

# FLUORIDE / AZIDE LIGAND EXCHANGE REACTIONS



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# Report Documentation Page

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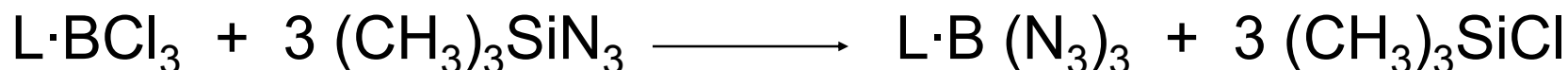
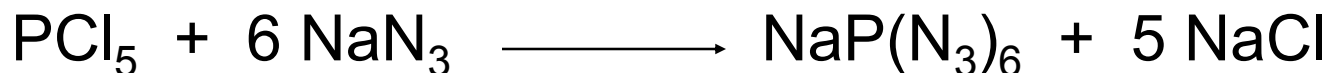
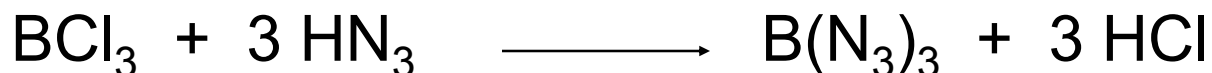
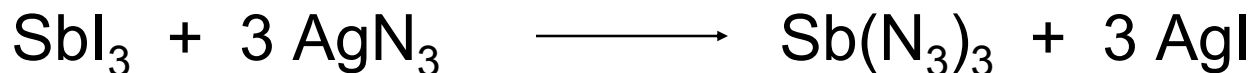


- Preparation and Characterization of High Energy Density Matter (HEDM) derived from binary covalent polyazides
- $\text{HN}_3$  was discovered in 1890 by Curtius, and binary covalent polyazides have been known for at least half a century ( $\text{B}(\text{N}_3)_3$ : Wiberg, 1954)
- Most compounds are extremely shock sensitive, difficult to handle and purify, and often have not been structurally characterized
- Important contributions to the field were made by Wiberg, Dehnicke, Schmidt, Roesky, Ang, Fillippou, and particularly Klapoetke

# Synthesis of Covalent Binary Polyazides



- Conventional methods involve the reactions of chlorides or iodides with either  $\text{HN}_3$ ,  $\text{NaN}_3$ ,  $\text{AgN}_3$ , or  $(\text{CH}_3)_3\text{SiN}_3$



- Potential Problems with these methods

➤ Shock sensitivity of  $\text{AgN}_3$  and  $\text{HN}_3$

➤ Cl /  $\text{N}_3$  ligand exchange is often incomplete

➤ Solvent problems  $(\text{CH}_2\text{Cl}_2 + 2 \text{MN}_3 \longrightarrow \text{CH}_2(\text{N}_3)_2)$

14<sup>th</sup> European Symposium on Fluorine Chemistry, Poznan, Poland

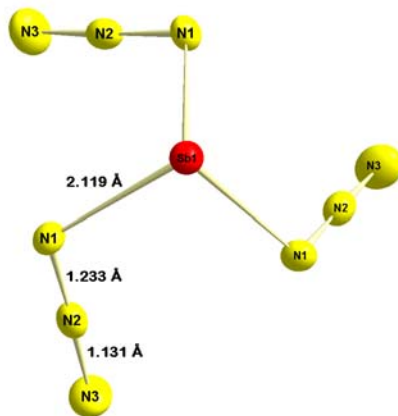
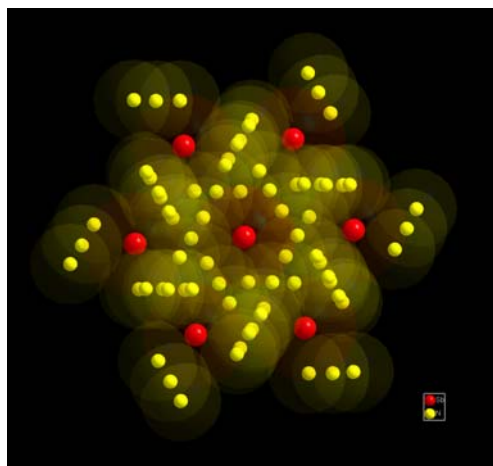


- Use of fluorides with  $(\text{CH}_3)_3\text{SiN}_3$  in a suitable solvent, such as  $\text{SO}_2$  (-64 C),  $\text{CH}_3\text{CN}$  (-40 C), or excess  $(\text{CH}_3)_3\text{SiN}_3$  (-40 C)
- Advantages
  - Rapid exchange
  - Complete conversions in a single step
  - Highly pure products
  - Easy product separation

# Results from our Studies, $As(N_3)_3$ and $Sb(N_3)_3$



- $As(N_3)_3$  and  $Sb(N_3)_3$  were previously known as highly explosive oil or powder, respectively, but no structures were known
- We obtained both compounds in crystalline form and determined their crystal structures




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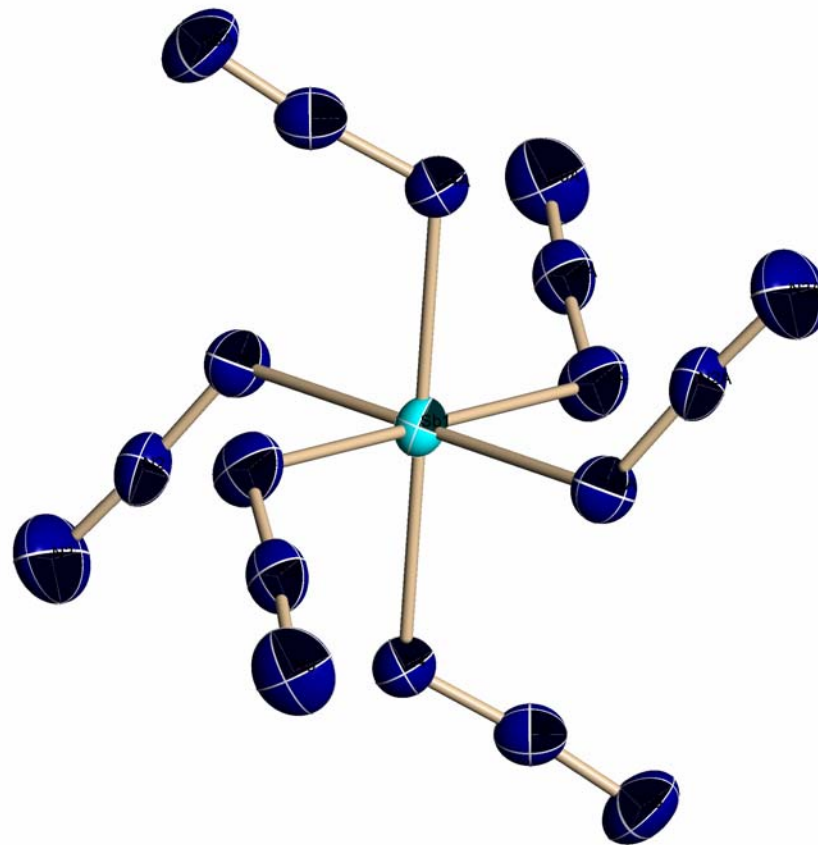
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# Crystal Structure of $[\text{Sb}(\text{N}_3)_6]^-$



- $\text{Sb}(\text{N}_3)_6^-$  anion had been known, but its structure was unknown
- We prepared the  $[\text{P}(\text{C}_6\text{H}_5)_4][\text{Sb}(\text{N}_3)_6]$  salt and determined its structure

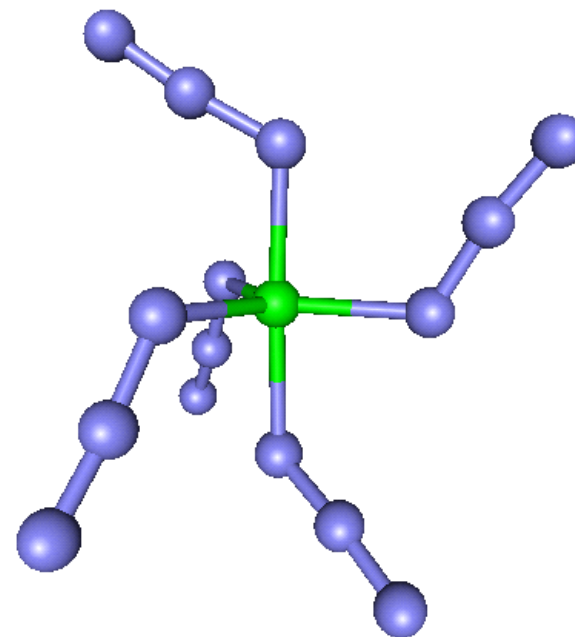
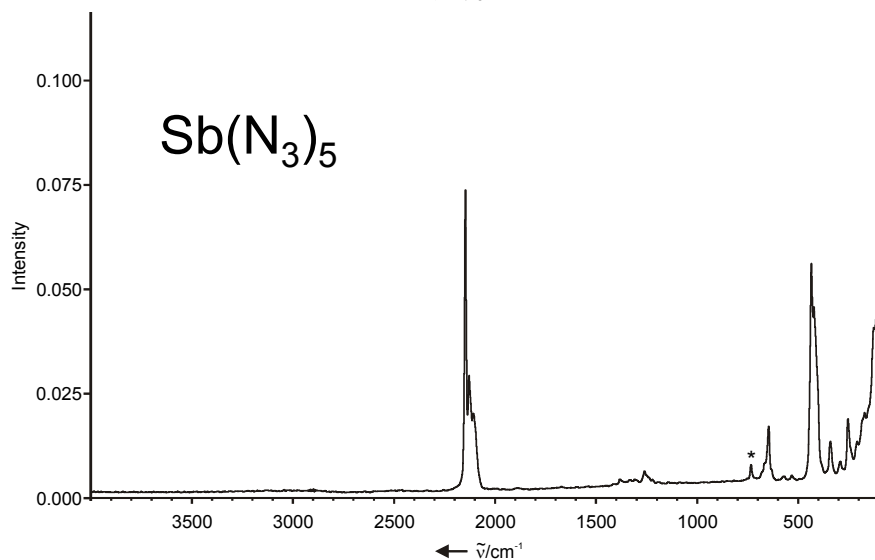
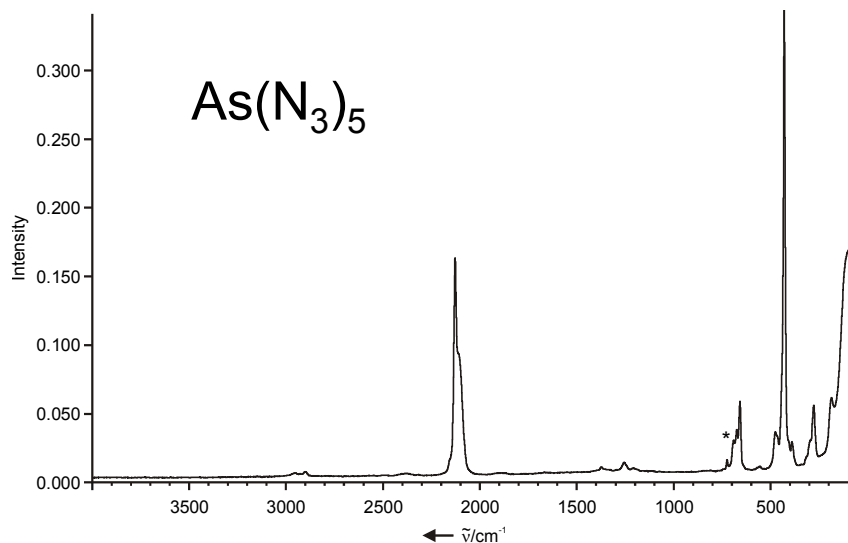


# Syntheses and Vibrational Spectra of $\text{As}(\text{N}_3)_5$ and $\text{Sb}(\text{N}_3)_5$



- Neutral polyazides are generally the most sensitive and, therefore, most difficult to prepare and characterize
- Unstable neutral polyazides can usually be stabilized by
  - negative charges (anion formation)
  - adduct formation with large organic bases
  - large bulky inert spacers, such as cations, to stop propagation
- Although  $\text{M}(\text{N}_3)_6^-$  anions and  $\text{M}(\text{N}_3)_5$  donor-acceptor adducts with amines ( $\text{M} = \text{As}$  or  $\text{Sb}$ ) had been known, the free pentaazides had been considered to be too sensitive for isolation
- The free pentaazides were now successfully prepared from the pentafluorides and TMSazide in  $\text{SO}_2$  solution and characterized by low-temperature Raman spectroscopy and theoretical calculations

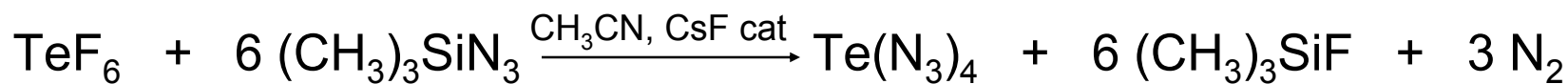
# Raman Spectra of $\text{As}(\text{N}_3)_5$ and $\text{Sb}(\text{N}_3)_5$



- Good agreement between observed spectra and those calculated for trigonal-bipyramidal monomers

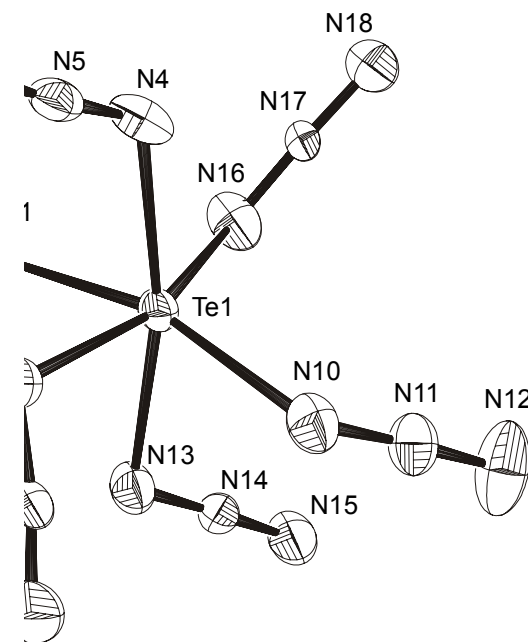
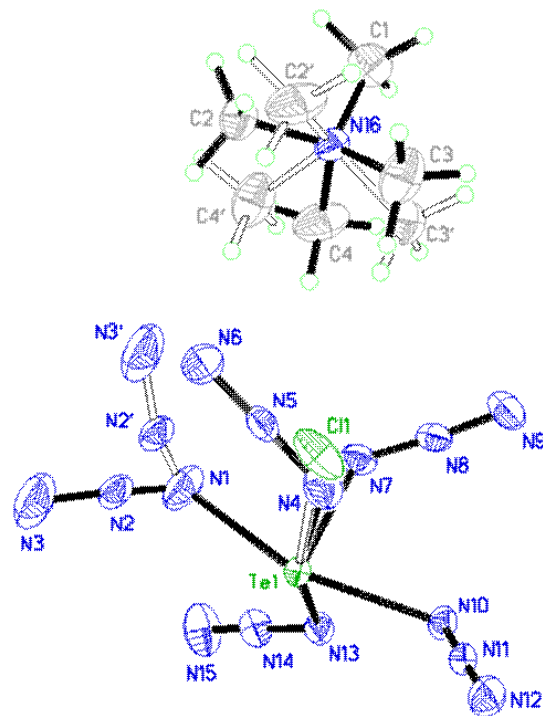


- We prepared and characterized the novel  $\text{Te}(\text{N}_3)_4$ ,  $[\text{N}(\text{CH}_3)_4][\text{Te}(\text{N}_3)_5]$ , and  $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Te}(\text{N}_3)_6]$



- $\text{Te}(\text{N}_3)_4$  is a shock sensitive, yellow solid and was characterized by vibrational and multinuclear NMR spectroscopy
- $\text{Te}(\text{N}_3)_5^-$  and  $\text{Te}(\text{N}_3)_6^{2-}$  were characterized by their crystal structures
- The results were published in *Angew. Chem. Int. Ed.* **2003**, 115, 1627 and highlighted in Chem. & Eng. News

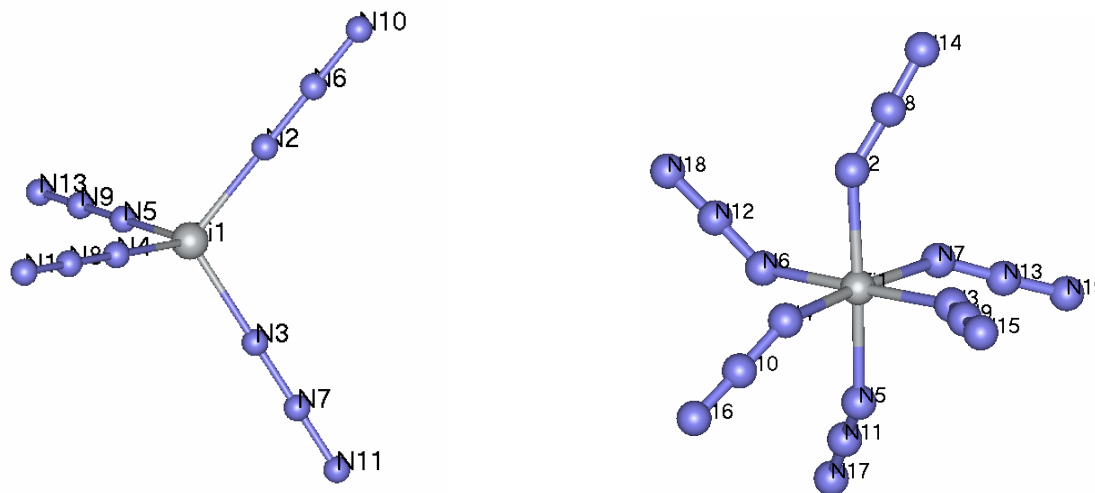
# Structures of $\text{Te}(\text{N}_3)_4$ , $\text{Te}(\text{N}_3)_5^-$ , and $[\text{Te}(\text{N}_3)_6]^{2-}$



# Titanium azide, does it possess linear Ti-N-N bonds?



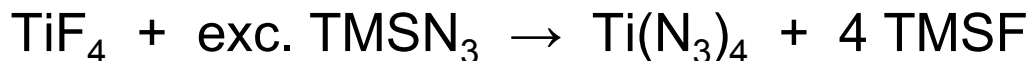
- Based on quantum chemical calculations, Gagliardi and Pyykkoe have recently predicted, (*Inorg. Chem.* **2003**, 42, 3074), for  $\text{Ti}(\text{N}_3)_4$ ,  $\text{Zr}(\text{N}_3)_4$ ,  $\text{Hf}(\text{N}_3)_4$ , and  $\text{Th}(\text{N}_3)_4$  a novel type of bonding involving linear M-N-N bonds.
- We have confirmed these calculations for  $\text{Ti}(\text{N}_3)_4$  and also predict that other azides, such as  $\text{Fe}(\text{N}_3)_2$  (Melanie Teichert), can form linear M-N-N bonds. However, based on our calculations, we expect that the  $\text{Ti}(\text{N}_3)_6^{2-}$  anion possesses the usual bent M-N-N bonds.



on Fluorine Chemistry, Poznan, Poland



- Synthesis



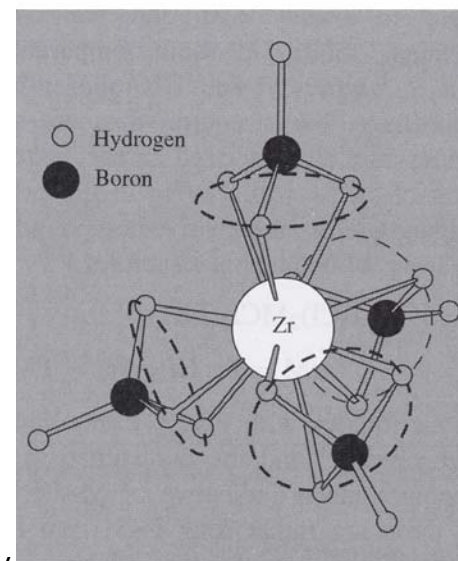
- Properties

- Yellow-orange solid
- Very shock-sensitive
- Very low volatility, decomposes on sublimation
- Could not get single crystals for structure determination, but Raman spectrum and comparison with calculated spectra suggest that CN is higher than 4 and the Ti-N-N angle is bent.
- Need a gas-phase structure of free  $Ti(N_3)_4$

# Possible explanations for linear M-N-N bonds



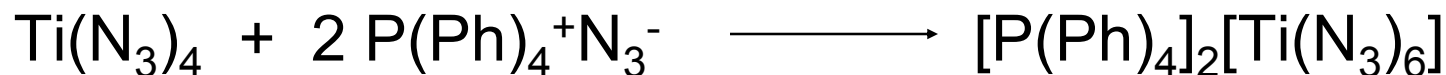
- Gagliardi and Pyykkoe invoke conjugation.
- We prefer the following interpretation because the calculated Ti-N bond distances are relatively long and are similar to single bonds. Also, the  $N_\beta$ - $N_\gamma$  bonds are quite short, and the Ti-N-N bonds in  $Ti(N_3)_6^{2-}$  are strongly bent.
  - The  $N_\alpha$  atom of the  $-N_3$  ligand has three free valence electron pairs which can act as a tridentate ligand and, in a tetrahedron, can perfectly overlap with three of the lobes of the Ti 3d-orbitals. This scheme is analogous to the structure of  $Zr(BH_4)_4$  which possesses 4 trihapto  $BH_4$  groups. In the usual covalent azides, the azide ligands utilize only one electron pair of the  $N_\alpha$  atom for the bonding, and the presence of two additional, sterically active free valence electron pairs results in a pyramidal configuration with an M-N-N angle of about  $120^\circ$ .



# Crystal Structure of $[\text{Ti}(\text{N}_3)_6]^{2-}$

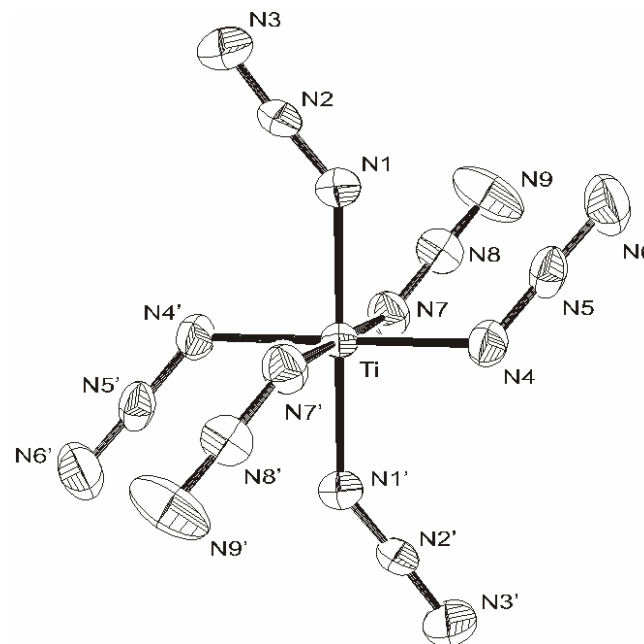


- Synthesized the  $[\text{Ti}(\text{N}_3)_6]^{2-}$  anion according to



and determined its crystal structure.

- Ti azide work has just appeared as a VIP paper in *Angew. Chem. Int. Ed.* **2004**, *116*, 3148.



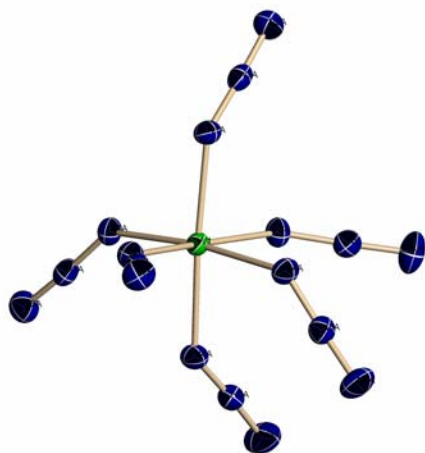
# Tantalum Azides



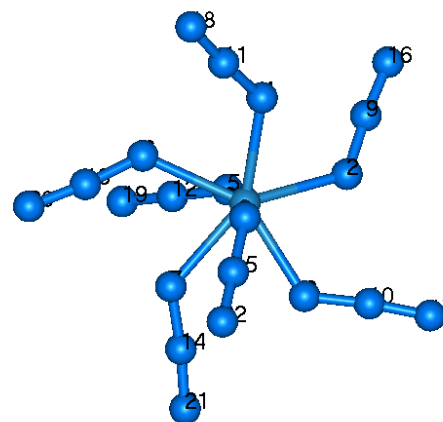
- $\text{Ta}(\text{N}_3)_5$  and  $\text{Ta}(\text{N}_3)_6^-$ , the first examples of binary Group V azides, were prepared from  $\text{TaF}_5$  and were characterized by vibrational spectroscopy.
- $\text{Ta}(\text{N}_3)_5$  is very sensitive and unstable, whereas the  $\text{P}(\text{C}_6\text{H}_5)_4^+\text{Ta}(\text{N}_3)_6^-$  salt is a stable white solid.



- $\text{Mo}(\text{N}_3)_6$  and  $\text{W}(\text{N}_3)_6$ , the first examples of binary Group VI azides, were prepared from  $\text{MoF}_6$  and  $\text{WF}_6$ , respectively.
- Both compounds are highly shock sensitive and were characterized by low-temperature Raman spectroscopy and, in the case of  $\text{WF}_6$ , also by its crystal structure.
- $\text{W}(\text{N}_3)_6$  can be stabilized as its  $\text{P}(\text{C}_6\text{H}_5)_4^+\text{W}(\text{N}_3)_7^-$  salt which was also characterized by vibrational spectroscopy.

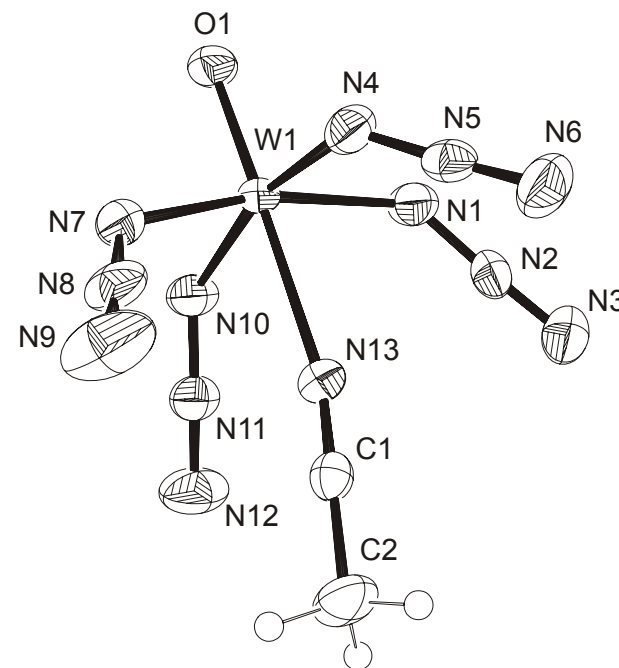


$\text{W}(\text{N}_3)_6$



$\text{W}(\text{N}_3)_7^-$

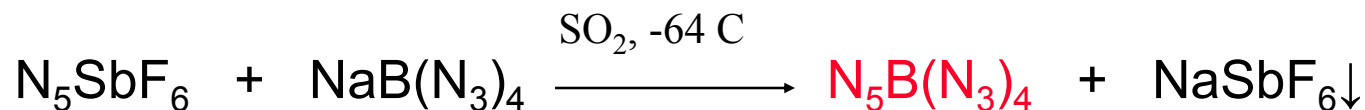
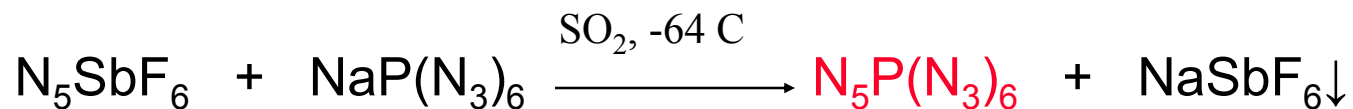
- $\text{WO}(\text{N}_3)_4$ , the first example of an oxoazide, was prepared from  $\text{WOF}_4$  and characterized by vibrational spectroscopy
- Recrystallization from  $\text{CH}_3\text{CN}$  solution resulted in a hexa-coordinated structure
- The  $\text{P}(\text{C}_6\text{H}_5)_4^+\text{WO}(\text{N}_3)_5^-$  salt was also prepared and characterized by vibrational spectroscopy



# Combination of $N_5^+$ with $P(N_3)_6^-$ and $B(N_3)_4^-$



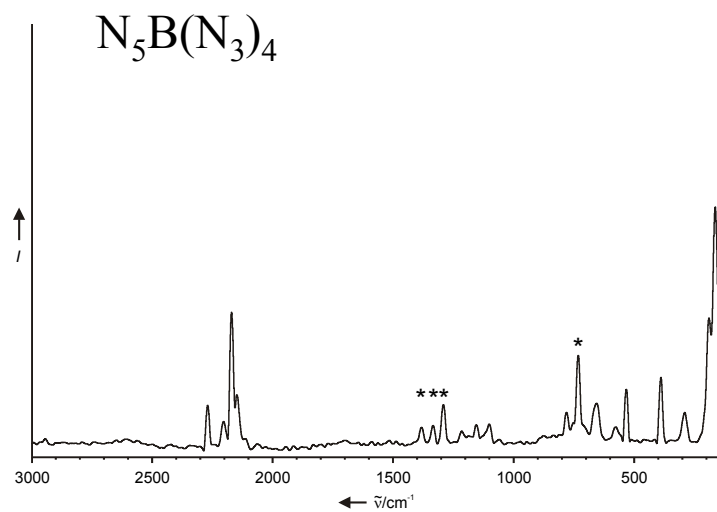
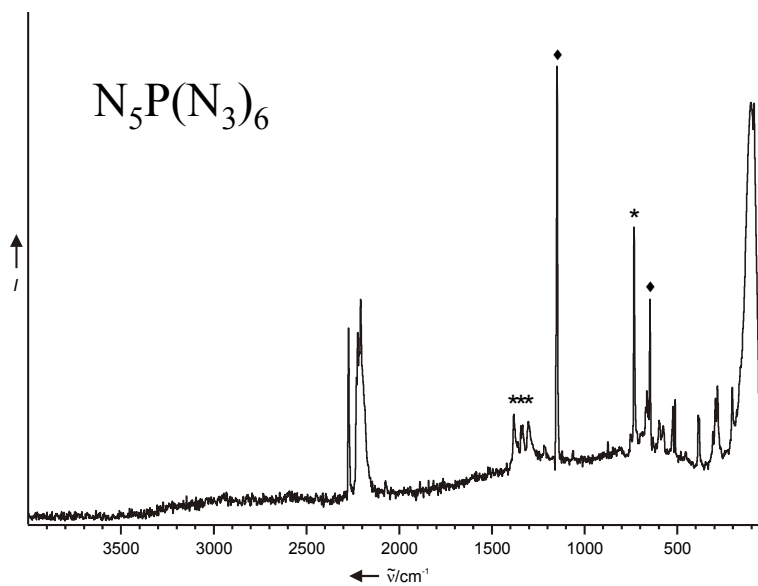
- First successful combinations of  $N_5^+$  with highly energetic anions:



- $NaP(N_3)_6$  and  $NaB(N_3)_4$  are already extremely shock-sensitive and their  $N_5^+$  salts are even more vicious.
- $N_5B(N_3)_4$  contains 96 weight % of energetic nitrogen.
- Paper has been accepted by Angewandte for publication.



- Low-temperature Raman spectra

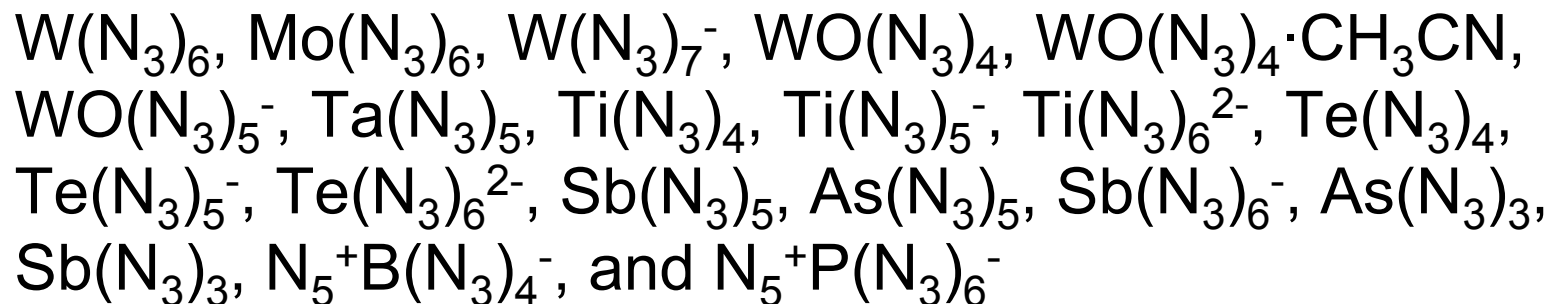


- Material balances
- Stable at  $-64\text{ }^\circ\text{C}$ , explode on warm-up toward room temperature



- Fluorine compounds and trimethylsilylazide undergo rapid and quantitative fluoride / azide ligand exchange
- This reaction is ideally suited for the preparation of binary polyazides in high purity and quantitative yield

- Compounds studied so far under this program include:



- This work is extremely challenging, because of the high energy content and explosiveness of these materials