ evidence the described pathway. The dibromo bridged bicyclus is made from $Cl_2Te(NSO)_2$ and $TeBr_4$ or by bromination of $Cl_2Te(N{=}S{=}N)_2TeCl_2$[16] (scheme 11). Dehalogenation of $Cl_6Te_2N_2S$ with $Sb(C_6H_5)_3$ provided $Cl_2\overline{TeTeNSN}$, an almost planar five membered ring with the two Cl-atoms bonded to tellurium. This reaction is reversible as chlorination with Cl_2 leads to the starting material (scheme 12).

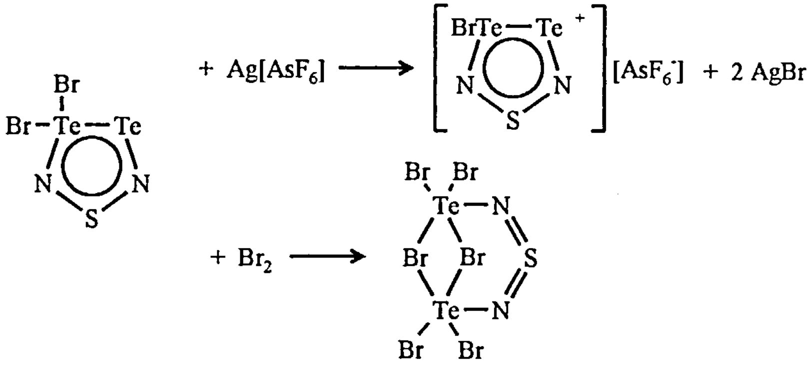

(12)

The thiaditelluradiazole ring is a very good starting material opening new possibilities. With AsF_5 (molar ratio 2:6) it forms a twice positively charged cage as proved by its X-ray structure determination. Another proof for the existence of such compounds. Supplemental reactions are shown in scheme 13.



(13)

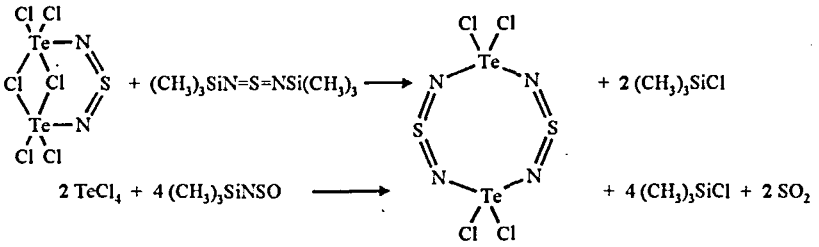
Again dibromositellurathiadiazole functions as a synthon forming with $Ag[AsF_6]$ or Br_2 the compounds shown in scheme 14.



(14)

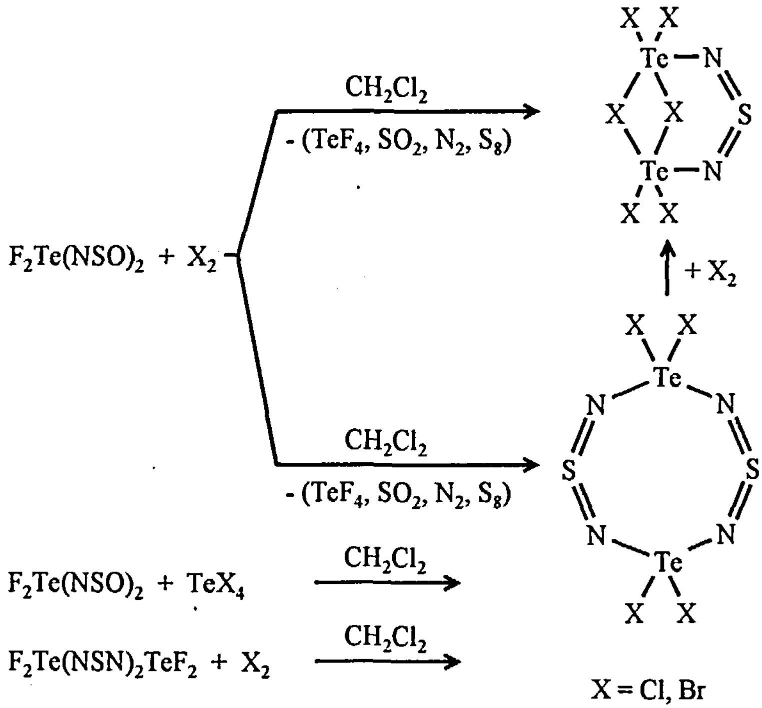
No iodo or fluoro substituted bicyclus could be made until now.

Other routes to substituted but neutral dithiaditelluratetraza heterocycles are reactions between $X_6Te_2N_2S$ and $(CH_3)_3SiN{=}S{=}NSi(CH_3)_3$ or TeX_4 and $(CH_3)_3SiNSO$ (scheme 15).



(15)

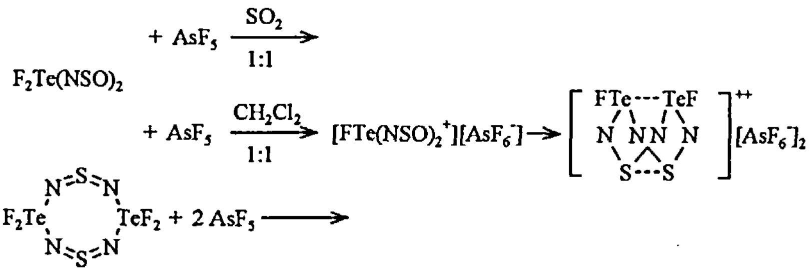
It was possible to demonstrate that $F_2Te(NSO)_2$ [made from TeF_4 and $(CH_3)_3SiNSO$] is a good access to eight membered rings, too. It starts to decompose at 20°C in THF already after half an hour with the precipitation of an orange product. After 5 days stirring the reaction is complete and 75% $F_2Te(NSN)_2TeF_2$[19] are isolated. Surprisingly $F_2Te(NSO)_2$ forms with chlorine or bromine (ratio 2:1) not fluorinated heterocycles but $X_2Te(NSN)_2TeX_2$ with X = Cl, Br. Additionally TeF_4, SO_2, N_2 and sulfur could be detected. If the ratio is 1:1 under similar reaction conditions $X_6Te_2N_2S$ (X = Cl, Br) is formed.



(16)

Analogously $F_2Te(NSN)_2TeF_2$ yields with X_2 in CH_2Cl_2 $X_2Te(NSN)_2TeX_2$ (scheme 16).

With Lewis acids such as AsF_5, SbF_5 and $F_2Te(NSO)_2$ new dicationic cages are formed in SO_2, molar ratio 2:1. Using CH_2Cl_2 as the solvent and AsF_5 the intermediate $[FTe(NSO)_2]^+[AsF_6^-]$ can be isolated and characterized. The reaction between $F_2Te(NSN)_2TeF_2$ and AsF_5 provides the double charged cage as well.



(17)

Meanwhile compounds such as $(C_6T_5)_2Te(NSO)_2$, $(CF_3)_2Ge(NSO)_2$, $Si(NSO)_4$ and $Ge(NSO)_4$ have been synthesized and characterized and it can be hoped that their chemistry is similarly manifold.

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