



Anorganische Chemie VI

Konzepte und Theorie an ausgewählten Stoffklassen (KTS)

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Institut für Chemie
Anorganische Chemie
der Universität Rostock
2026*



Chalokogen-Stickstoff-Chemie

■ Inhalt

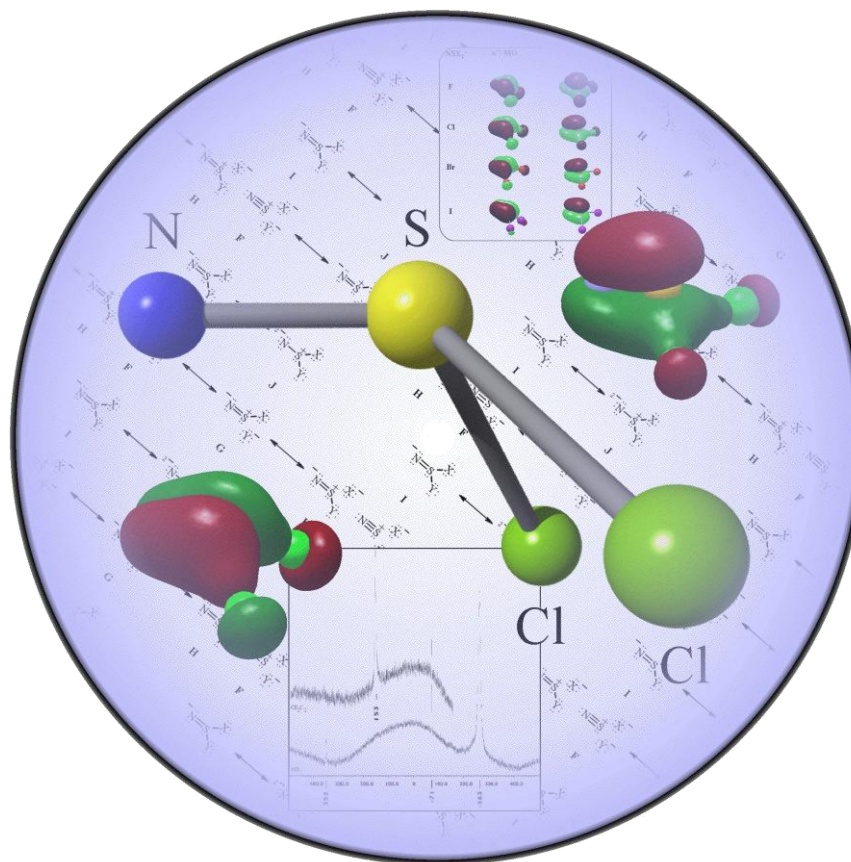
- **SN-Aromaten**
- **SN-Halogene**
- **Kombination Theorie-Experiment**

Alle Folien sind im Internet als pdf Dokument erhältlich:

<http://www.schulz.chemie.uni-rostock.de/>



„Neue Schwefel-Stickstoff-Spezies: Synthese, Struktur und Bindung“





Schwefel-Stickstoffverbindungen

■ Lehrbücher

R. Steudel, *Chemie der Nichtmetalle*, W. de Gruyter, 1998;

T. M. Klapötke, I. C. Tornieporth-Oetting, *Nichtmetallchemie*, VCH, 1994;

J. D. Woolins, *Non-Metal Rings, Cages and Cluster*, Wiley & Sons, New York, 1987;

N. Burford, J. Passmore, J. C. P. Sanders in *From Atoms to Polymers*, (Hrsg.: J. F. Liebman, A. Greenberg), VCH, Weinheim **1989**, S. 53.

T. Chivers, *Chemical Reviews*, **1985**, 85, 341.

T. Chivers, *A Guide to Chalcogen-Nitrogen-Chemistry*, **2005**

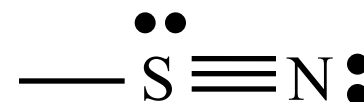
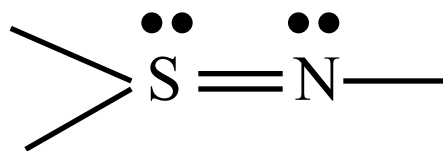
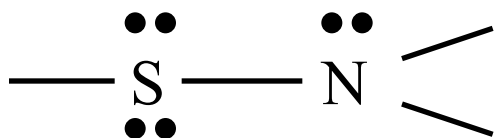
Binäre SN-Spezies



Ternäre SN-Spezies

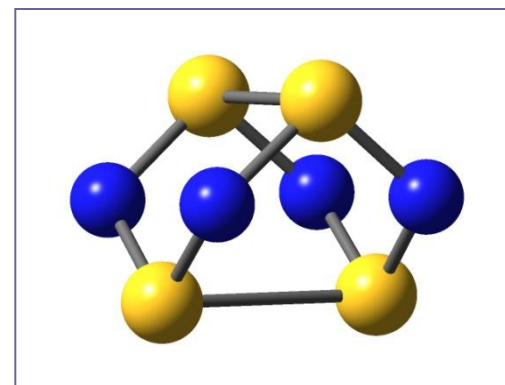


Einleitung



- kontinuierliche Übergänge
- auch höhere Oxidationszahlen
- höhere Koordinationszahlen
- gesättigt oder ungesättigt
- kettenförmig, cyclisch oder polycyclisch
- neutral, kationisch oder anionisch

1835: S₄N₄





Tetraschwefeltetranitrid: S₄N₄

178°-198° Zersetzung

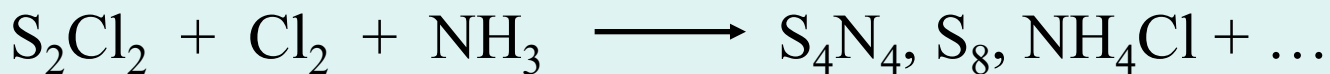
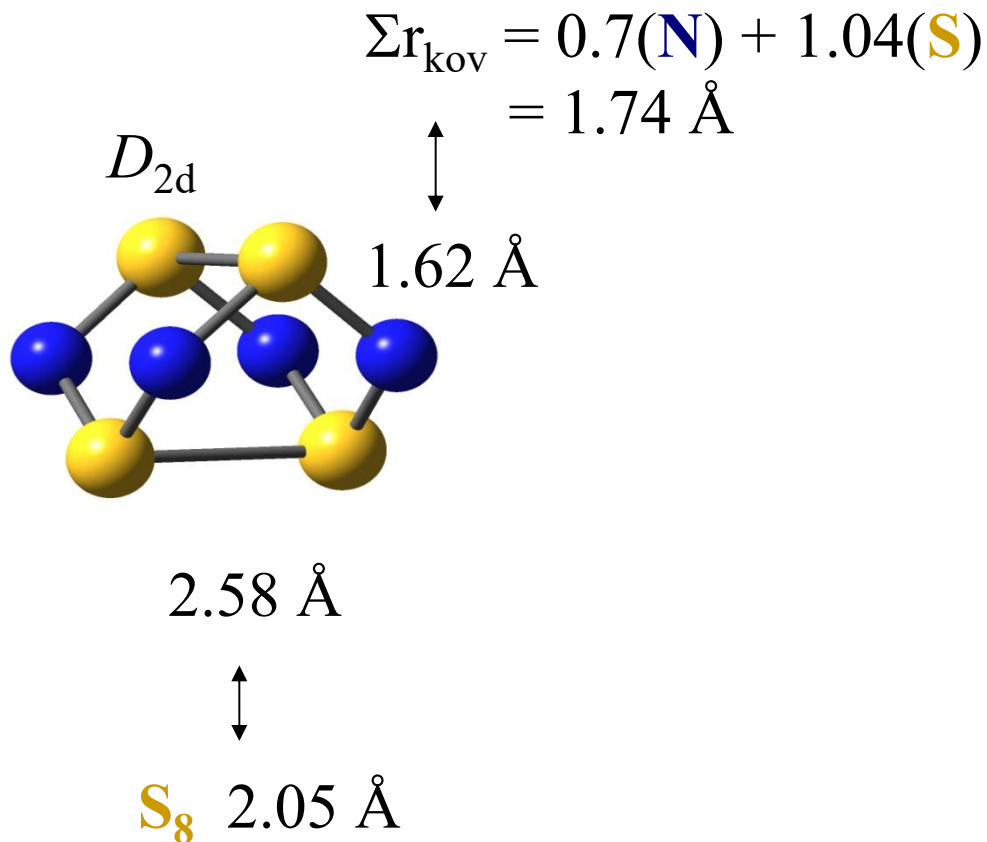
orange Kristalle

thermochrom

$\Delta H_B^\circ = 460 \text{ kJ/mol}$

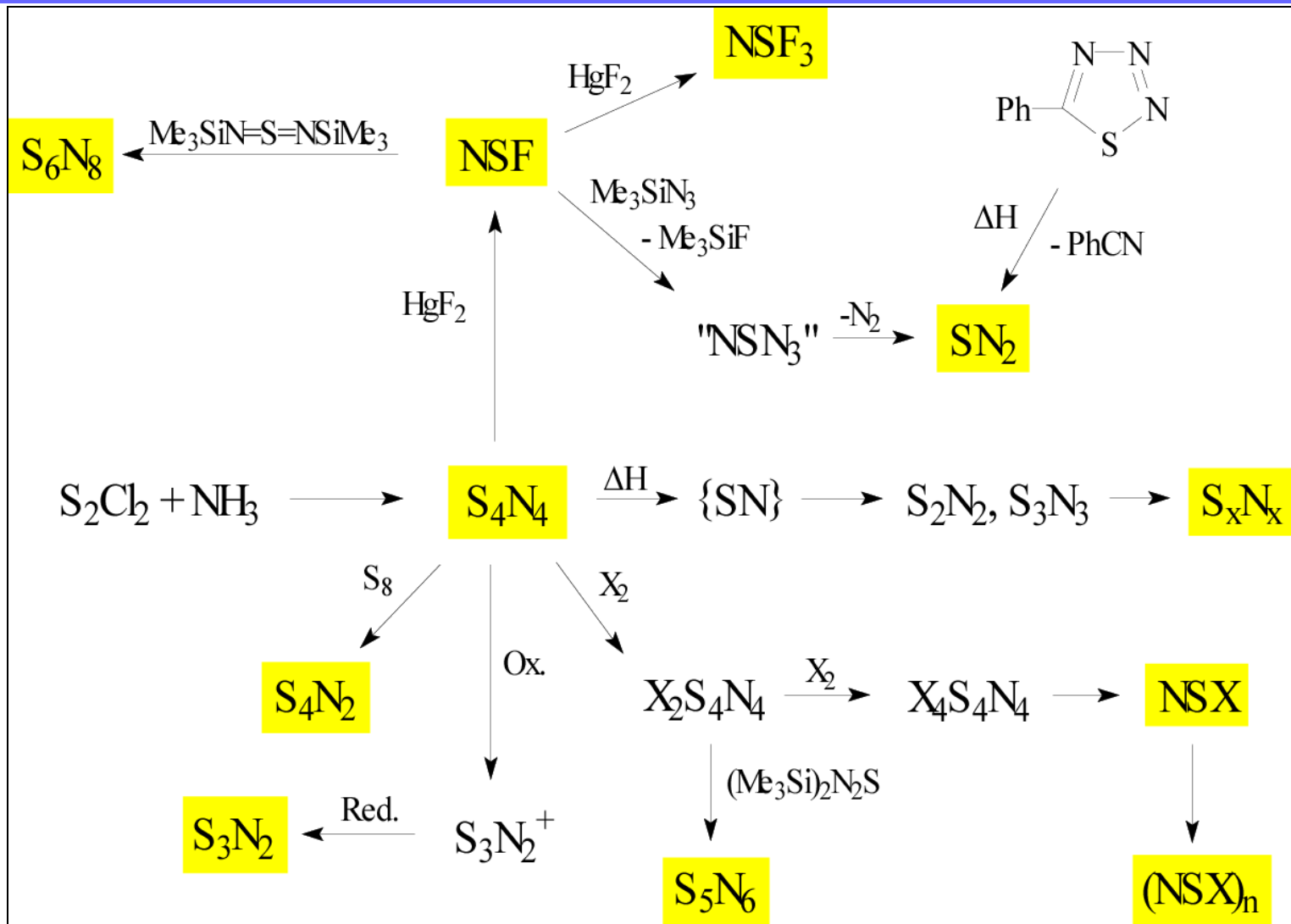
cf.

$\Delta H_B^\circ(4 \times \text{NO}) = 321 \text{ kJ/mol}$



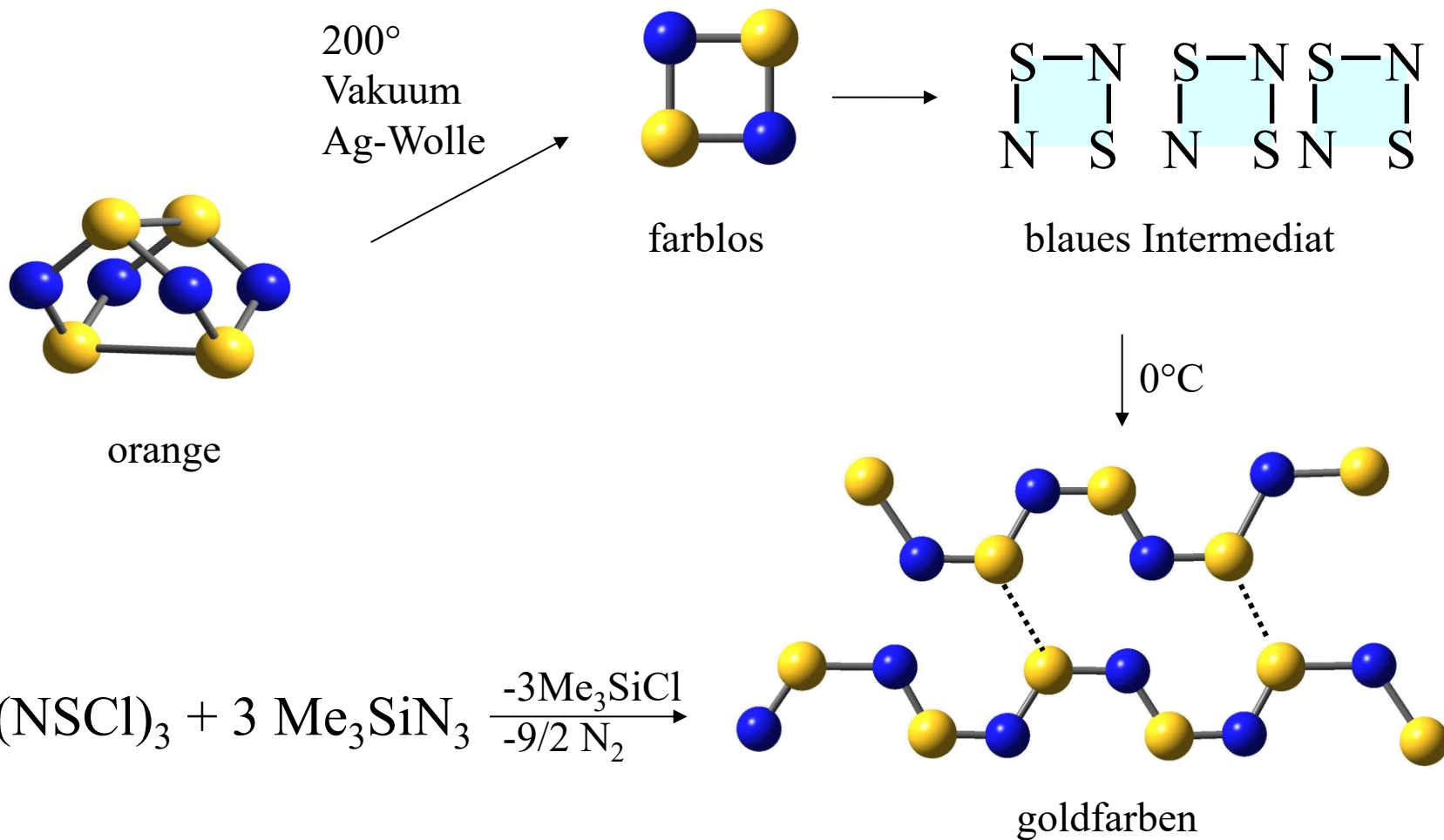


S_4N_4 ein Tor zur SN-Chemie



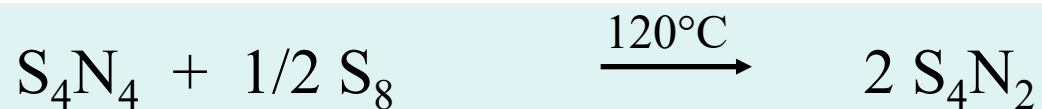
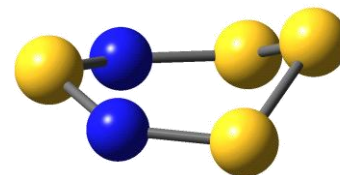
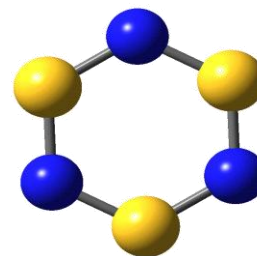
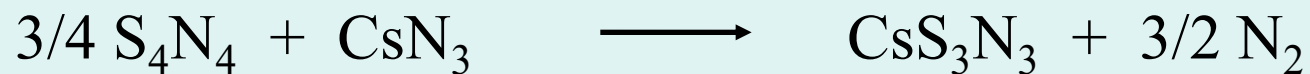


Thermolyse von S₄N₄



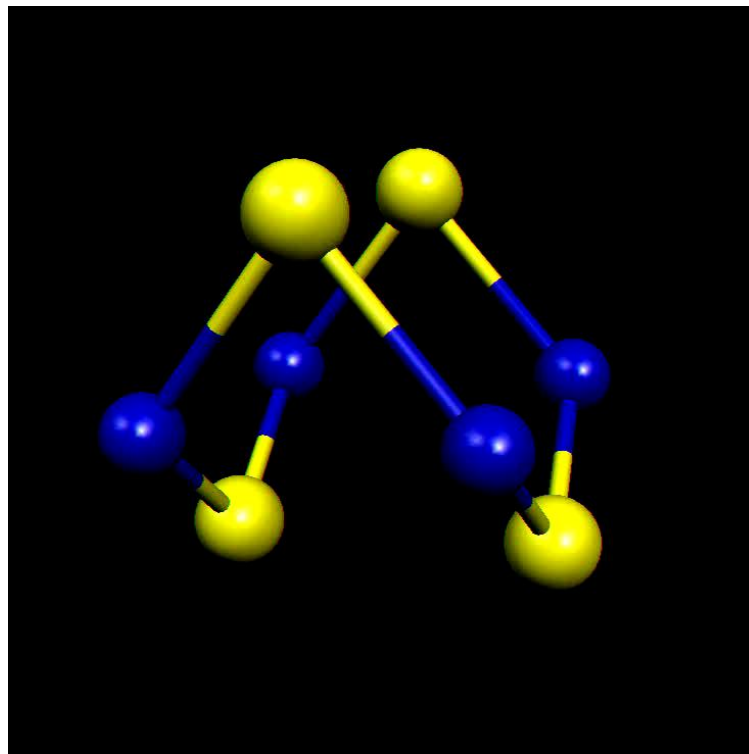
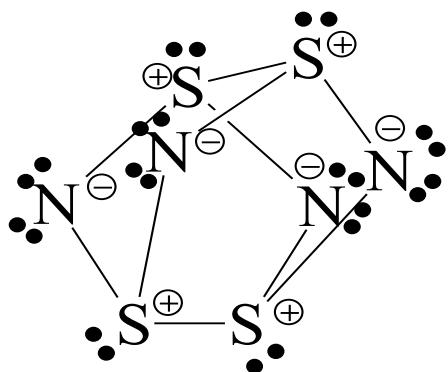


Weitere binäre SN-Spezies



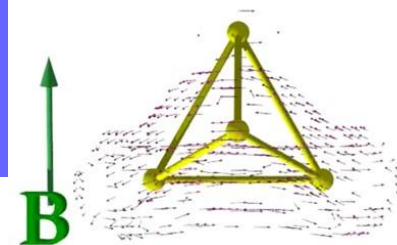


Was passiert, wenn S_4N_4 oxidiert wird?





Aromatizität – KEINE Observable



Klassische Merkmale

- Cyclisch-konjugiert
- $4n + 2$ π -Elektronen (Hückel-Regel)
- planar
- sp^2 -hybridisiert
- diamagnetischen Ringstromeffekten, Anisotropie der magnetische Suszeptibilität
- Entartung (3-zählige Symmetrie)
- Bindungslängenausgleich
- antiaromatisch – JT-Verzerrung

Erweiterung

- NICS-Werte (negativ)
- HOMO-LUMO Differenz (groß), antiaromatisch klein (häufig Biradikalcharakter)

π -Aromatizität

Hetero-Aromatizität

σ -Aromatizität

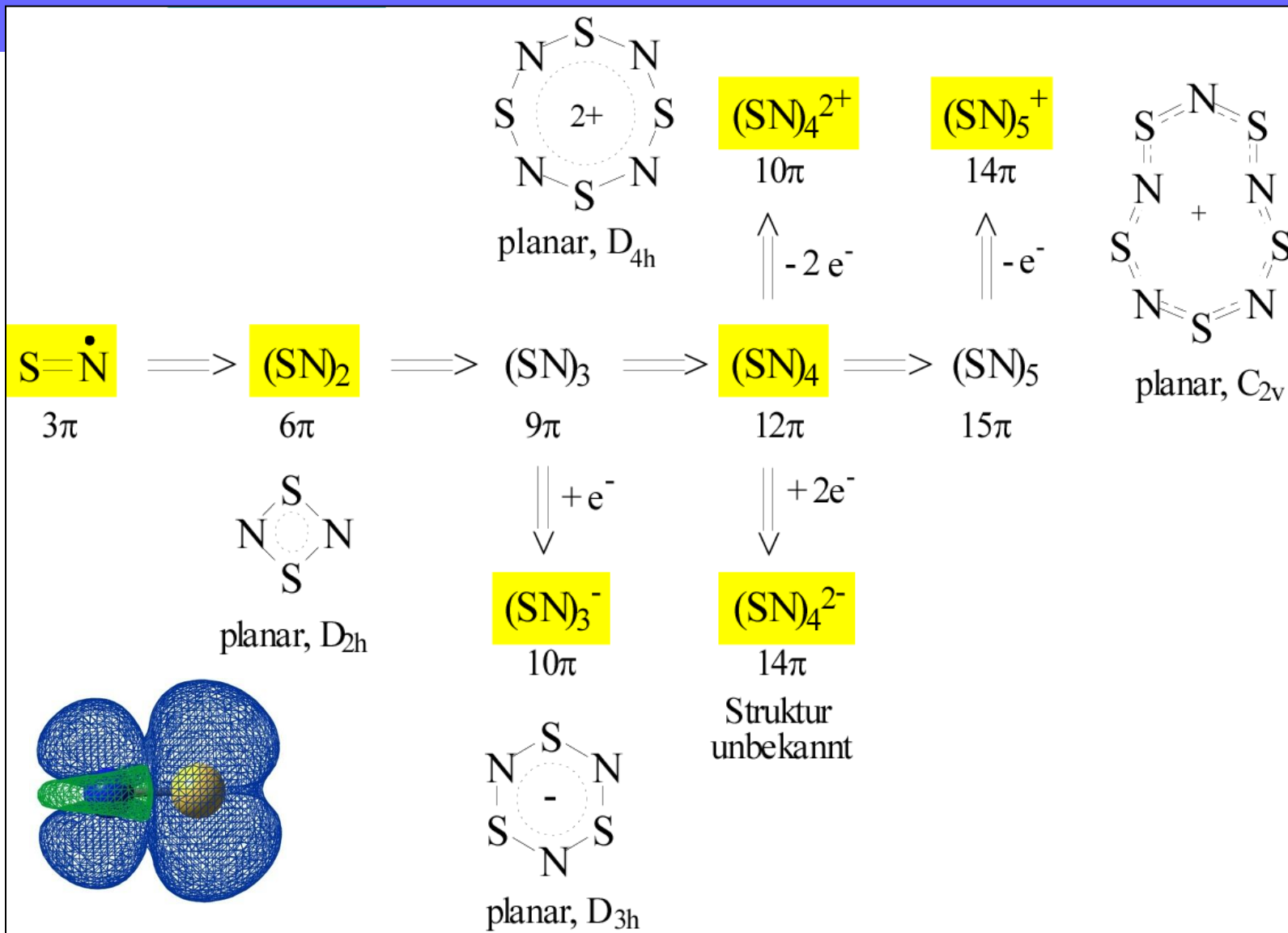
Homoaromatizität

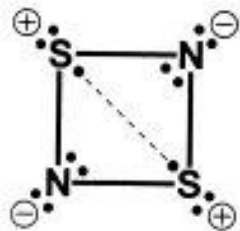
σ -Homoaromatizität

**Sphärische Aromatizität
(Räumliche Aromatizität,
3D-Aromatizität)**

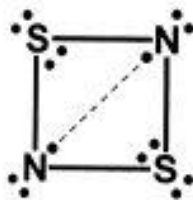


Binäre planare SN-Ringe

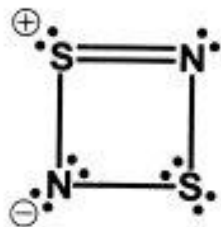




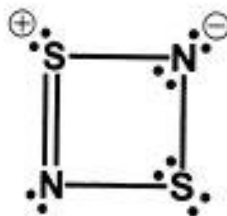
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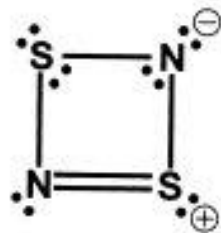
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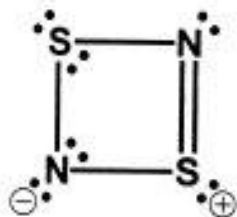
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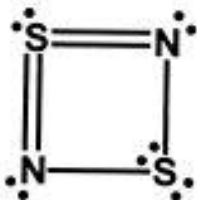
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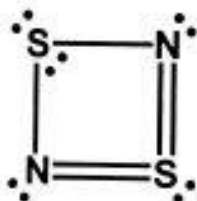
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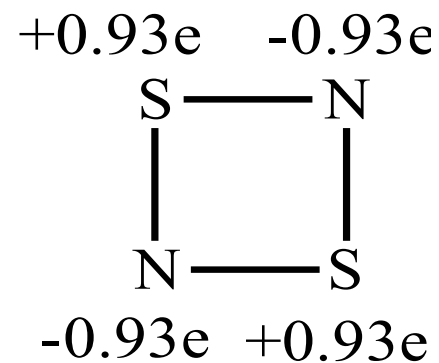


g



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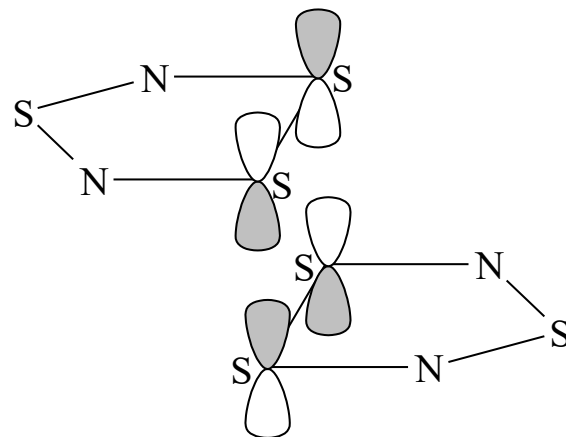
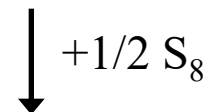
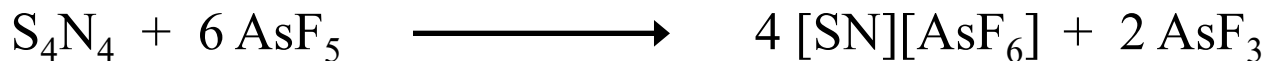
S₂N₂: 6π-Aromat ?



R.D. Harcourt, A. Schulz et. al
J. Chem. Phys., **1998**, 1850.

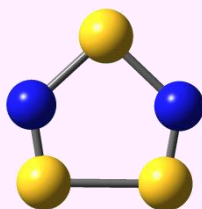


$\pi^*-\pi^*$ -Wechselwirkung zweier $S_3N_2^+$ -Radikal-Kationen



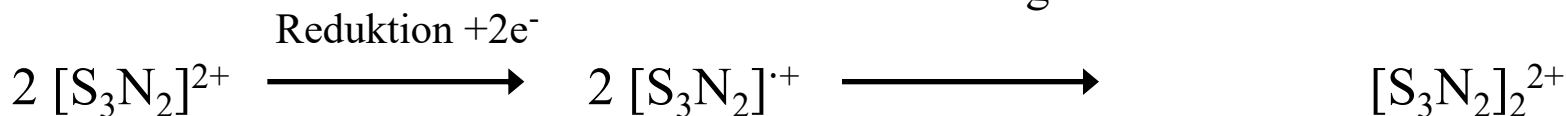
$[S_3N_2]^{2+}$: Ermitteln der π -Elektronen ausgehend von den Valenzelektronen

Elektronen S:	18
Elektronen N:	10
Ladung:	-2
<hr/> Gesamtzahl:	<hr/> 26



5- σ -Bindungen:	-10
5 freie e^- -Paare:	-10
<hr/> π -Elektronen:	<hr/> 6

entspricht $(4n+2)$, $n = 1$



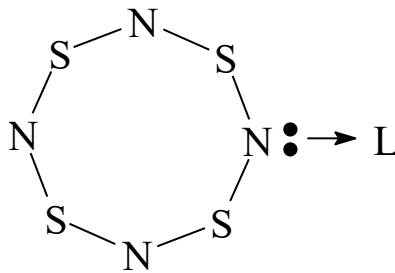
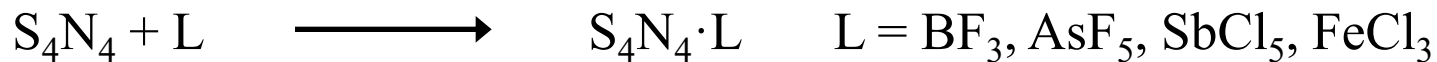
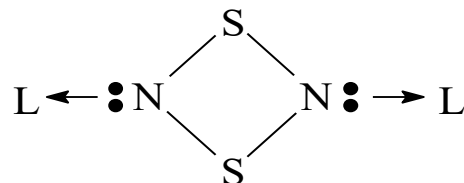
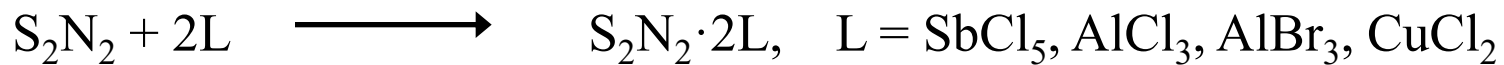
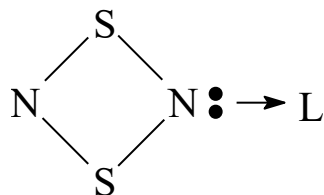
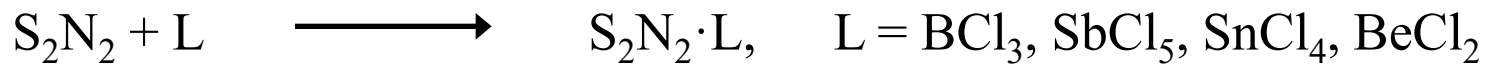


Schwere Elemente und Doppelbindung ?

- kinetisch stabilisiert z.B. $R_2Si=SiR_2$
- durch positive Ladungen stabilisiert z.B. SN^+ , I_2^+
- durch Delokalisation stabilisiert z.B. S_4^{2+} , S_2N_2
- Adduktbildung bzw. Koordination an Übergangsmetallfragment z.B. $S_4N_4-SbCl_5$
z.B. $NbCl_5(S_2N_2)NbCl_5$
- durch $\pi^*-\pi^*$ -Wechselwirkung stabilisiert z.B. $S_3N_2^{\cdot+}$ -Radikal

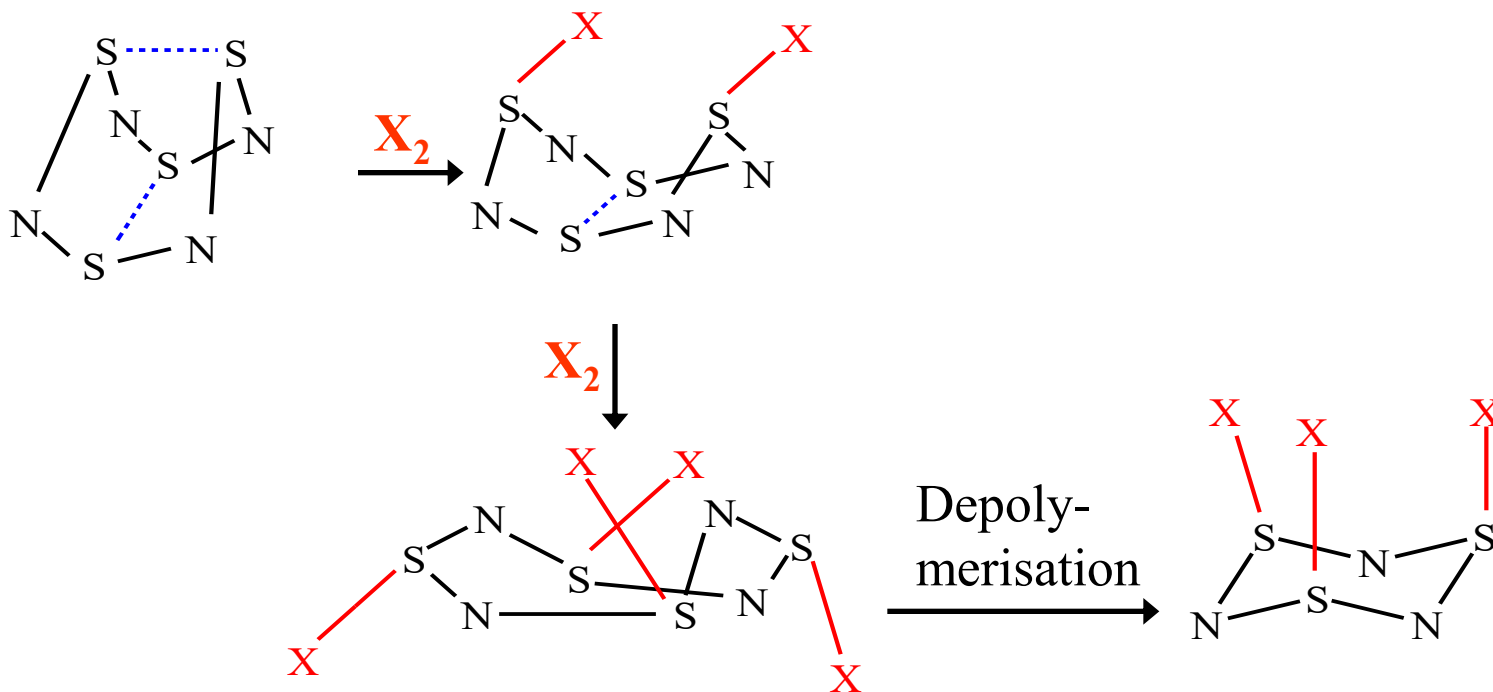


Adduktbildung





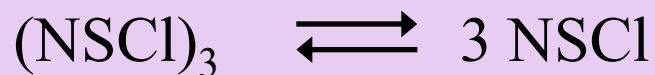
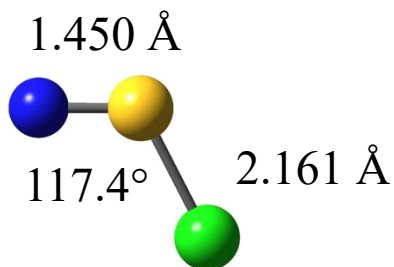
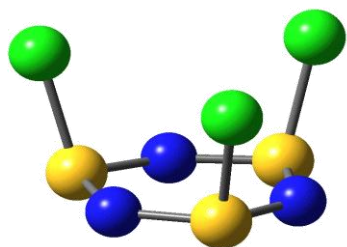
Ternäre NSX-Spezies (X = Halogen)





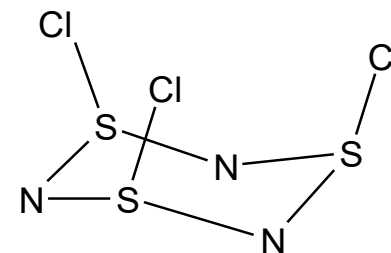
Ternäre NSCI-Spezies

- $(\text{NPCl}_2)_x$ vs. $(\text{NSCl})_x$
- PCl_2 durch SCl substituieren



$$\Delta H^\circ = 65 \pm 13 \text{ kJ mol}^{-1}, \Delta S^\circ = 206 \pm 20 \text{ J mol}^{-1} \text{ K}^{-1}$$

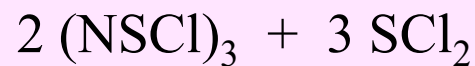
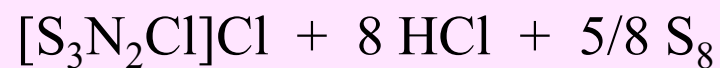
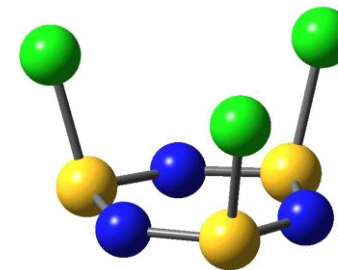
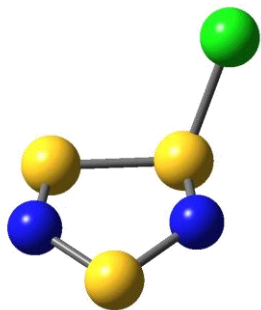
J. Passmore, M. Schriver, *Inorg. Chem.* **1988**, 27, 2749.



flacher Sesselkonformation

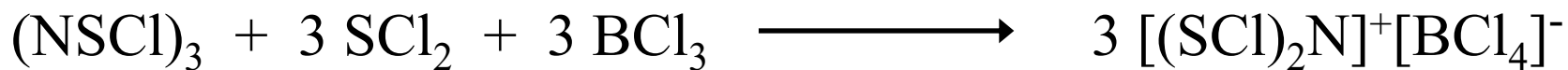
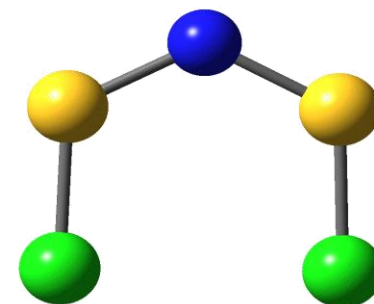
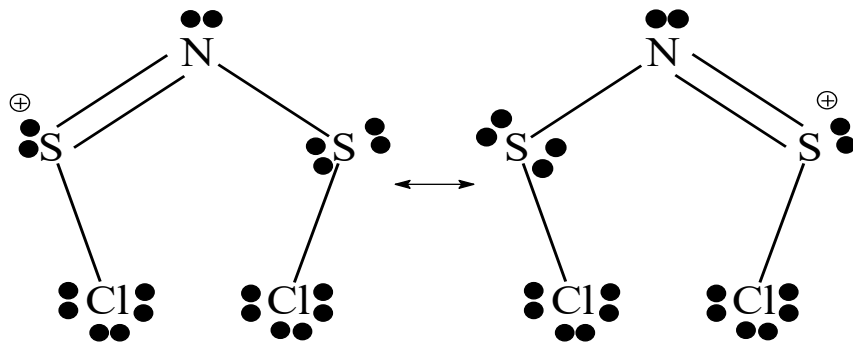
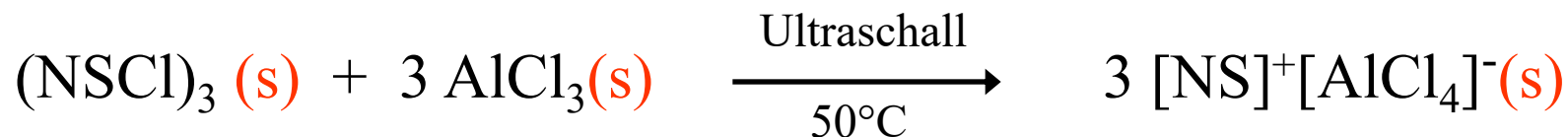


Thiazylchlorid



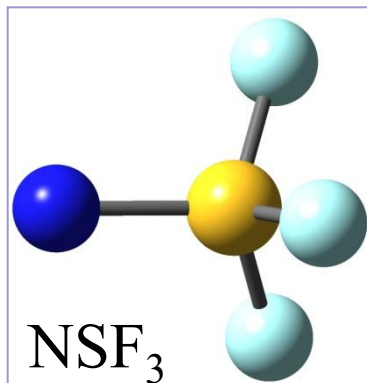
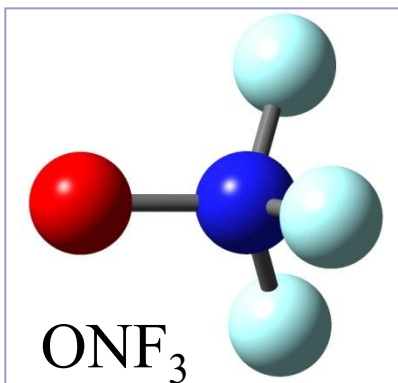
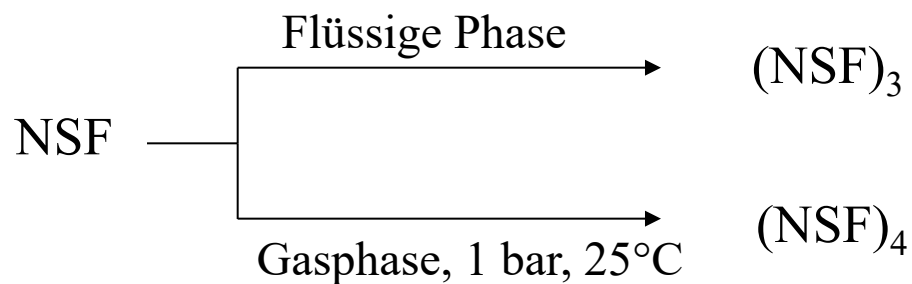
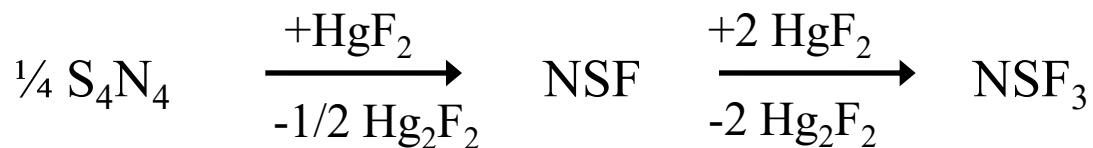


(NSCl)₃ + Lewis-Säure





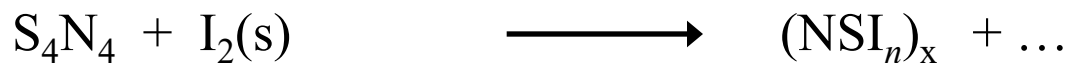
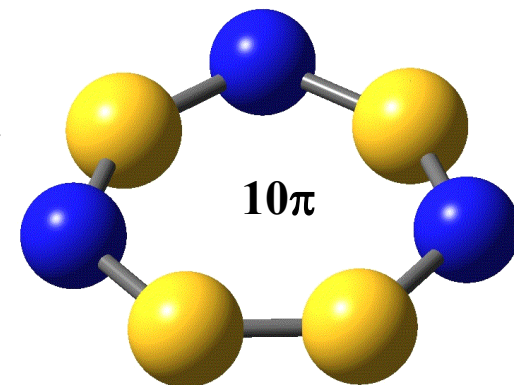
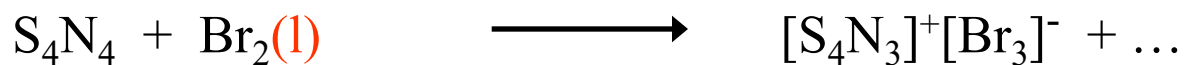
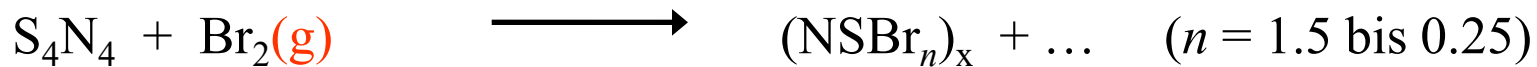
Thiazylfluoride



vs. SF₆

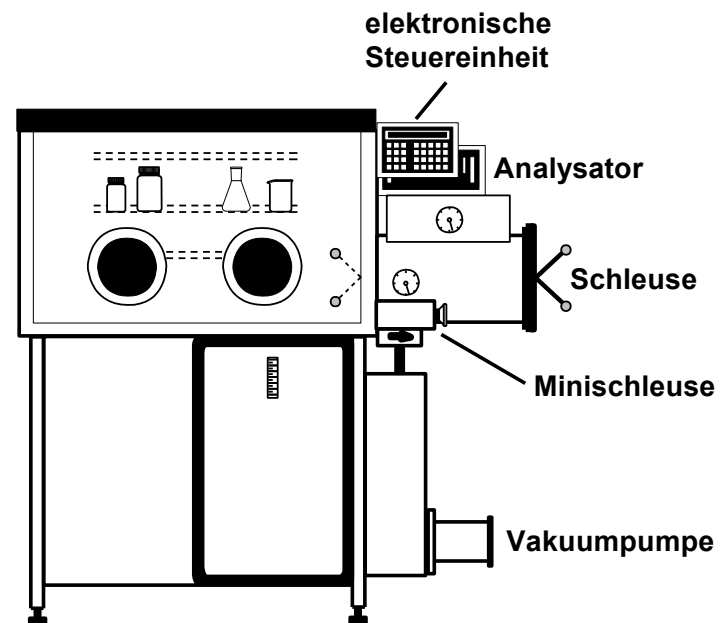
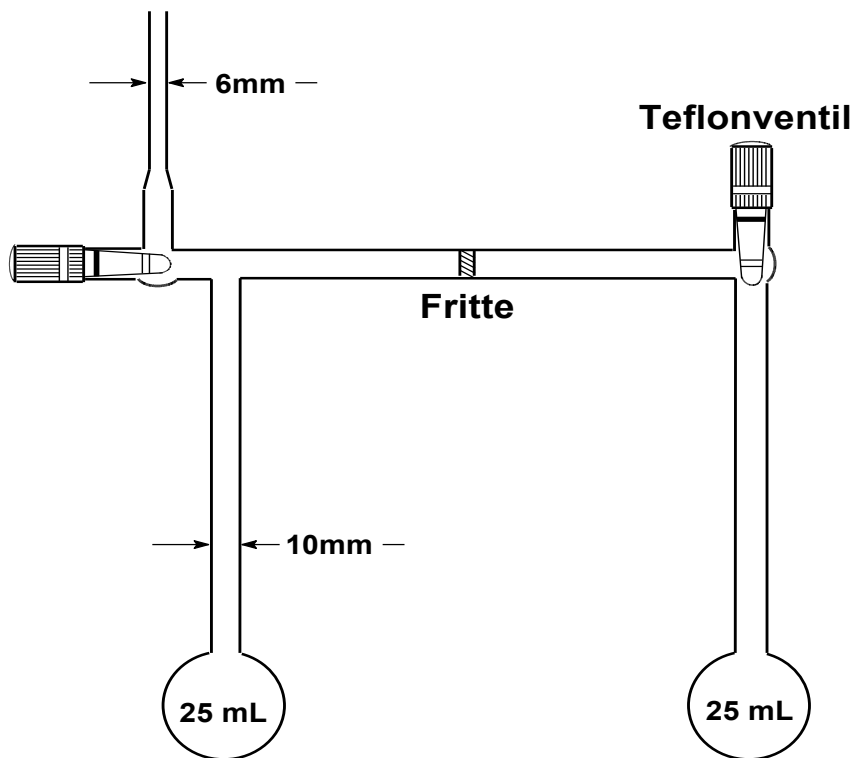


Thiazylbromide und – iodide?



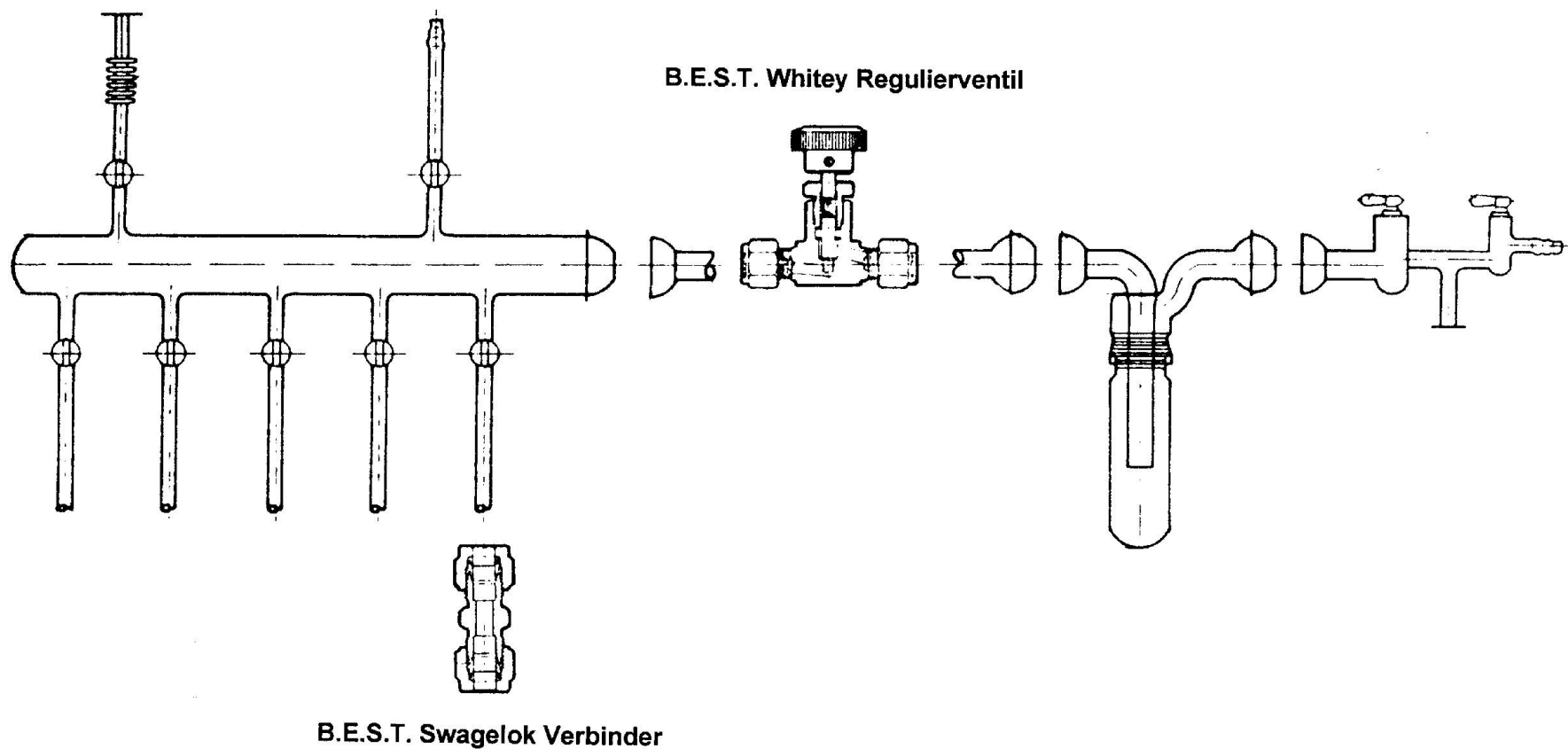


Zweikugelkolben





Vakuumanlage aus Stahl





Zusammenfassung - Binäre SN-Spezies

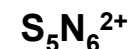
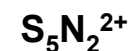
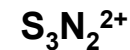
Anionen



Neutrale Moleküle

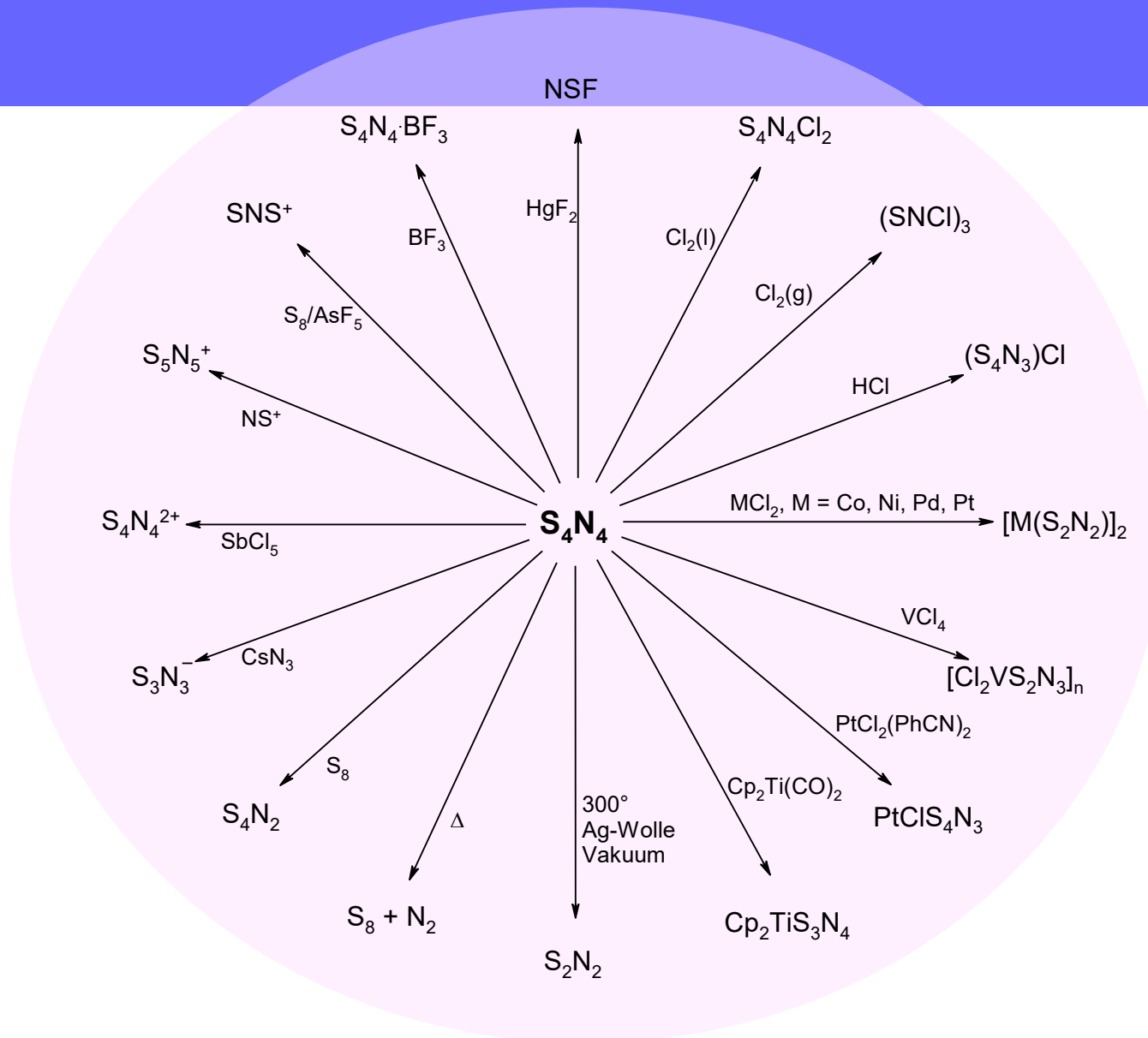


Kationen





Zusammenfassung - Synthese von SN-Spezies



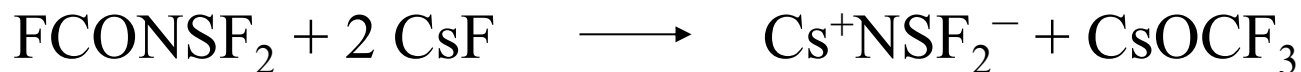
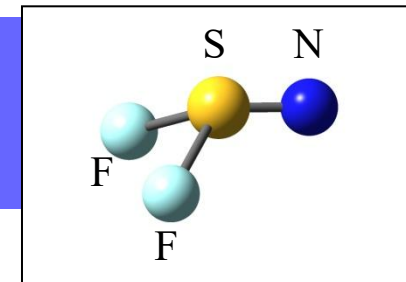


Aus dem AK-Schulz

„Neue Schwefel-Stickstoff-Spezies: Synthese, Struktur und Bindung“



Thiazyldifluorid: NSF_2^-



TAS-Fluorid = $(\text{Me}_2\text{N})_3\text{S}^+ \text{Me}_3\text{SiF}_2^-$

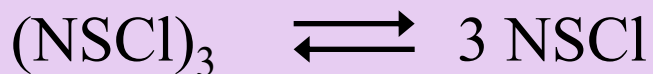
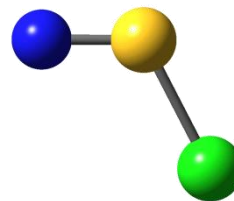
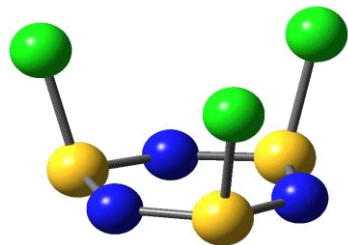
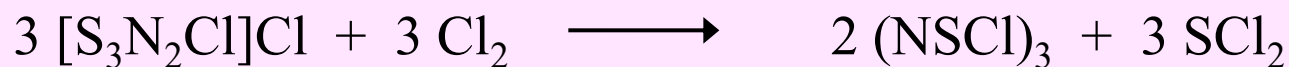
Tris(dimethylamino)sulfonium-difluorotrimethylsilikat

W. Heilemann, R. Mews, *Chem. Ber.* **1988**, *121*, 461;

B. Krebs, E. Meyer-Hussein, O. Glemser, R. Mews, *Chem. Comm.* **1968**, 1578.



Thiazylchlorid

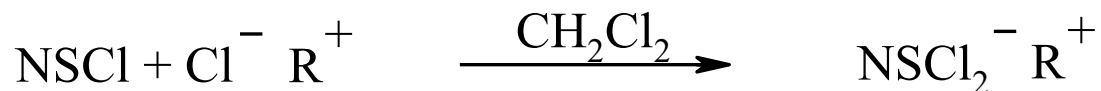


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J. Passmore, M. Schriver, *Inorg. Chem.* **1988**, 27, 2749.

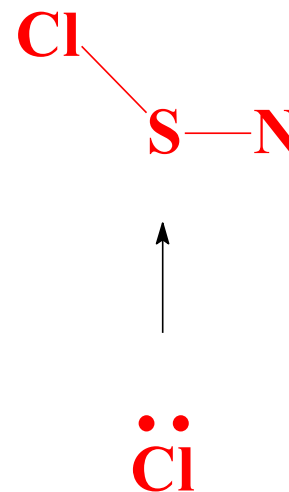
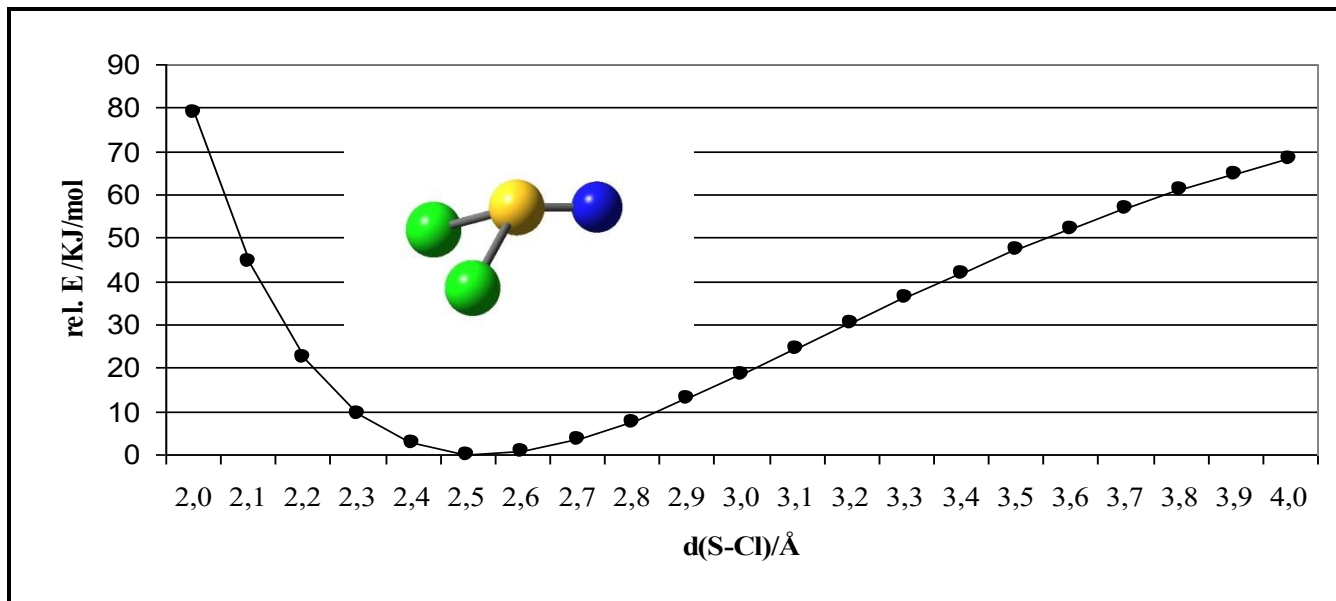


Thiazyldichlorid: NSCl_2^-



$$Q_{\text{CT}} = 0.385e$$

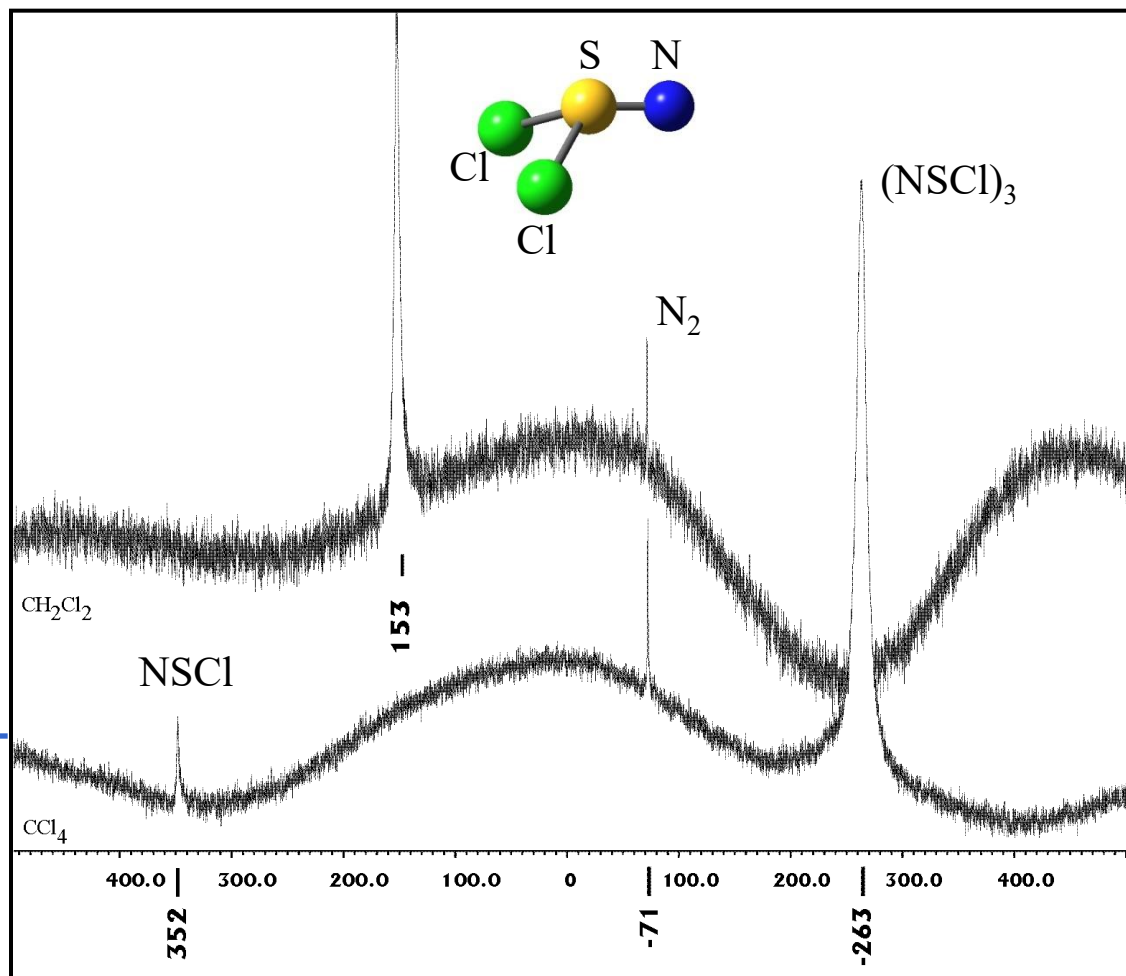
Energiepotential (B3LYP/6-311+G(3df)) für die Reaktion $\text{NSCl} + \text{Cl}^-$

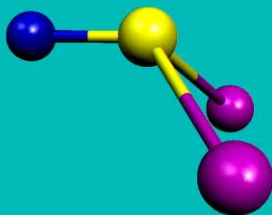




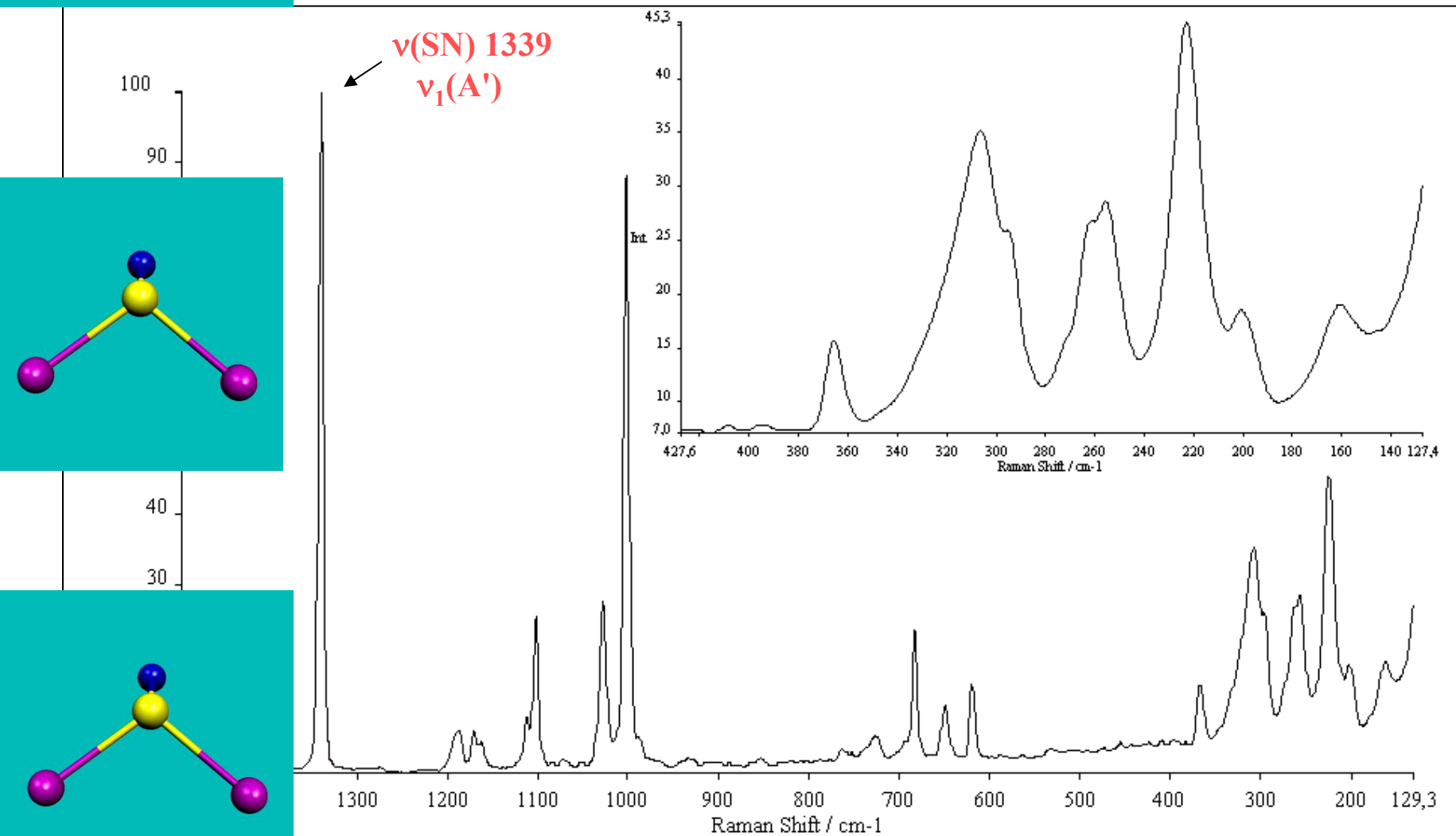
^{14}N - und ^{15}N -NMR-Verschiebungen

Verbindung	Kern	δ	$\Delta\nu^{1/2}$
$[\text{Ph}_4\text{P}]^+[\text{NSCl}_2]^-$	^{14}N	+153	140
$[\text{Ph}_4\text{P}]^+[\text{NSCl}_2]^-$	^{15}N	+148	
$[\text{Ph}_4\text{P}]^+[\text{NSCl}_2]^-$	^{15}N MAS	+147	
$[\text{Ph}_3\text{BzP}]^+[\text{NSCl}_2]^-$	^{14}N	+153	140
$[(\text{PPh}_3\text{N})_2\text{SCl}]^+[\text{NSCl}_2]^-$	^{14}N	+153	140
$(\text{NSCl})_3$	^{14}N	-263	260
NSCl	^{14}N	+352	80



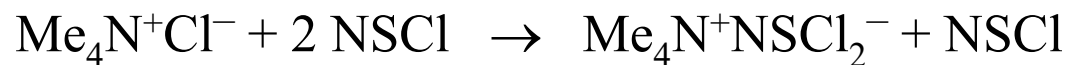
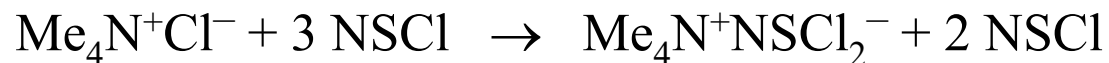


Raman Spektrum von $[\text{Ph}_4\text{P}]^+[\text{NSCl}_2]^-$





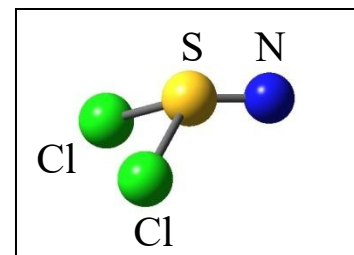
Einfluss der Stöchiometrie



H,C,N,S – Analyse

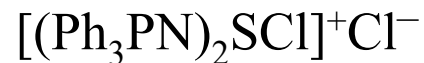
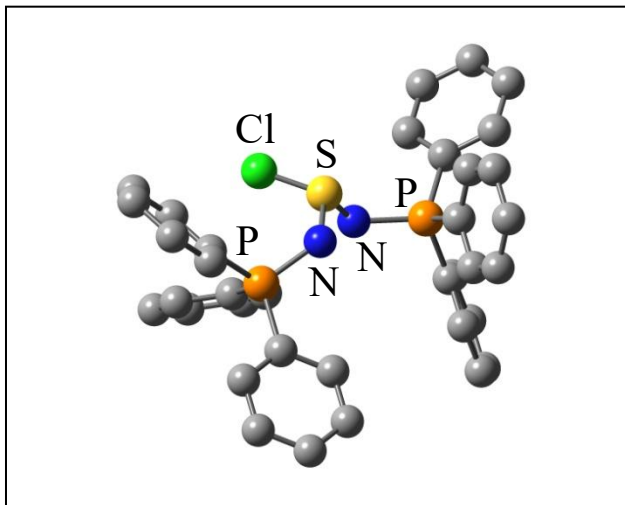
Pulverdiffraktometrie

IR-, Raman-Experimente





Auf der Suche nach Einkristallen von einem NSCl_2^- -Salz



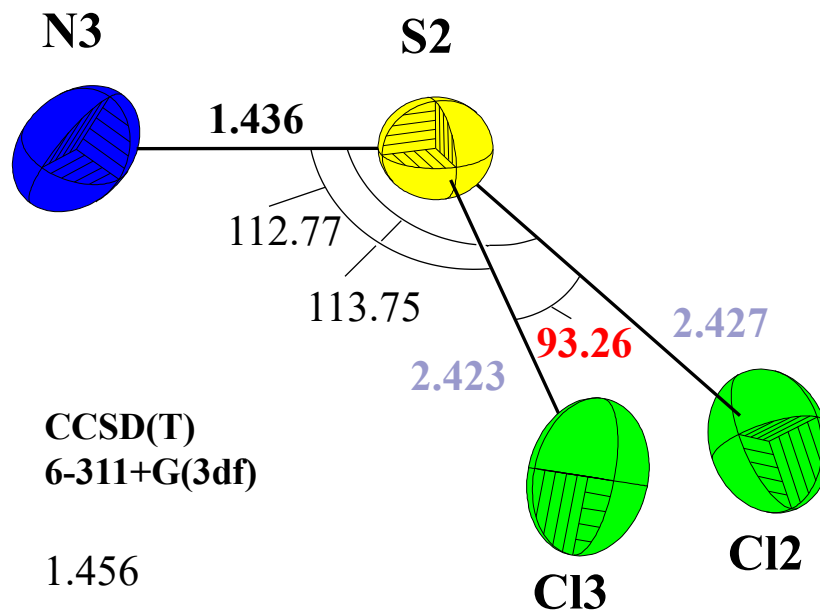
H. Folkerts, D. Nußhär, F. Weller,
K. Dehnicke, J. Maghull, W. Hiller
Z. Anorg. Allg. Chem. **1994**, 620, 1986.



10 % Ausbeute



Molekülstruktur des NSCl_2^- -Ions

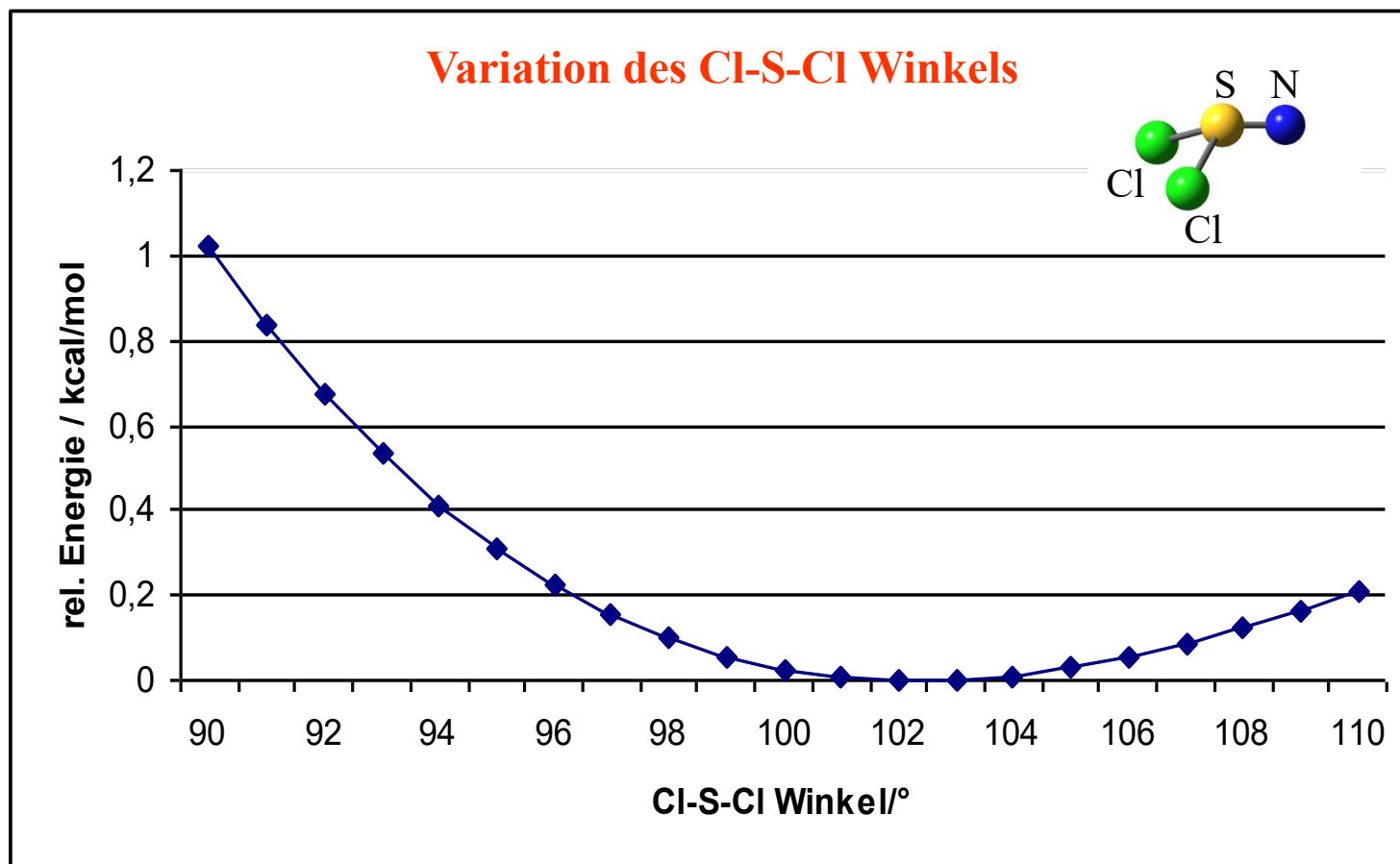


	$[(\text{Ph}_3\text{PN})_2\text{SCI}]^+[\text{NSCl}_2]^-$	B3LYP 6-311+G(3df)	CCSD(T) 6-311+G(3df)
SN	1.436(6)	1.445	1.456
SCI	2.423(2), 2.427(2)	2.487	2.453
$\langle\text{NSCl}$	112.76(19), 113.8(3)	114.4	113.9
$\langle\text{ClSCI}$	93.26 (8)	102.4	99.9

monoklin, $P21/c$



Einfluss von Gittereffekten I





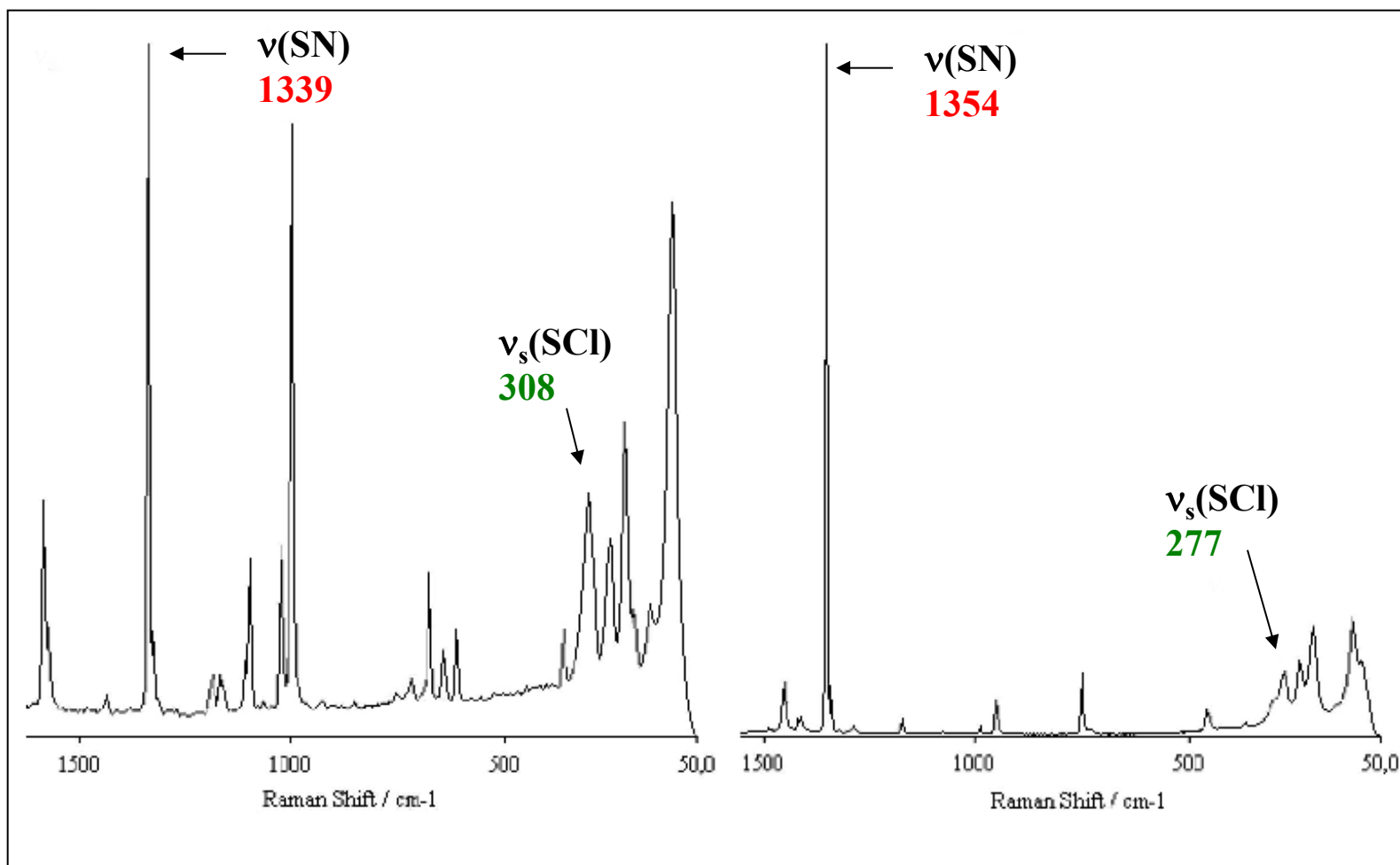
Einfluss von Gittereffekten II



$$d(\text{SN}) = 1.436 \text{ \AA}, d(\text{SCl}) = 2.423 \text{ \AA}$$

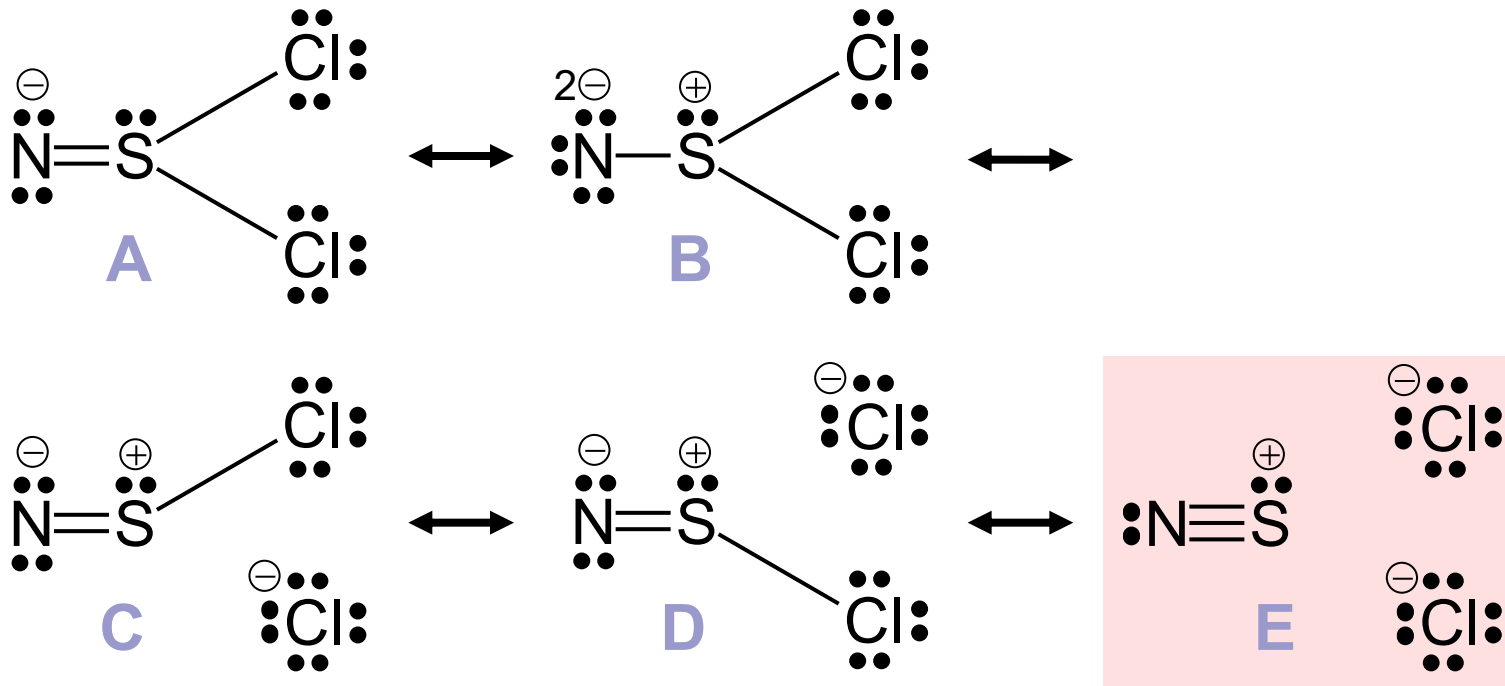
vs

$$d(\text{SN}) = 1.42 \text{ \AA}, d(\text{SCl}) = 2.52 \text{ \AA}$$





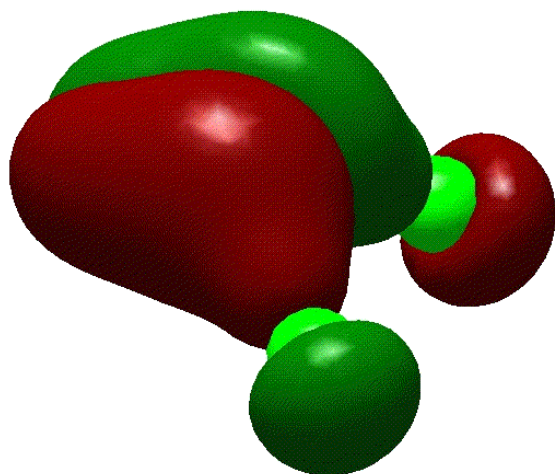
Standard-VB-Darstellung des NSCl_2^- -Ions



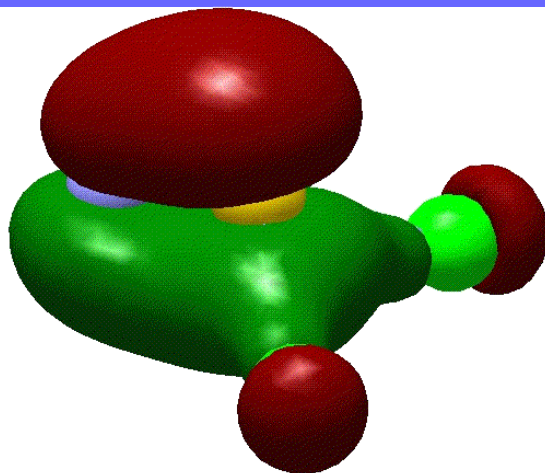
Verbindung	NSCl_2^-		NS^+	NSCl	
	NS	SCI	NS	NS	SCI
Bindungsordnung	2.21	0.23	2.76	2.16	0.45



Die Chemische Bindung in NSCl_2^- : MO-Darstellung

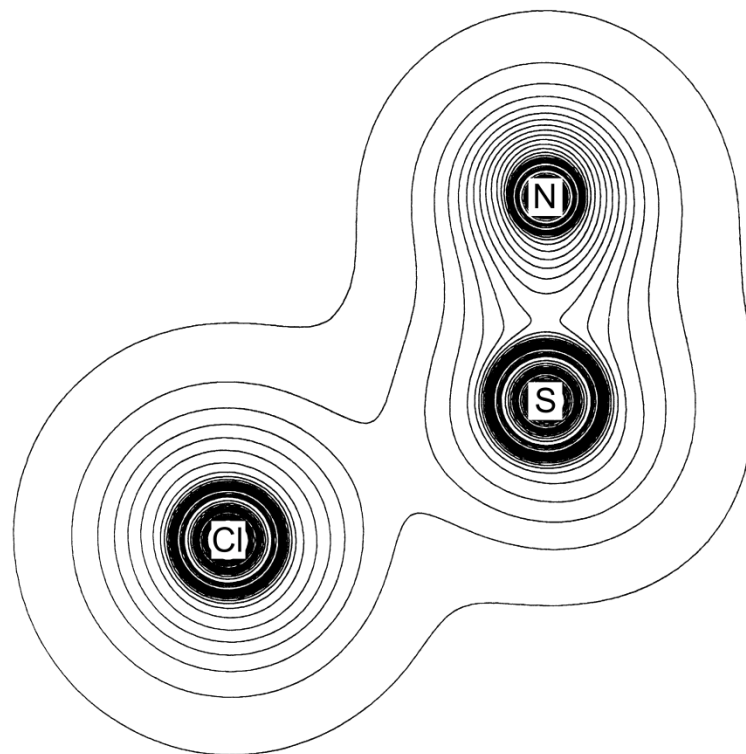


HOMO-8
(a'')



HOMO-7
(a')

Elektronendichte in NSCl_2^- ,
Schnitt durch eine NSCl-Ebene





4-Elektronen-3-Zentrenbindung im NSCl_2^-

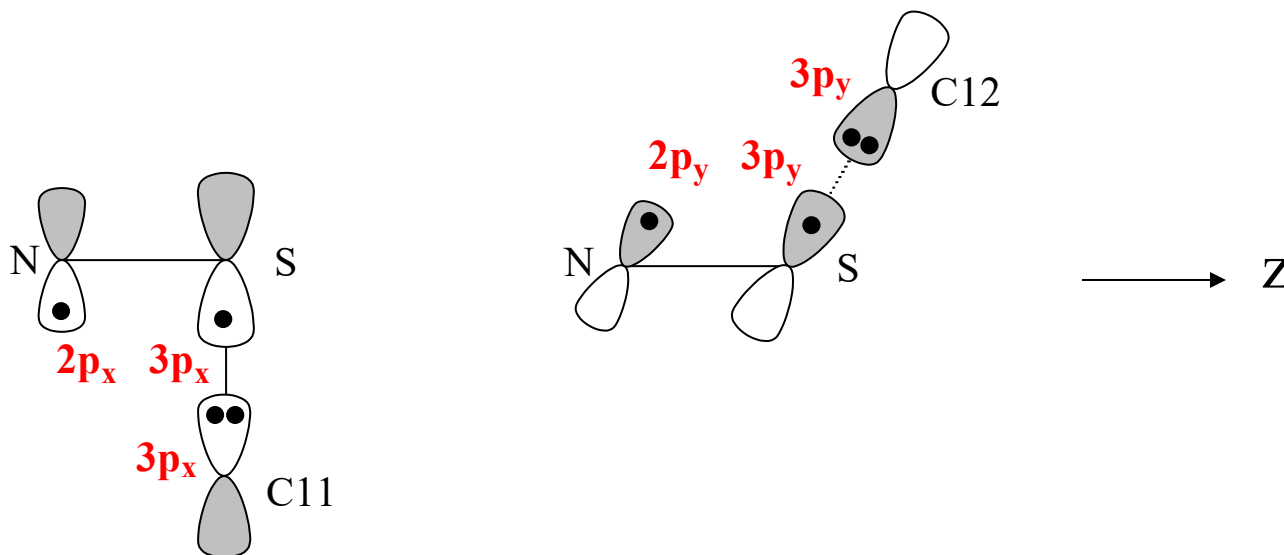
$$\psi^{\text{HOMO-7}} = 0.3 p_x(\text{N}) - 0.3 p_y(\text{N}) + 0.3 p_x(\text{S}) - 0.3 p_y(\text{S}) - 0.2 s(\text{Cl1}) - 0.2 p_x(\text{Cl1}) - 0.2 s(\text{Cl2}) + 0.2 p_y(\text{Cl2})$$

$$\psi^{\text{HOMO-8}} = 0.3 p_x(\text{N}) + 0.3 p_y(\text{N}) + 0.3 p_x(\text{S}) + 0.3 p_y(\text{S}) - 0.2 s(\text{Cl1}) - 0.2 p_x(\text{Cl1}) + 0.2 s(\text{Cl2}) - 0.2 p_y(\text{Cl2})$$

Lineare Transformation \Rightarrow Zwei entartete 4-Elektronen-3-Zentrenbindungen

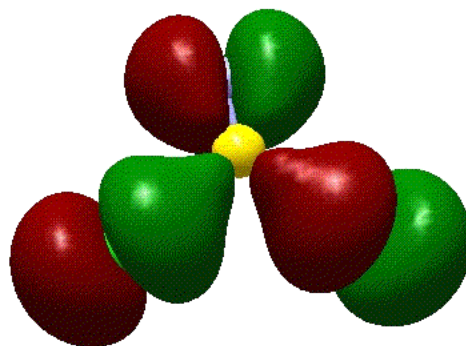
$$\psi^{\text{HOMO-8}} + \psi^{\text{HOMO-7}} = 0.6 * [p_x(\text{N}) + p_x(\text{S})] - 0.4 * [s(\text{Cl1}) + p_x(\text{Cl1})]$$

$$\psi^{\text{HOMO-8}} - \psi^{\text{HOMO-7}} = 0.6 * [p_y(\text{N}) + p_y(\text{S})] + 0.4 * [s(\text{Cl2}) - p_y(\text{Cl2})]$$





Stabilisierung der nichtbindenden MOs

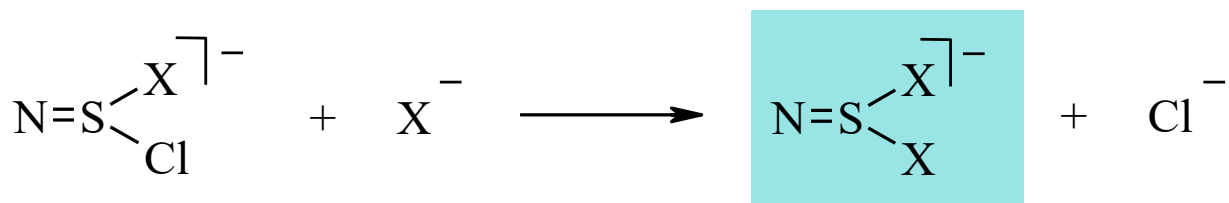
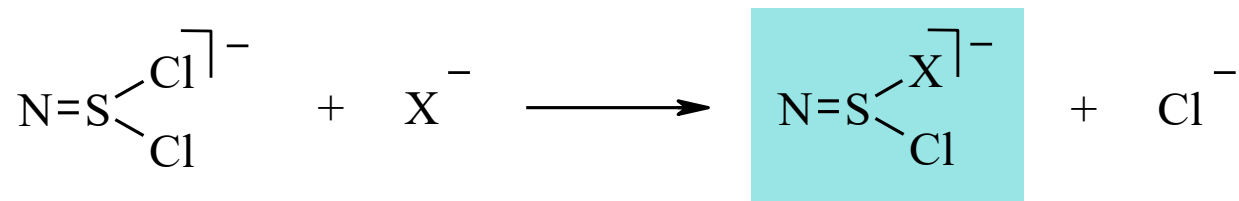


geringe d-Orbitalbeteiligung am Schwefel



Thiazyldihalogenide

NSX_2^- mit $X = F, Br, I$

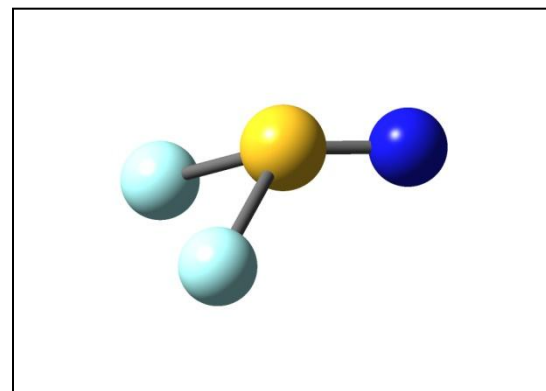




Thiazyldifluorid: NSF_2^-

^{19}F -NMR: 160 ppm NSF_2^-

W. Heilemann, R. Mews, *Chem. Ber.* **1988**, 121, 461.

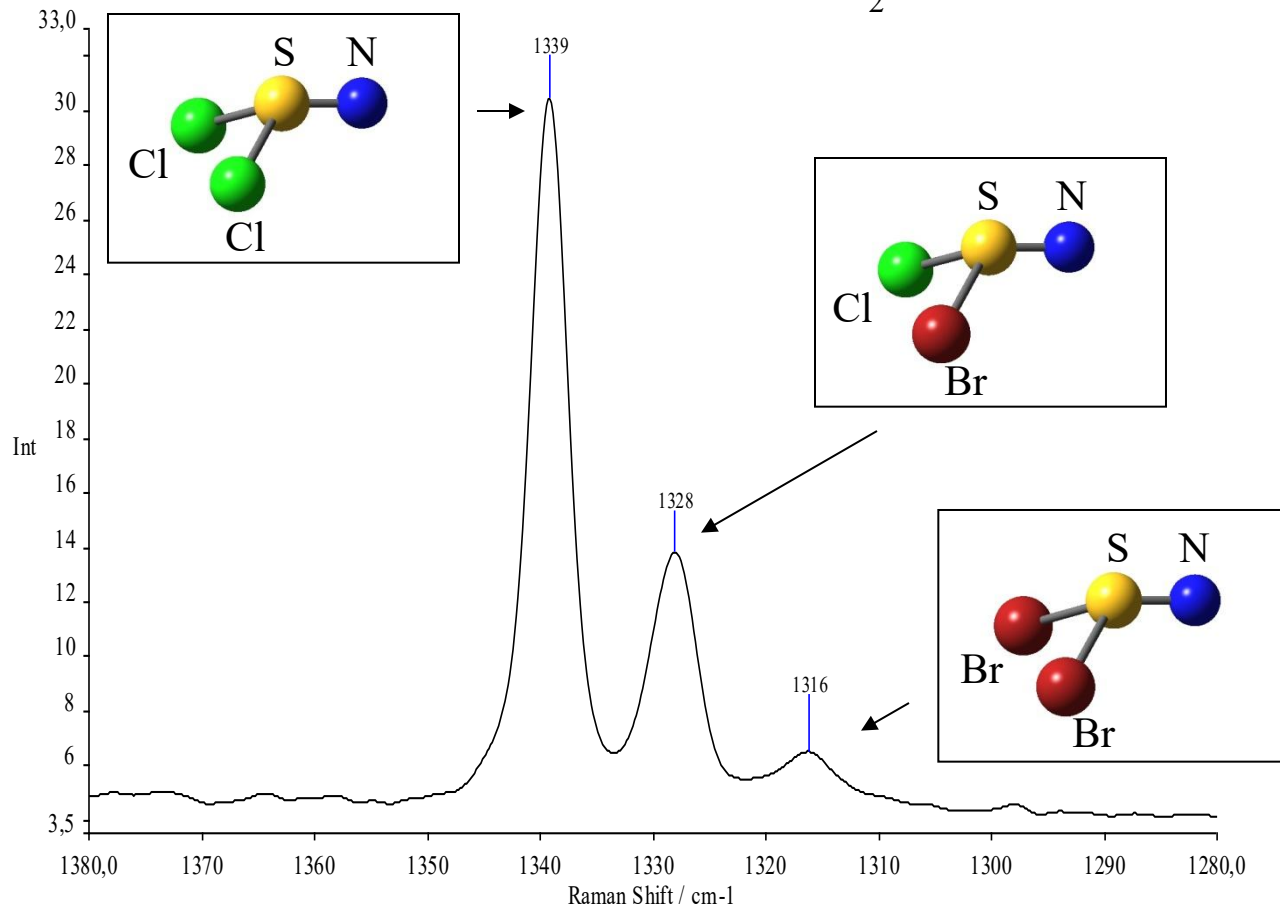


Problem „nacktes“ Fluorid: -170 ppm CH_2ClF , -155 ppm HF_2^-

K. O. Christe, W. W. Wilson *J. Fluor. Chem.* **1990**, 47, 117.



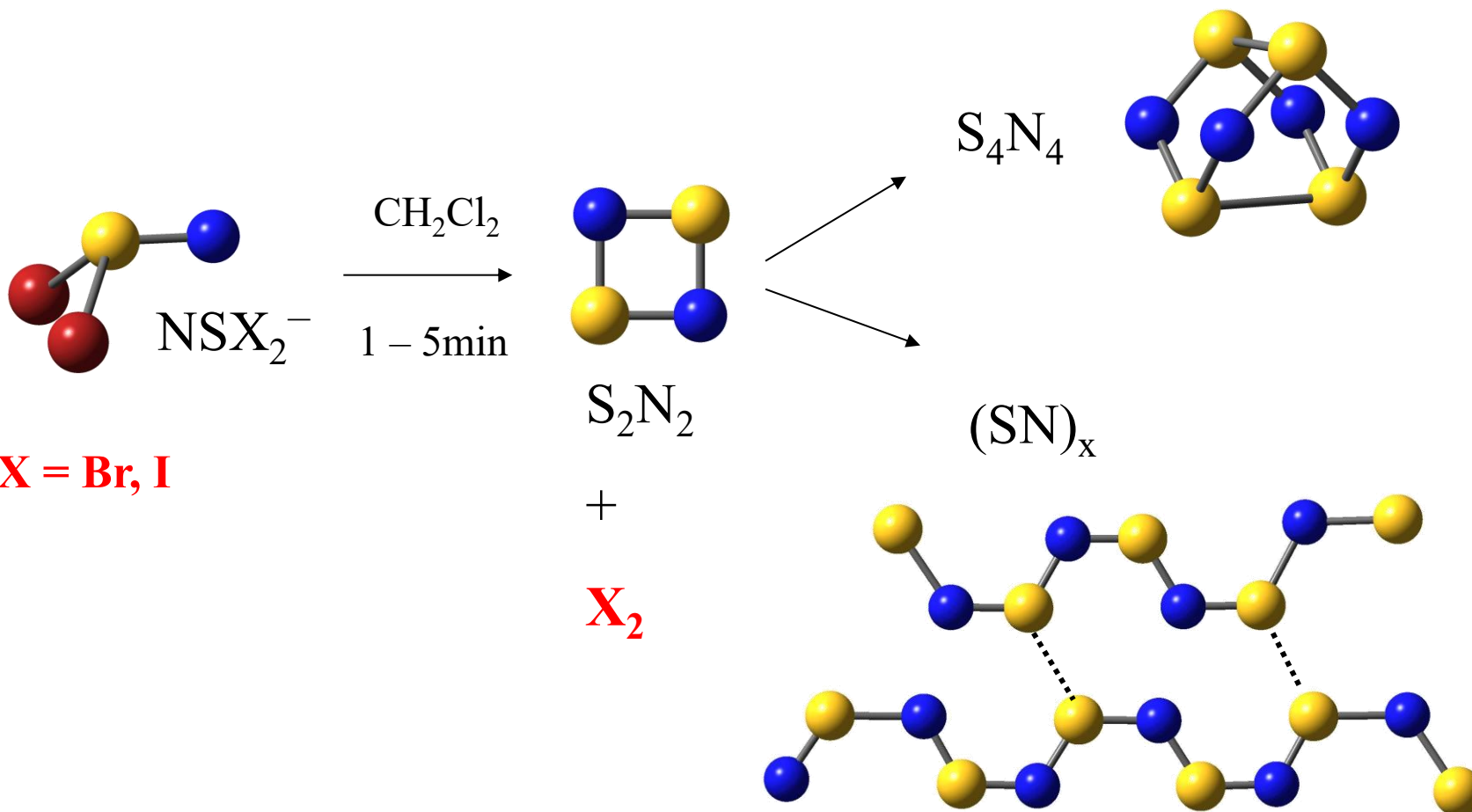
Thiazylidibromid: NSBr_2^- ?



Raman-Spektrum: Aufspaltung der S-N-Streckschwingung bei Zugabe von Br^- zu NSCl_2^-



Der Zerfall von „Thiazyldibromid und –iodid“

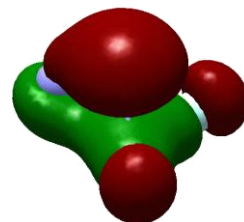
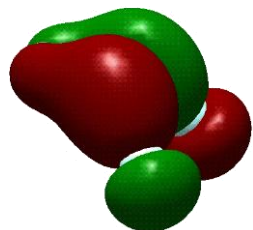




MO-Bild der Vier-Elektronen-Drei-Zentren-Bindungen

 NSX_2^-
 $a''\text{-MO}$
 $a'\text{-MO}$
 $\Delta_R G_{298}$

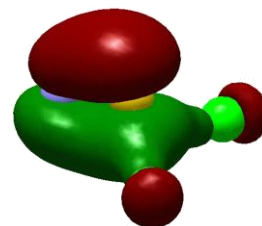
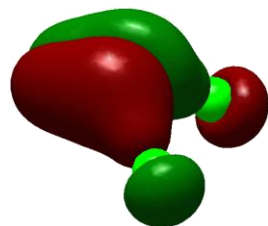
F



kcal/mol

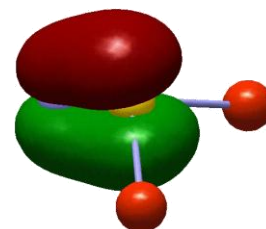
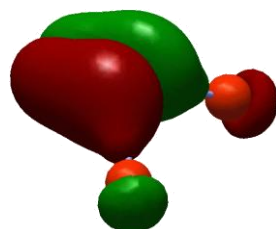
-62.3

Cl



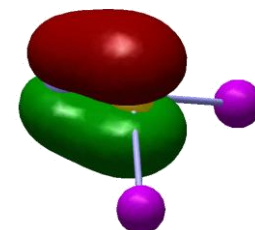
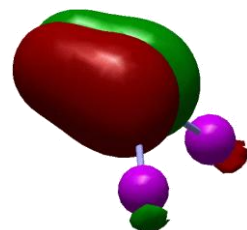
-29.1

Br

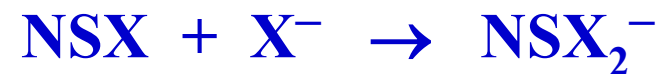


-20.0

I

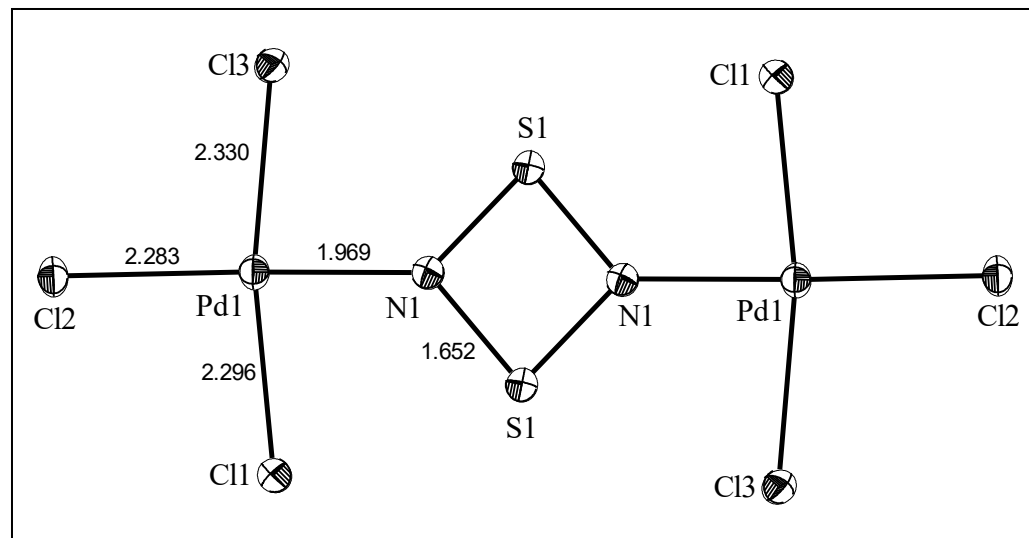
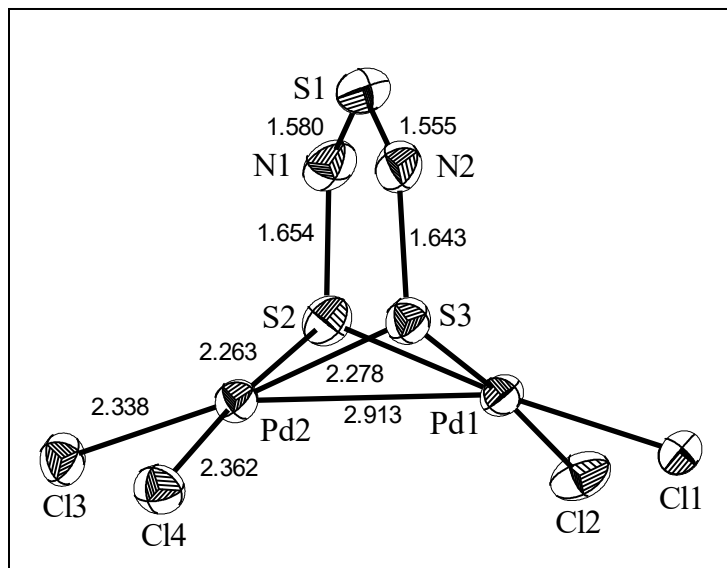


-18.2





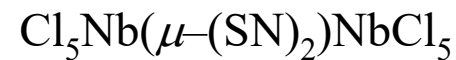
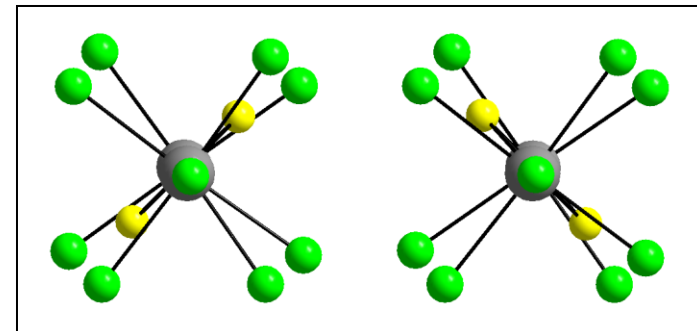
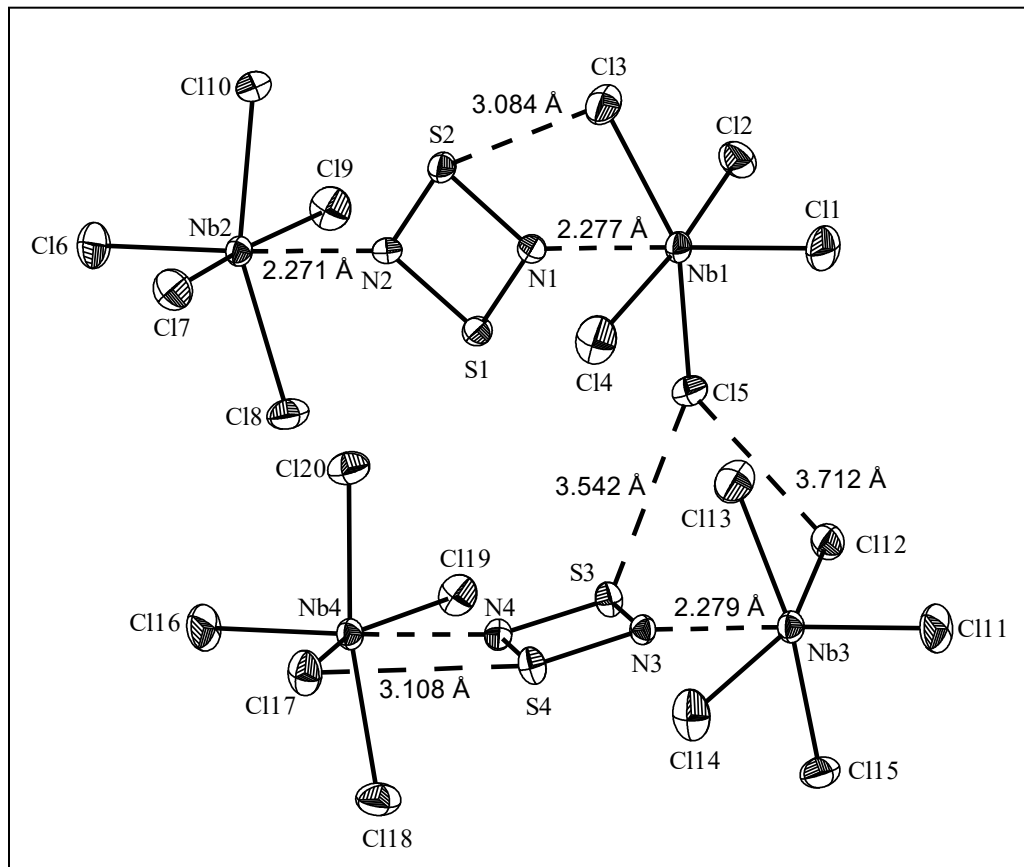
Reaktion von $[\text{Ph}_4\text{P}]^+[\text{NSCl}_2]^-$ mit $[(\text{Et}_3\text{P})\text{ClPd}(\mu\text{-Cl})]_2$



$[\text{Ph}_4\text{P}]_2^+[\text{Pd}_2\text{Cl}_6]^{2-}$ mit S_4N_4 : P.F. Kelly, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *Polyhedron* **1991**, 10, 2337.



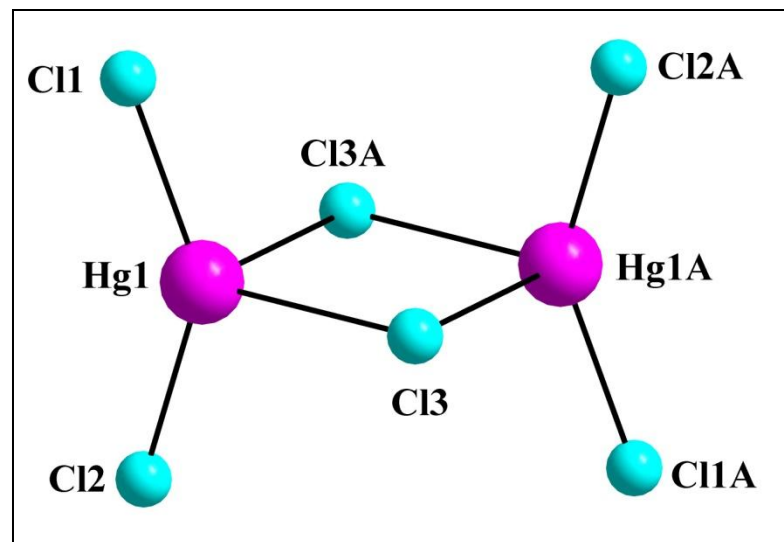
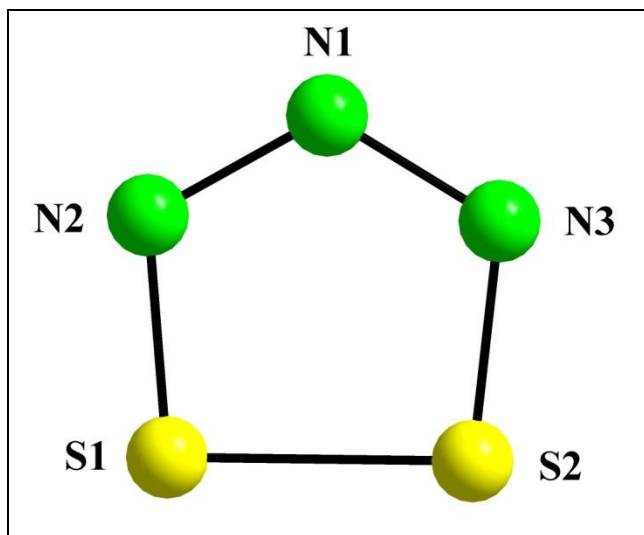
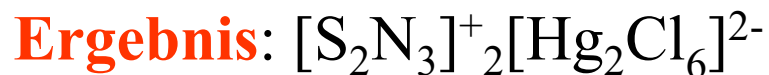
Reaktion von $[\text{Ph}_4\text{P}]^+[\text{NSCl}_2]^-$ mit NbCl_5



$\text{Cl}_5\text{Sb}(\mu\text{-(SN)}_2)\text{SbCl}_5$: L. Patton, K. Raymond, *Inorg. Chem.* **1969**, *8*, 2426.



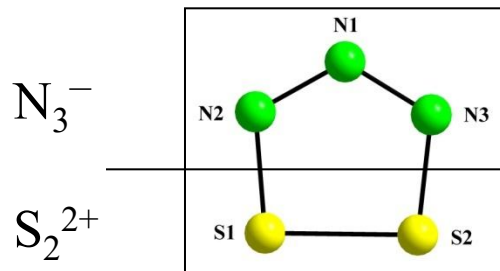
$S_2N_3^+$: Ein aromatischer SN-Ring mit einer N_3 -Einheit (1,2,3,4,5-Dithiatriazoliumkation)



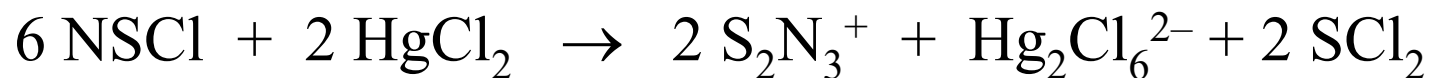
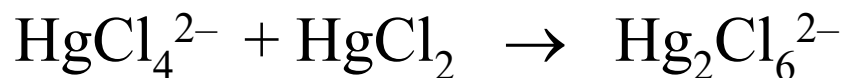
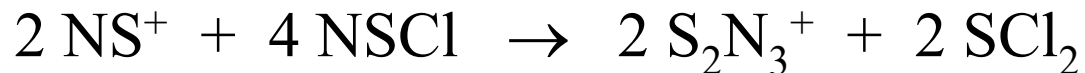
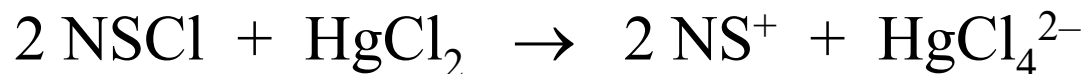
Angew. Chem. **2001**, *113*, 327.



Mechanismus Vorschlag

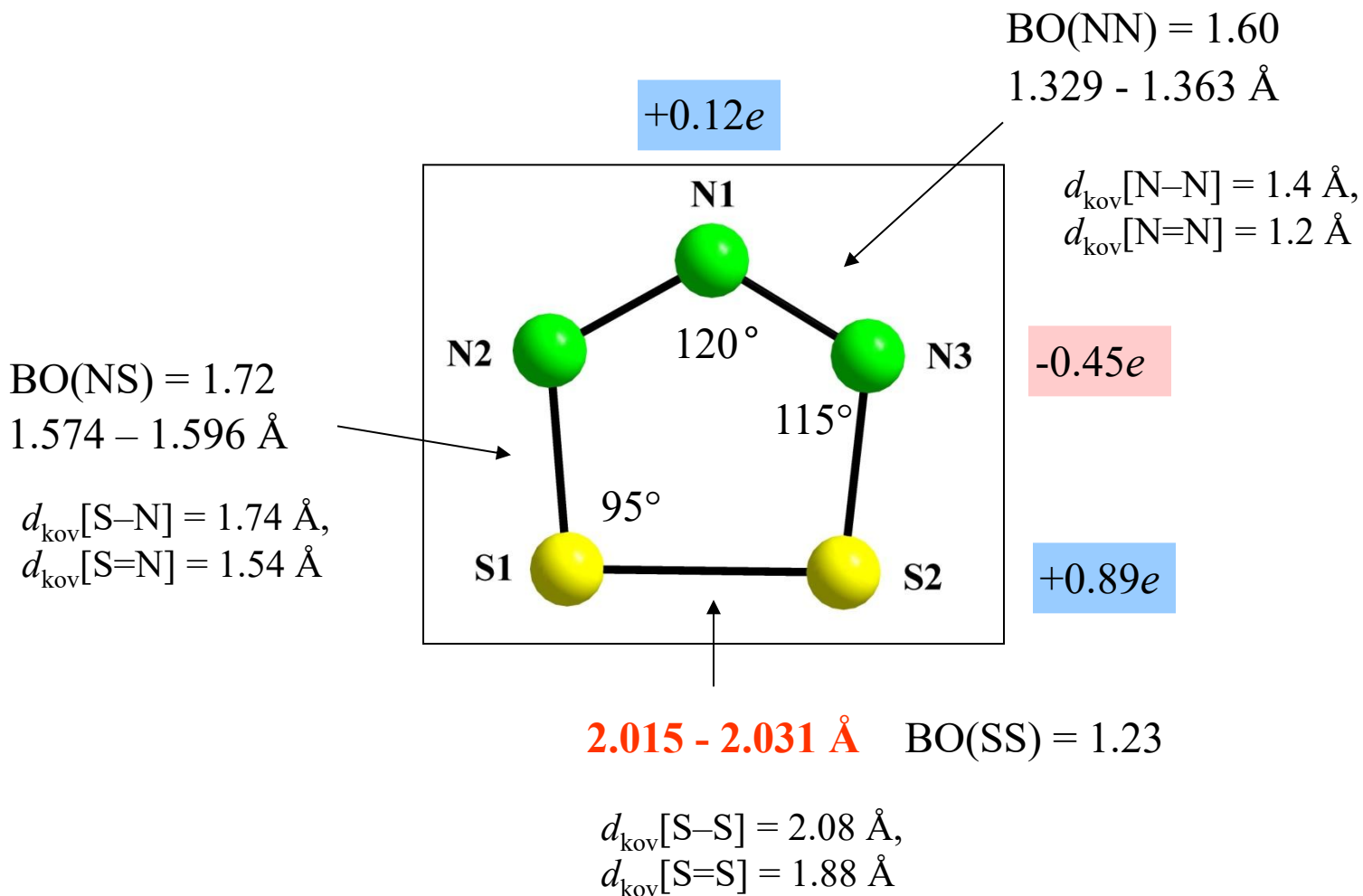


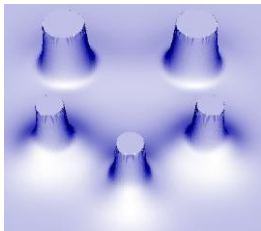
[3+2] Cycloaddition?





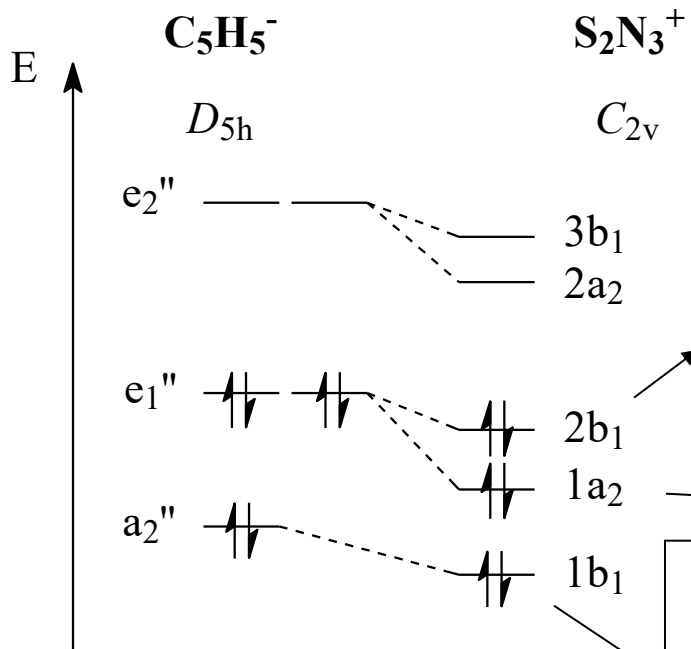
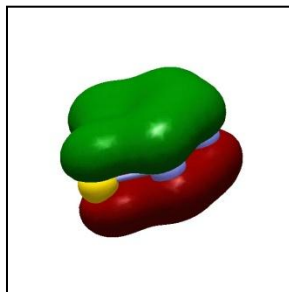
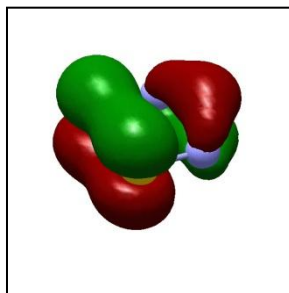
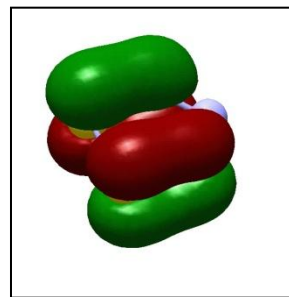
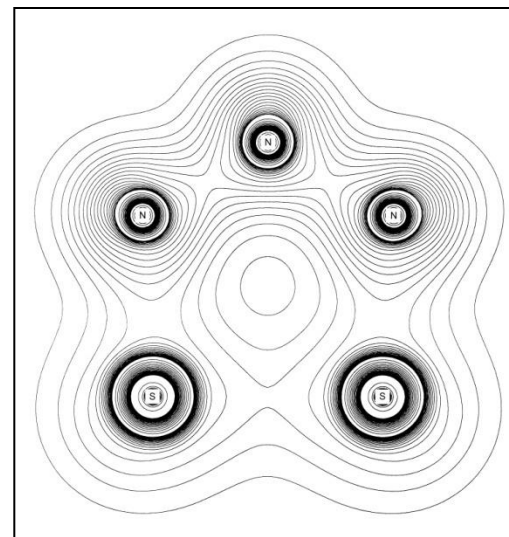
Molekülstruktur des $S_2N_3^+$ -Ions





$S_2N_3^+$ versus $C_5H_5^-$

Berechnete Elektronendichte

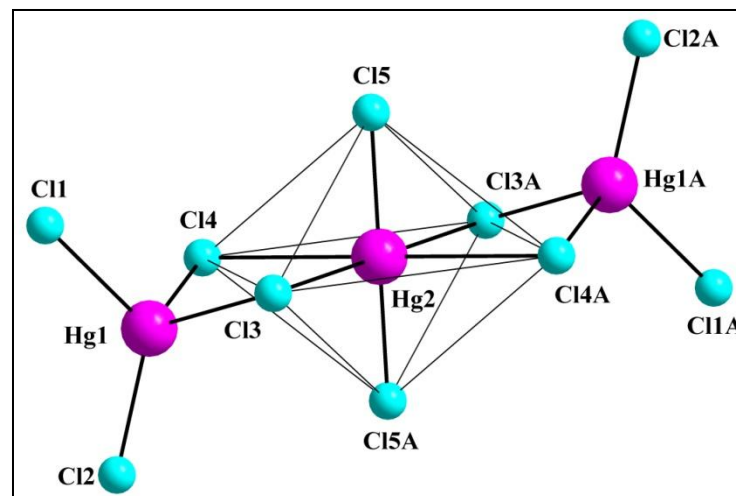
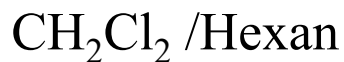
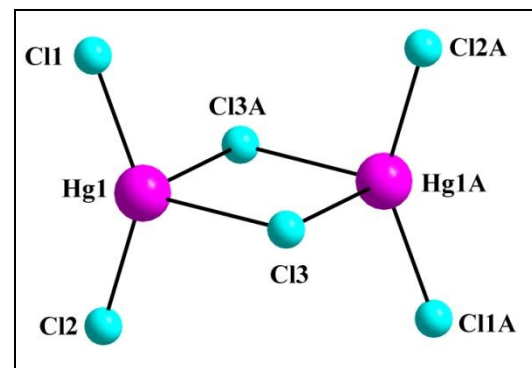
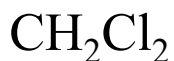




Einfluss des Lösemittels I

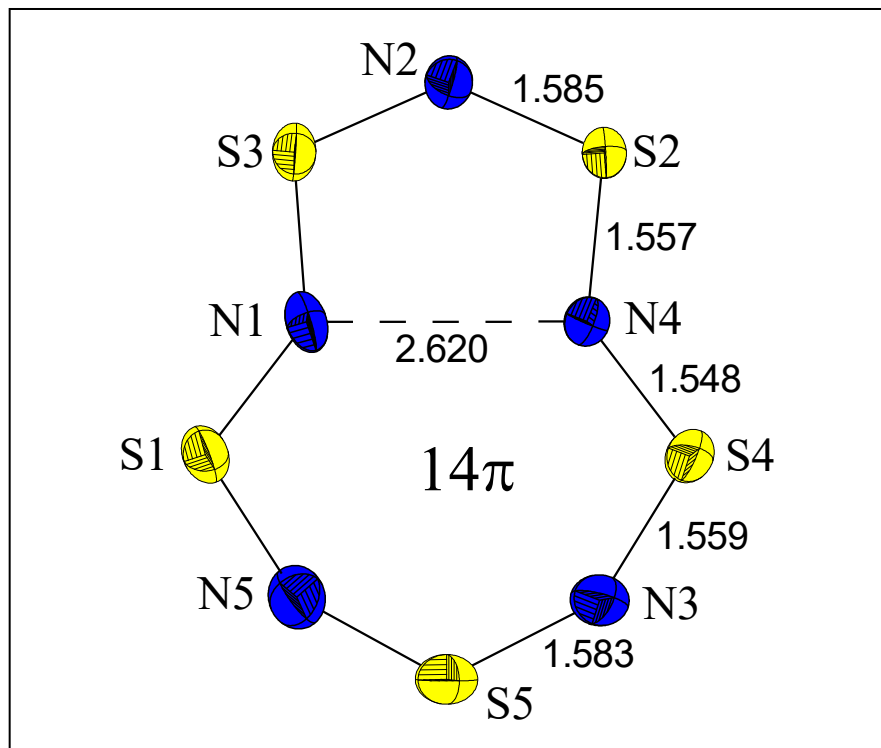
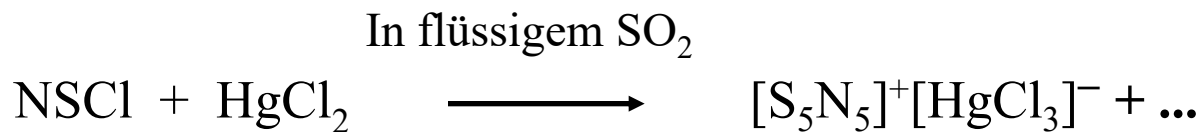
In Lösung:

mononukleare (HgCl_4^{2-}),
 di- ($\text{Hg}_2\text{Cl}_6^{2-}$, $\text{Hg}_2\text{Cl}_7^{3-}$),
 tri- ($\text{Hg}_3\text{Cl}_9^{3-}$, $\text{Hg}_3\text{Cl}_{12}^{6-}$),
 tetra- ($\text{Hg}_4\text{Cl}_{14}^{6-}$)
 oligo- oder
 polynukleare Chloromercurate



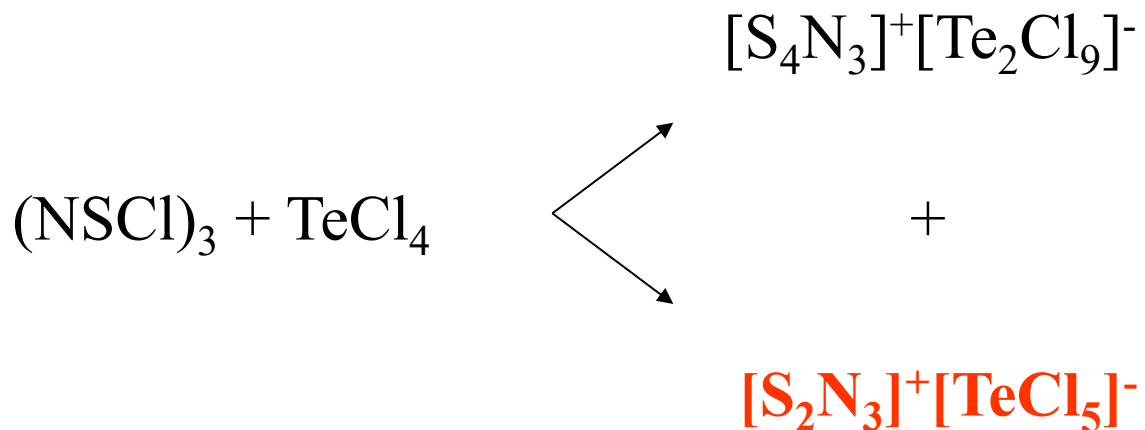


Einfluss des Lösemittels II





Ein alternativer Weg zum $S_2N_3^+$ -Salz



A. Olteanu, Dissertation, Ruhr-Universität Bochum, **2000**;

A. Haas, E. Hoppmann, A. Olteanu, Poster, *16th International Symposium on Fluorine Chemistry*, University of Durham, Durham, UK, **2000**.