FLUORIDE / AZIDE LIGAND EXCHANGE REACTIONS

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Project Sponsors

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Objective and Background

- Preparation and Characterization of High Energy Density Matter (HEDM) derived from binary covalent polyazides

- HN₃ was discovered in 1890 by Curtius, and binary covalent polyazides have been known for at least half a century (B(N₃)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 HN₃, NaN₃, AgN₃, or (CH₃)₃SiN₃

  SbI₃ + 3 AgN₃ → Sb(N₃)₃ + 3 AgI
  BCl₃ + 3 HN₃ → B(N₃)₃ + 3 HCl
  PCl₅ + 6 NaN₃ → NaP(N₃)₆ + 5 NaCl
  L·BCl₃ + 3 (CH₃)₃SiN₃ → L·B (N₃)₃ + 3 (CH₃)₃SiCl

• Potential Problems with these methods
  ➢ Shock sensitivity of AgN₃ and HN₃
  ➢ Cl / N₃ ligand exchange is often incomplete
  ➢ Solvent problems (CH₂Cl₂ + 2 MN₃ → CH₂(N₃)₂)
Our Method

• Use of fluorides with (CH$_3$)$_3$SiN$_3$ in a suitable solvent, such as SO$_2$ (-64 C), CH$_3$CN (-40 C), or excess (CH$_3$)$_3$SiN$_3$ (-40 C)

• Advantages
  - Rapid exchange
  - Complete conversions in a single step
  - Highly pure products
  - Easy product separation
Results from our Studies, $\text{As(\text{N}_3)_3}$ and $\text{Sb(\text{N}_3)_3}$

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

- 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 As(N₃)₅ and Sb(N₃)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 M(N₃)₆⁻ anions and M(N₃)₅ donor-acceptor adducts with amines (M = As or 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 SO₂ solution and characterized by low-temperature Raman spectroscopy and theoretical calculations
Raman Spectra of $\text{As(N}_3\text{)}_5$ and $\text{Sb(N}_3\text{)}_5$

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

As($\text{N}_3\text{)}_5$

Sb($\text{N}_3\text{)}_5$

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Tellurium Azides

• We prepared and characterized the novel Te(N₃)₄, [N(CH₃)₄][Te(N₃)₅], and [P(C₆H₅)₄]₂[Te(N₃)₆]

\[
\text{TeF}_6 + 6 \left(\text{CH}_3\right)_3\text{SiN}_3 \xrightarrow{\text{CH}_3\text{CN, CsF cat}} \text{Te(N}_3\text{)}_4 + 6 \left(\text{CH}_3\right)_3\text{SiF} + 3 \text{N}_2
\]

• Te(N₃)₄ is a shock sensitive, yellow solid and was characterized by vibrational and multinuclear NMR spectroscopy

• Te(N₃)₅⁻ and Te(N₃)₆²⁻ 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 $\text{Te}(N_3)_4$, $\text{Te}(N_3)_5^-$, and $[\text{Te}(N_3)_6]^{2-}$
Titanium azide, does it possess linear Ti-N-N bonds?

• Based on quantum chemical calculations, Gagliardi and Pyykköe have recently predicted, (*Inorg. Chem.* 2003, 42, 3074), for Ti(N₃)₄, Zr(N₃)₄, Hf(N₃)₄, and Th(N₃)₄ a novel type of bonding involving linear M-N-N bonds.

• We have confirmed these calculations for Ti(N₃)₄ and also predict that other azides, such as Fe(N₃)₂ (Melanie Teichert), can form linear M-N-N bonds. However, based on our calculations, we expect that the Ti(N₃)₆²⁻ anion possesses the usual bent M-N-N bonds.
Synthesis and Characterization of Ti(N₃)₄

• Synthesis

\[ \text{TiF}_4 + \text{exc. TMSN}_3 \rightarrow \text{Ti(N}_3\text{)}_4 + 4 \text{TMSF} \]

• 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(N₃)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 $\text{Ti(N}_3\text{)}_6^{2-}$ 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 $\text{Zr(BH}_4\text{)}_4$ 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 °.
Crystal Structure of $[\text{Ti}(\text{N}_3)_6]^{2-}$

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

$$\text{Ti}(\text{N}_3)_4 + 2 \text{P(Ph)}_4^+\text{N}_3^- \rightarrow [\text{P(Ph)}_4]^2[\text{Ti}(\text{N}_3)_6]$$

and determined its crystal structure.

Tantalum Azides

• Ta(N₃)₅ and Ta(N₃)₆⁻, the first examples of binary Group V azides, were prepared from TaF₅ and were characterized by vibrational spectroscopy.

• Ta(N₃)₅ is very sensitive and unstable, whereas the P(C₆H₅)₄⁺Ta(N₃)₆⁻ salt is a stable white solid.
Molybdenum and Tungsten Azides

• Mo(N₃)₆ and W(N₃)₆, the first examples of binary Group VI azides, were prepared from MoF₆ and WF₆, respectively.

• Both compounds are highly shock sensitive and were characterized by low-temperature Raman spectroscopy and, in the case of WF₆, also by its crystal structure.

• W(N₃)₆ can be stabilized as its P(C₆H₅)₄⁺W(N₃)₇⁻ salt which was also characterized by vibrational spectroscopy.
Oxoazides

• WO(N$_3$)$_4$, the first example of an oxoazide, was prepared from WOF$_4$ and characterized by vibrational spectroscopy

• Recrystallization from CH$_3$CN solution resulted in a hexa-coordinated structure

• The P(C$_6$H$_5$)$_4$$^+$WO(N$_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:

$$\text{N}_5\text{SbF}_6 + \text{NaP(N}_3\text{)}_6 \xrightarrow{\text{SO}_2, -64 \text{ C}} \text{N}_5\text{P(N}_3\text{)}_6 + \text{NaSbF}_6$$

$$\text{N}_5\text{SbF}_6 + \text{NaB(N}_3\text{)}_4 \xrightarrow{\text{SO}_2, -64 \text{ C}} \text{N}_5\text{B(N}_3\text{)}_4 + \text{NaSbF}_6$$

- $\text{NaP(N}_3\text{)}_6$ and $\text{NaB(N}_3\text{)}_4$ are already extremely shock-sensitive and their $N_5^+$ salts are even more vicious.

- $\text{N}_5\text{B(N}_3\text{)}_4$ contains 96 weight % of energetic nitrogen.

- Paper has been accepted by Angewandte for publication.
Characterization of $N_5P(N_3)_6$ and $N_5B(N_3)_4$

- Low-temperature Raman spectra

- Material balances

- Stable at -64 °C, explode on warm-up toward room temperature
Summary

• 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:
  
  $W(N_3)_6, Mo(N_3)_6, W(N_3)_7^-, WO(N_3)_4, WO(N_3)_4\cdot CH_3CN, WO(N_3)_5^-, Ta(N_3)_5, Ti(N_3)_4, Ti(N_3)_5^-, Ti(N_3)_6^{2-}, Te(N_3)_4, Te(N_3)_5^-, Te(N_3)_6^{2-}, Sb(N_3)_5, As(N_3)_5, Sb(N_3)_6^-, As(N_3)_3, Sb(N_3)_3, N_5^+B(N_3)_4^-, and N_5^+P(N_3)_6^-$

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