A cage rule for structures of chalcogen-nitrogen compounds – Applied to the resolution of fundamental issues

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Introduction
Cage rule
Discussion of reaction pathways based on isolated or spectroscopically detected intermediates. Three examples:

1) **$Se(NSO)_2 + MF_5$ → ? → ? → final product (Bicyclue)**

2) **$Te(NSO)_2 + SbCl_5$ → ? → ? → final product (Coordinated Ring)**

3) **$TeCl_4 + (CH_3)_3SiNSNSi(CH_3)_3$ → ? → ? → final product (Cage)**

Benzene, multinuclear benzene like systems and other cyclic conjugated polyenes are aromatic, if their number of π-electrons comply with the Hückel-rule

$$\Sigma\pi = 4n + 2 \ (n = 0, 1, 2, 3......)$$

This rule is also valid for charged molecular ions.

Banister correlated in 1972 the number of π-electrons for molecules- such as S_4N_3 (10π), $[S_5N_5]^{-}$ (14π), S_2N_2 (6π), $[S_3N_5]^{-}$ (6π), S_4N_2 (14π)- with their structures and chemical stability. The number of π-electrons obey the Hückel-rule and the examples are, classified as electron rich, inorganic, (aromatic)heterocycles.

R. Gleiter confirmed this statement.

In the last 10 years several neutral, charged and halogenated chalcogen – nitrogen heterocycles have been synthesized.

Their structures are determined by X-ray structure analyses.

These include [$S_2N_3^+$] (6π), $Cl_2TeS_2N_2$ (6π), [$ClTe_2SN_2^+$] (6 π), [$ClSe_2N_2S^+$] (6π) and Cl_2TeSeN_2S (6π).

Exocyclic single bonds reduce the π- electron count by one.

Is there a similar rule for cage structures ?

The binary neutral and charged molecules S_4N_4 (8π-), [$S_4N_5^+$] (8π-), [$S_4N_5^-$] (8π-), and S_5N_6 (12π-), have cage - like structures.

Two transanular S-S bonds in S_4N_4, d = 2.666 Ǻ (sum of van der Waals radii 3.6 Ǻ) must be taken into account.

Each N and S atom contributes one electron to the π- system.

The numbers 8 and 12, are multiples of 4 e.g. 4x2 for S_4N_4, [$S_4N_5^+$], [$S_4N_5^-$] and 4x3 for S_5N_6.

One can postulate tentatively a Cage rule: $\Sigma\pi = 4n^*$

But are there cages with fewer or more π- electrons ?

For $n^* = 1$; $\Sigma\pi = 4$. This ought to be the smallest cage with $n^* = 1,2,3,...$

How is this proposed cage rule connected to Hückel`s rule?

$$\Sigma\pi = 4n + 2 \quad \text{with } n = 0,1,2,3,...$$

The answer is: transforming n* (1,2,3) into n with n* = n + 1 or n = n*- 1.

Replacing n* by n in $\Sigma\pi = 4n^*$ provides 4 (n + 1) or

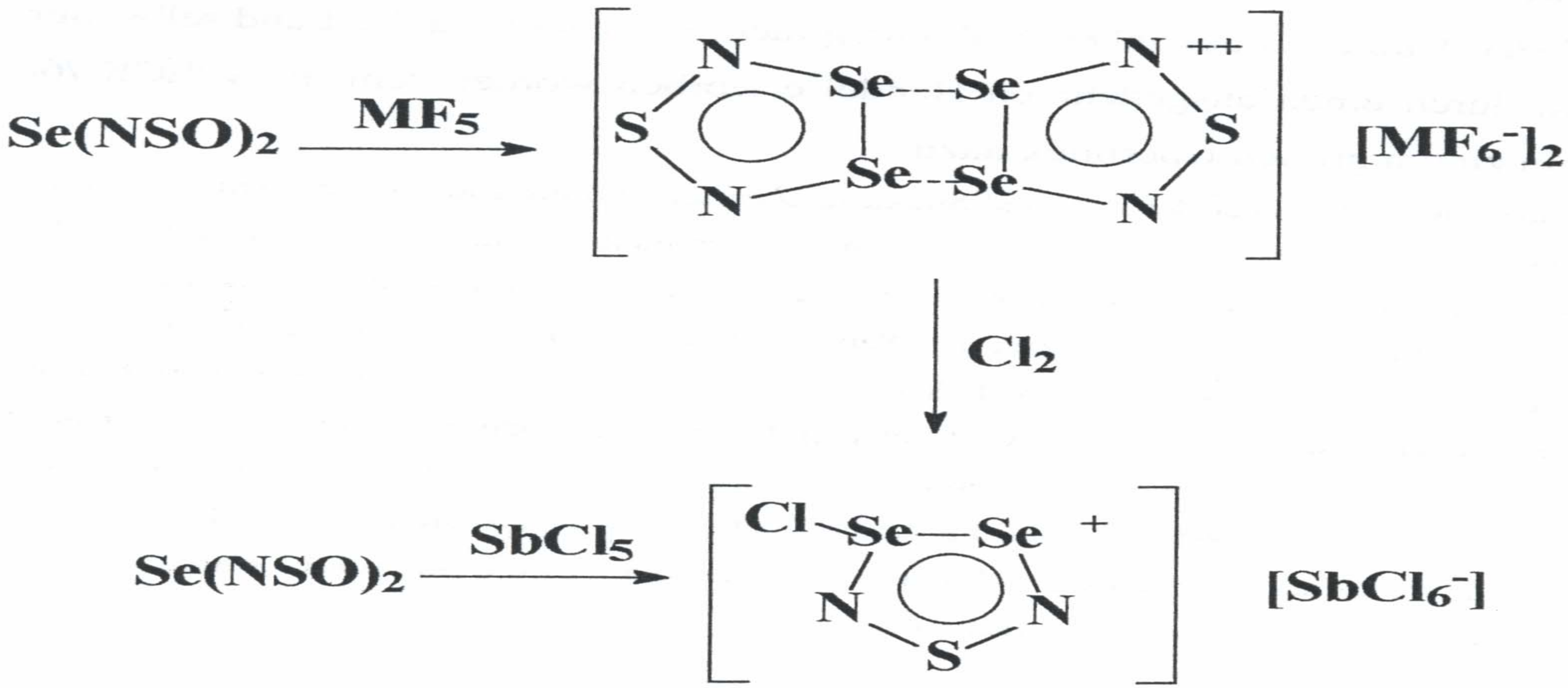
$$\text{Cage rule: } \Sigma\pi = 4n + 4 \quad (n = 0,1,2,3\cdots\cdots);$$

$$\text{Hückel`s rule: } \Sigma\pi = 4n + 2;$$

Additional evidence?

Recently synthesized compounds and ions such as: $Se_2S_2N_4$ (8π), [$Te_2S_2N_4^{++}$](8π), (no transanular S-S bonds), [$FTeSeS_2N_4^{+}$] (8π), (no transanular S-S bond), [$SeS_3N_5^{+}$] (8π), and $Cl_3TeNSNTeCl_3$ (4π) follow the cage rule.

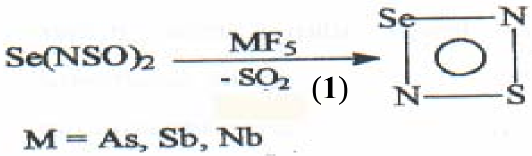
The cage structures have been confirmed by x-ray structure analyses.



$Se(NSO)_2 + MF_5 \rightarrow ? \rightarrow ? \rightarrow$ endproduct

„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“.

R. T. Oakley, Prog. Inorg. Chem. 1988, *36*, 299.



(**1**) Isolating $(SeNSN{\cdot}TiCl_4)_n$ and quantitative estimation of the SO_2 formed.

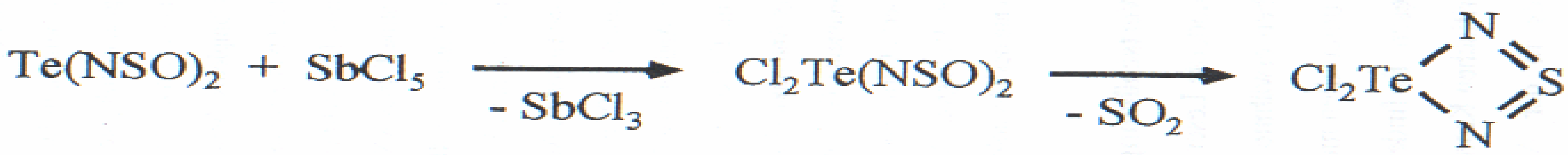
(**2**) Synthesis and x-ray structure of $Se_2S_2N_4$ by Laitinen, Chivers et al.

(**3**) Synthesis and x-ray structure of $[FTeSeS_2N_4^+]$.

(**4**) Prove of $[SeSeNSN^{\cdot+}]$ by esr spectroscopy.

(**5**) X-ray structure of the dimeric product.

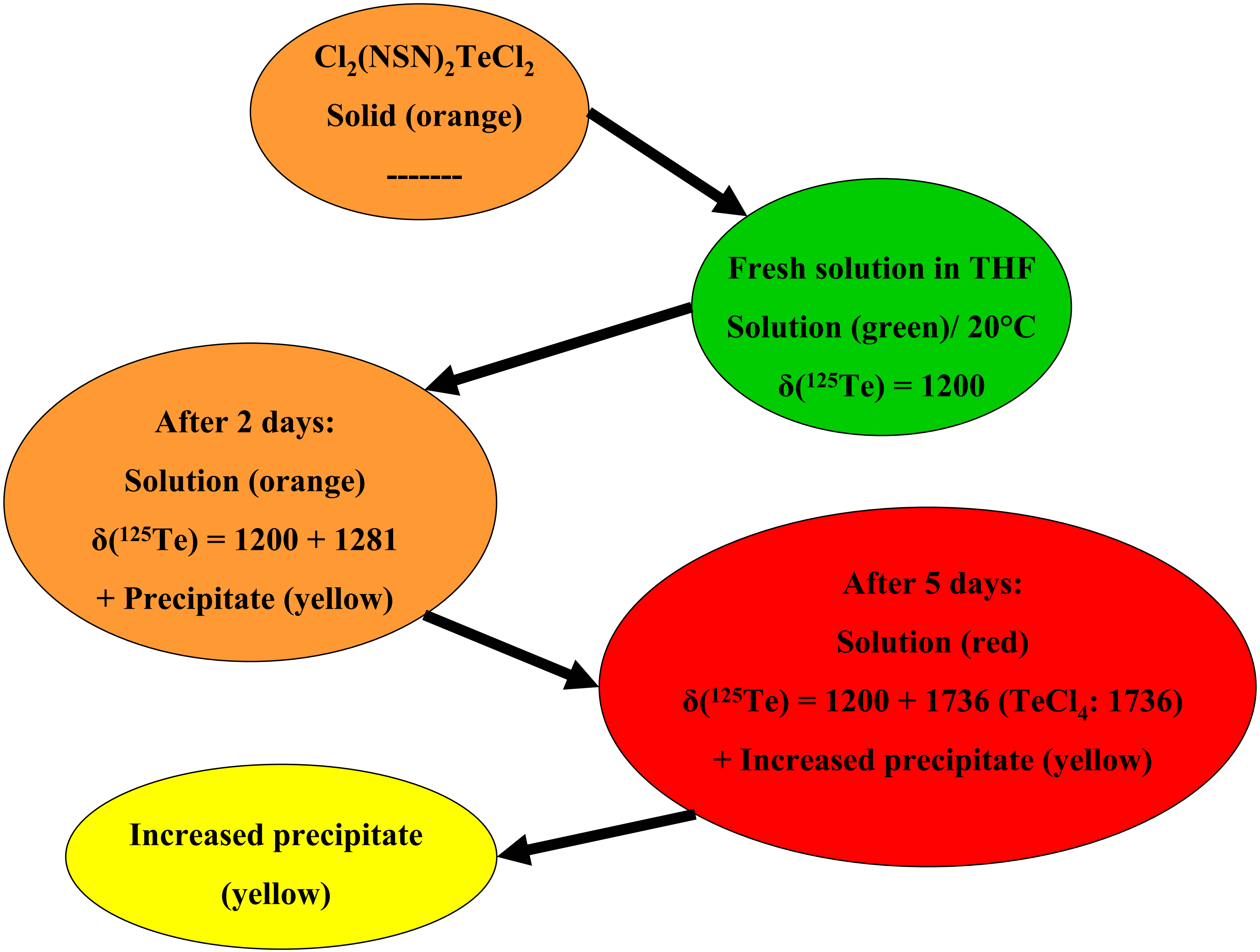

Te(NSO)2
+
SbCl5
?
?..
Cl3Sb---Cl---Te
Cl
S
N
N
S


Te(NSO)2 + SbCl5
- SbCl3
Cl2Te(NSO)2
- SO2
Cl2Te
N
S
N

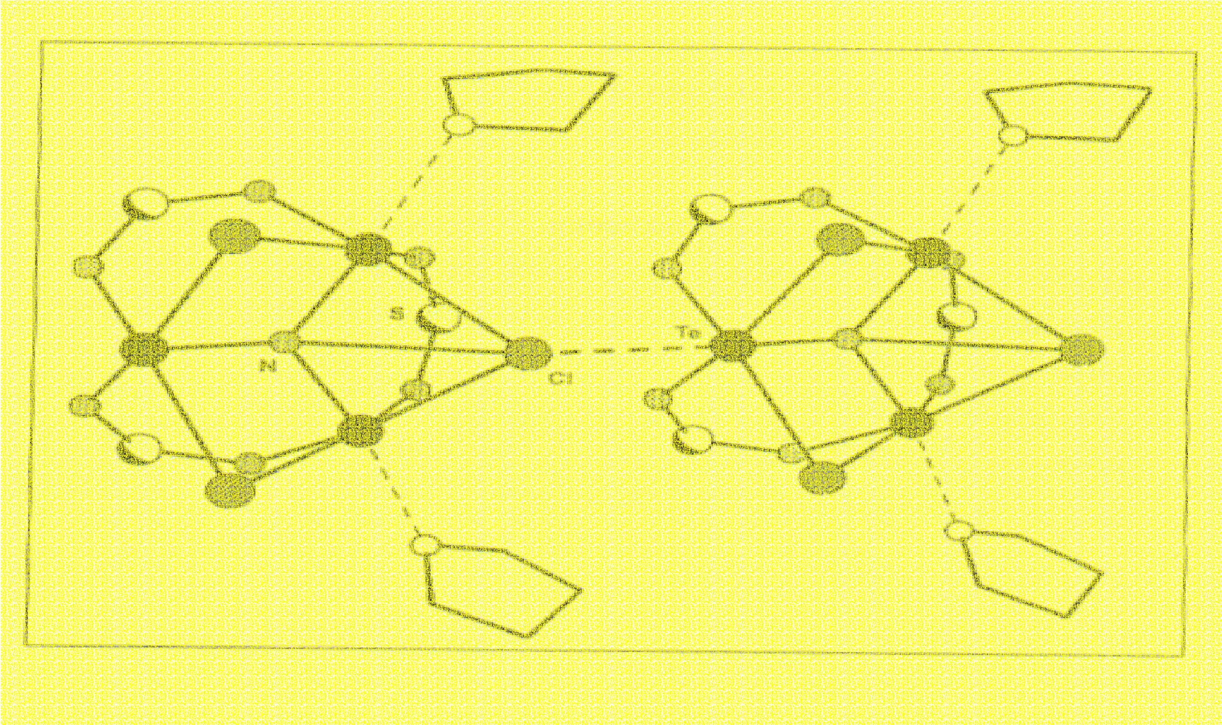
$$Cl_2Te(NSO)_2 + SbCl_{3(5)} \longrightarrow Cl_3TeNSO + SbCl_{2(4)}NSO$$

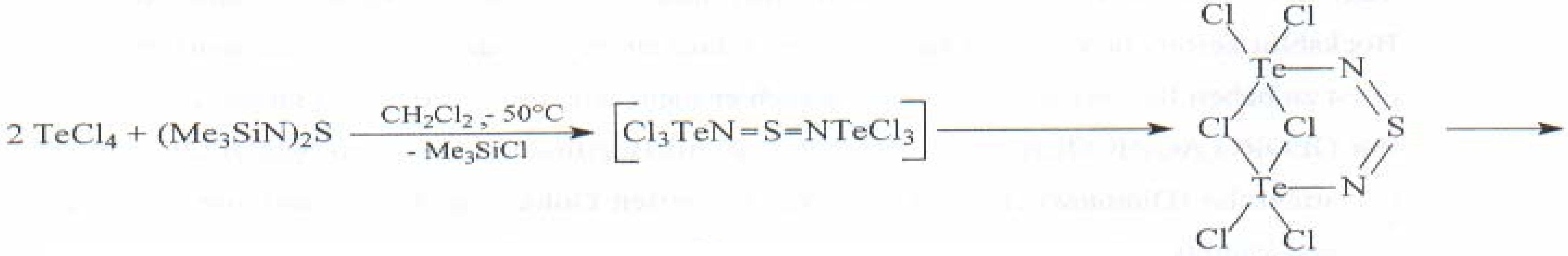
$$2Cl_2Te(NSO)_2 + 2CF_3SCl \longrightarrow Cl_3TeNSO + 2CF_3SNSO$$

$$2Cl_3TeNSO \longrightarrow Cl_3TeNSNTeCl_3 + SO_2$$

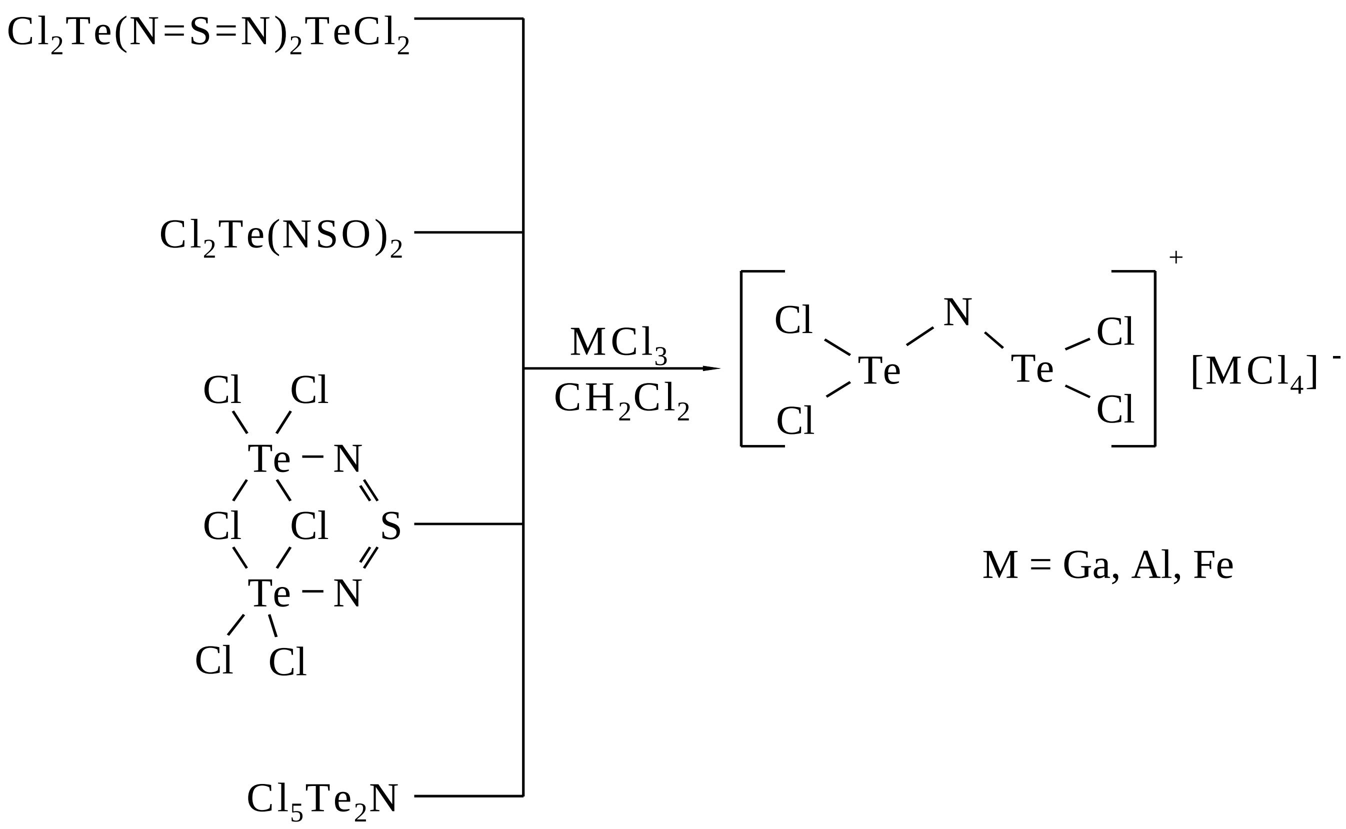

$Cl_2(NSN)_2TeCl_2$
Solid (orange)

Fresh solution in THF
Solution (green)/ 20°C
$\delta(^{125}Te) = 1200$
After 2 days:
Solution (orange)
$\delta(^{125}Te) = 1200 + 1281$
+ Precipitate (yellow)
After 5 days:
Solution (red)
$\delta(^{125}Te) = 1200 + 1736$ ($TeCl_4$: 1736)
+ Increased precipitate (yellow)
Increased precipitate
(yellow)


S
N
Cl
Te

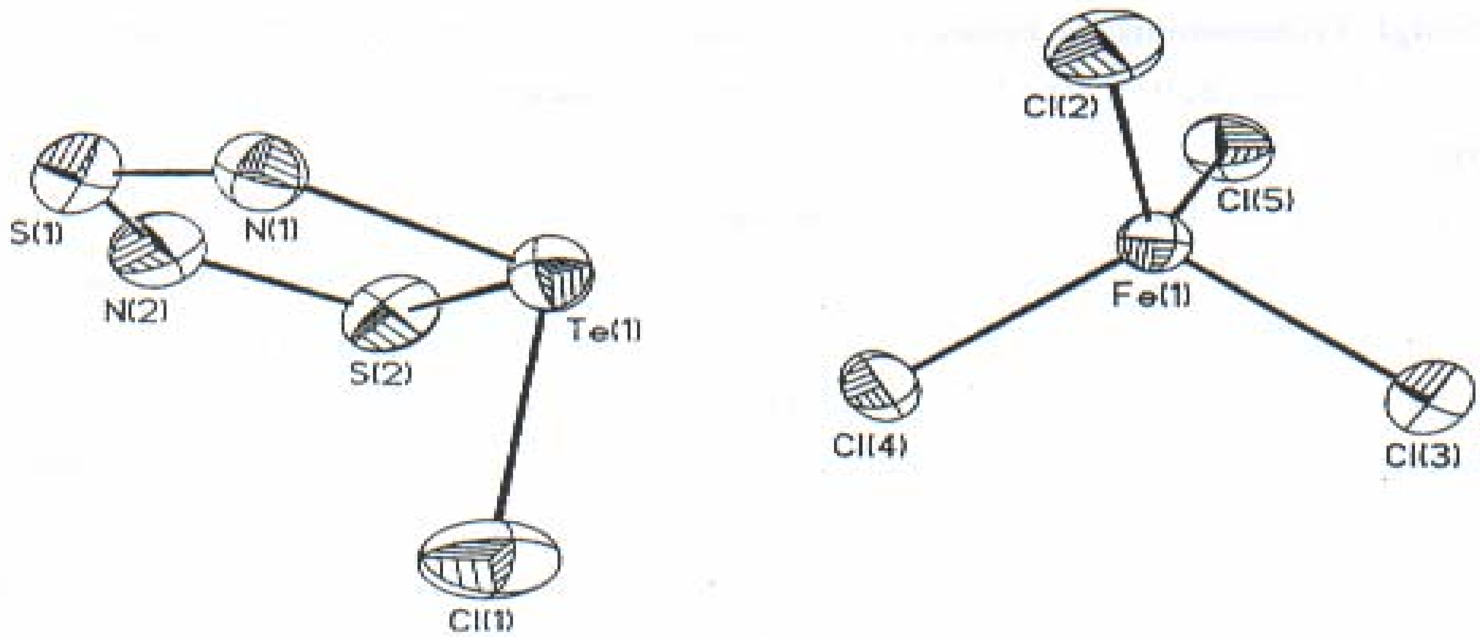


3

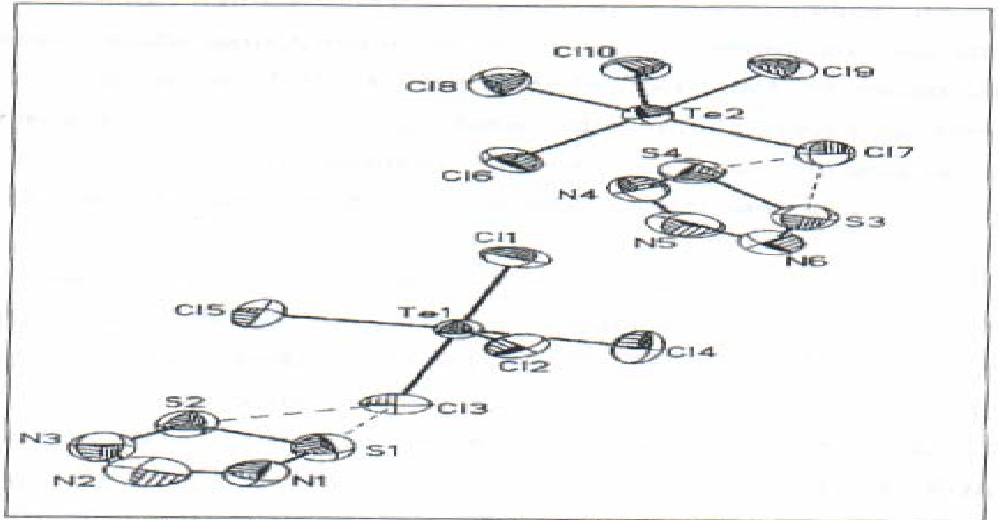


$$3\ TeCl_4 + [(CH_3)_3Si]_3N \longrightarrow (Cl_3Te)_3N + 3\ (CH_3)_3SiCl$$

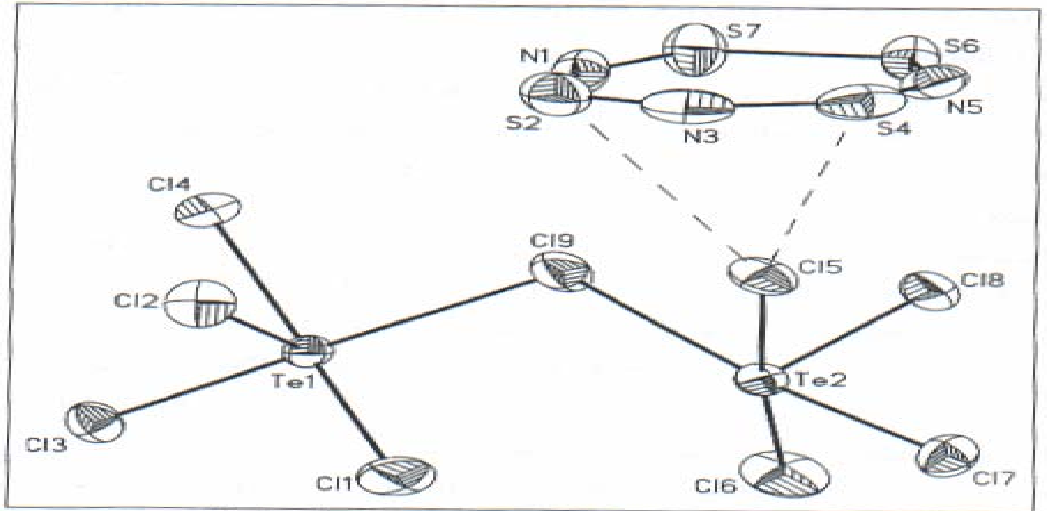
$$(Cl_3Te)_3N \longrightarrow Cl_5Te_2N + TeCl_4$$



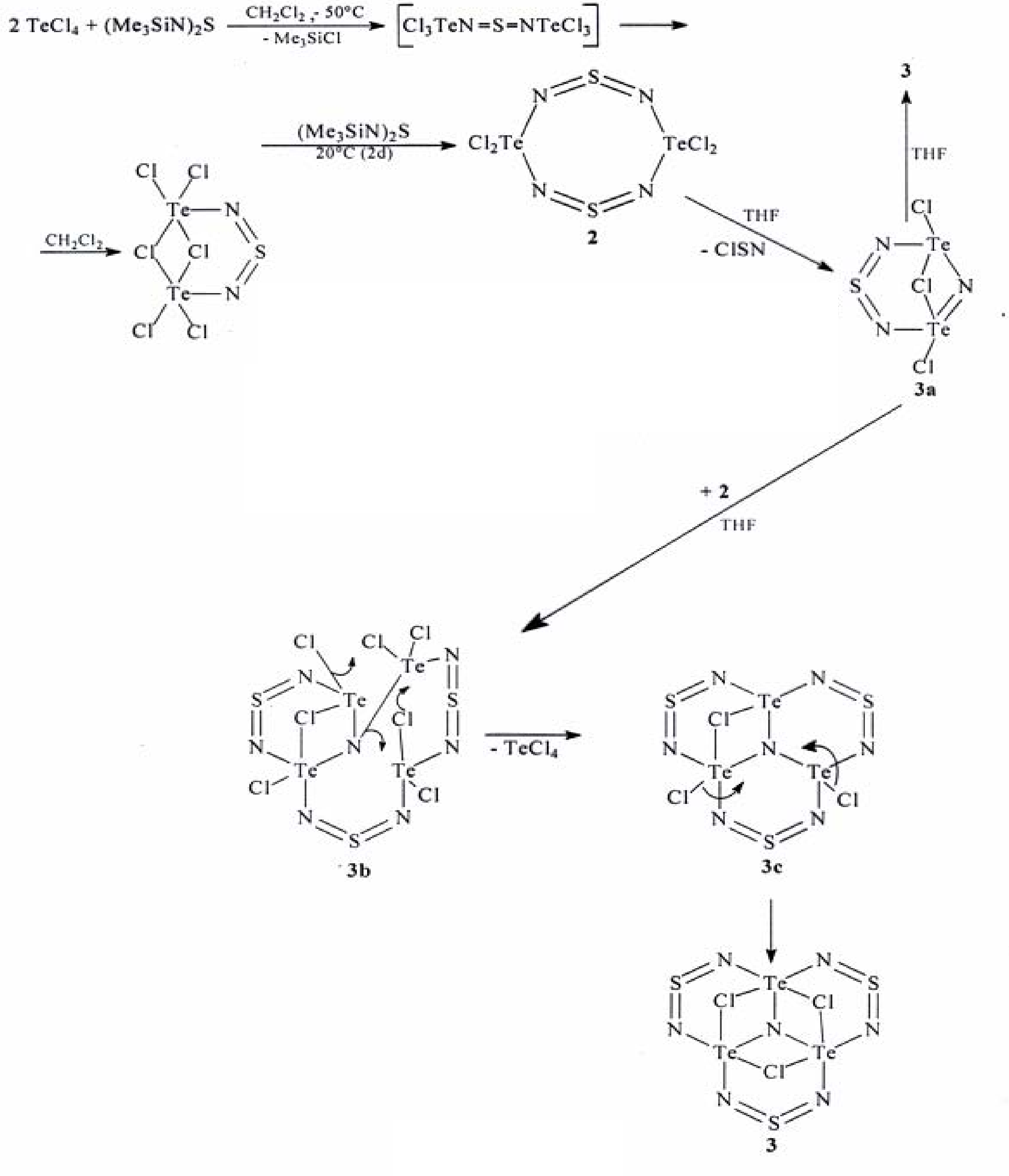
S(1)
N(1)
N(2)
S(2)
Te(1)
Cl(1)
Cl(2)
Cl(5)
Fe(1)
Cl(4)
Cl(3)



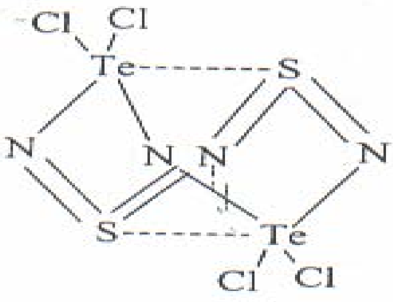
Molecular structure of $[S_2N_3]^+[TeCl_5^-]$



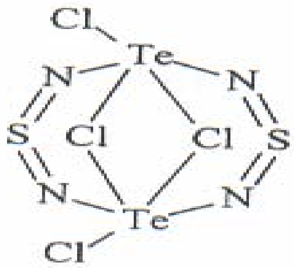
Molecular structure of $[S_4N_3^-][Te_2Cl_9^-]$


2 TeCl4 + (Me3SiN)2S
CH2Cl2 , - 50°C
- Me3SiCl
Cl3TeN=S=NTeCl3
(Me3SiN)2S
20°C (2d)
CH2Cl2
2
THF
- ClSN
3
3a
+ 2
THF
3b
- TeCl4
3c
3

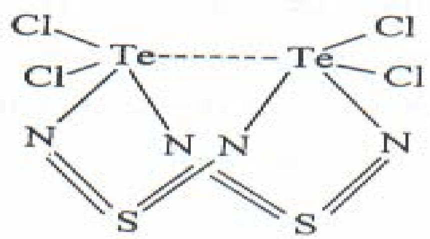
Structures of $Cl_2Te(NSN)_2TeCl_2$



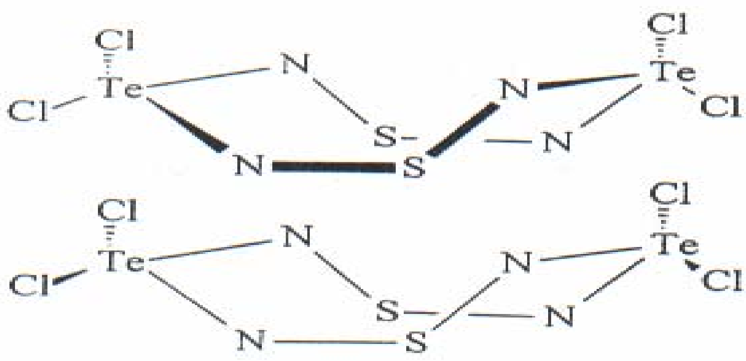
A



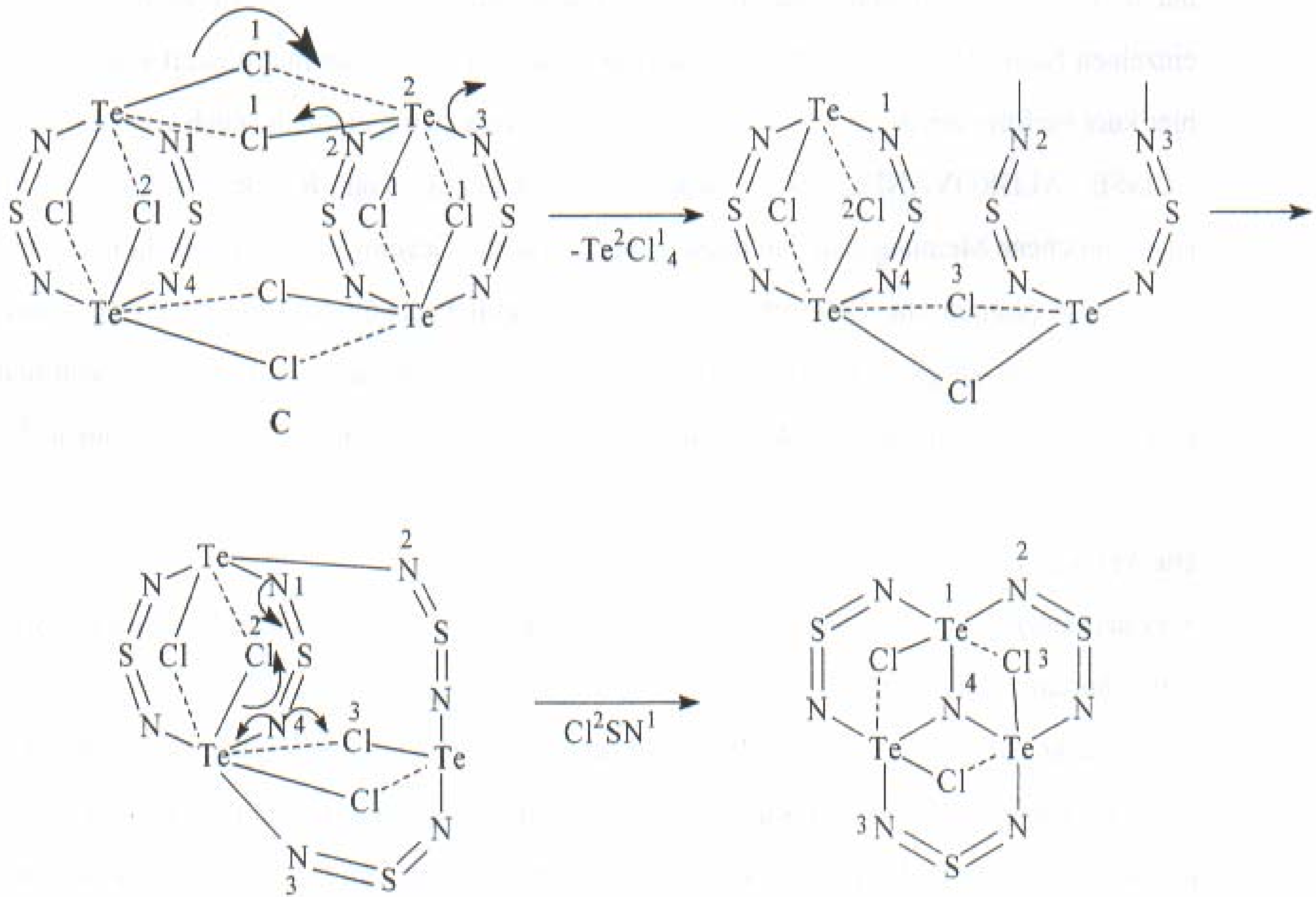
B



C



D


C
$-Te^{2}Cl^{1}_{4}$
$Cl^{2}SN^{1}$