New High Energy Density Materials. Synthesis and Characterization of $N_5^+P(N_3)_6^-$, $N_5^+B(N_3)_4^-$, $N_5^+HF_2^-\cdot nHF$, $N_5^+BF_4^-$, $N_5^+PF_6^-$, and $N_5^+SO_3F^-$[**]

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During the past two decades, polynitrogen compounds have received increasing attention as promising candidates for High Energy Density Materials (HEDM).[1-17] While most of the efforts were devoted to theoretical studies, the long-known existence of the stable azide anion (N_3^-)[18] and the recent syntheses of stable salts of the pentanitrogen cation (N_5^+)[1-3] have demonstrated the feasibility of experimentally pursuing such materials. The only known direct method for preparing N_5^+ compounds is their synthesis from an N_2F^+ salt with HN_3 in HF solution according to Equation 1. [1,2]

$$N_2F^+MF_6^- \ + \ HN_3 \ \xrightarrow{\text{HF}} \ N_5^+MF_6^- \ + \ HF \quad (M = As, Sb) \tag{1}$$

This direct synthesis route is restricted by the small number of N_2F^+ salts available. Except for N_2FAsF_6 and N_2FSbF_6 and reports on unstable N_2FBF_4 [19] and N_2FPF_6 [20] salts, no other N_2F^+ compounds have been described in the literature.

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14. ABSTRACT
During the past two decades, polynitrogen compounds have received increasing attention as promising candidates for High Energy Density Materials (HEDM).[1-17] While most of the efforts were devoted to theoretical studies, the long-known existence of the stable azide anion (N3-)[18] and the recent syntheses of stable salts of the pentanitrogen cation (N5+)[1-3] have demonstrated the feasibility of experimentally pursuing such materials. The only known direct method for preparing N5+ compounds is their synthesis from an N2F+ salt with HN3 in HF solution according to Equation 1. [1, 2]

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Other N_5^+ salts can be prepared by an indirect method using metathetical reactions[3] (Equation 2).

$$N_5^+SbF_6^- \ + \ M^+Y^- \ \longrightarrow \ N_5^+Y^- \ + \ M^+SbF_6^-? \qquad\qquad (2)$$
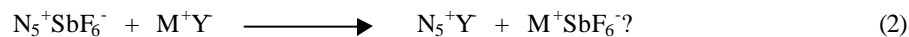
For a successful metathetical reaction, each ion must be compatible with the solvent, and both starting materials and one of the products must be highly soluble, while the second reaction product must exhibit low solubility. Because of its highly oxidizing nature, N_5SbF_6 is compatible with only a limited number of solvents, e.g. HF, SO_2 and CHF_3, thus severely restricting the general usefulness of the metathetical approach. Because SbF_5 is among the strongest known Lewis acids,[21] the displacement of SbF_5 in $N_5^+SbF_6^-$ by a stronger Lewis acid is also rarely feasible. Therefore, the development of a more general method for the syntheses of N_5^+ compounds was desirable. Furthermore, in the interest of preparing N_5^+ salts of higher energy content, the combination of N_5^+ with highly energetic counter-ions was pursued. Previous attempts to combine N_5^+ with either N_3^-, ClO_4^-, NO_3^-, or $N(NO_2)_2^-$ had been unsuccessful.[22]

While in theory, F^- abstraction from FN_5 by a strong Lewis acid, such as SbF_5, could provide a general synthesis for N_5^+ salts (Equation 3),

$$FN_5 \ + \ SbF_5 \qquad ? \qquad N_5^+SbF_6^- \qquad\qquad (3)$$

the required FN_5 precursor is unknown. A theoretical study identified at least 6 vibrationally stable isomers of FN_5 but, in accordance with experimental results, the predicted lifetimes of these species are only in the nanosecond range.[23]

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During attempts to prepare $N_5^+N(CF_3)_2^-$ by metathesis from $N_5^+SbF_6^-$ and $Cs^+N(CF_3)_2^-$ in HF solution at -78 °C (Equation 4),

$$N_5^+SbF_6^- + Cs^+N(CF_3)_2^- \longrightarrow N_5^+N(CF_3)_2^- + CsSbF_6? \qquad (4)$$

the expected $CsSbF_6$ precipitate was formed and removed by filtration. However, after pumping off all volatile material from the filtrate at -64 °C, the low-temperature Raman spectrum of the resulting clear liquid residue exhibited only bands attributable to N_5^+ (see Figure 1). This finding reminded us of a situation encountered 24 years ago with the metathetical reaction of NF_4SbF_6 and CsF in HF (Equation 5).

$$NF_4^+SbF_6^- + CsF + (n+1) HF \longrightarrow NF_4HF_2 \cdot nHF + CsSbF_6? \qquad (5)$$
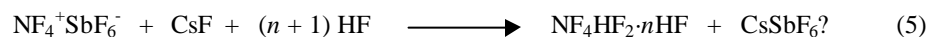
This reaction resulted in the formation of thermally unstable, liquid $NF_4HF_2 \cdot nHF$,[24] which exhibited characteristics very similar to those observed in the above N_5^+ reaction, i. e., a failure to observe anion bands because a polybifluoride anion is an extremely weak Raman scatterer. The formation of $N_5HF_2 \cdot nHF$ in reaction (4) can be explained if liquid HF is capable of displacing $HN(CF_3)_2$ from its $N(CF_3)_2^-$ salts according to Equation 6.

$$Cs^+N(CF_3)_2^- + 2 HF \longrightarrow Cs^+HF_2^- + HN(CF_3)_2 \qquad (6)$$
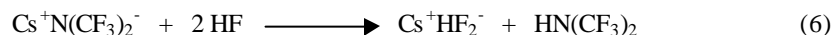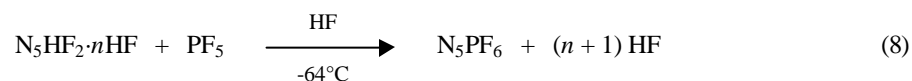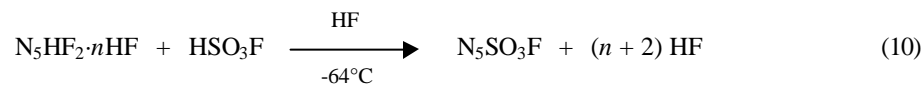
The above assumptions were confirmed by carrying out a reaction of N_5SbF_6 with CsF in anhydrous HF at –64 ℃ which resulted in the expected precipitation of $CsSbF_6$ and the formation of a polybifluoride of N_5^+ according to Equation 7.

$$N_5SbF_6 \ + \ CsHF_2 \ + \ n \, HF \ \xrightarrow[\text{-64°C}]{\text{HF}} \ N_5HF_2 \cdot n HF \ + \ CsSbF_6\downarrow \qquad (7)$$
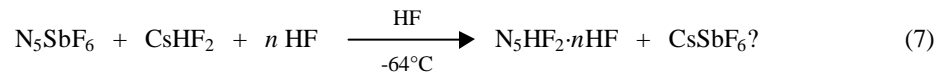
$N_5HF_2 \cdot n HF$ was isolated as a clear, colorless liquid after filtering off the $CsSbF_6$ precipitate and removing all volatiles at –64 °C from the filtrate. The observed low-temperature Raman spectrum was identical to that shown in Figure 1. It exhibits, in addition to some weak bands due to the Teflon-FEP sample container and a trace of SbF_6^- from the starting material, only bands due to N_5^+. The experimental Raman frequencies and assignments are listed in Table 1. On warm-up to room temperature, the $N_5HF_2 \cdot n$ HF salt decomposed under formation of *trans*-N_2F_2, NF_3 and N_2, which were identified by checking for non-condensible gas at –196 °C and FT-IR spectroscopy.

The usefulness of the $N_5HF_2 \cdot n HF$ salt as a reagent for the synthesis of other N_5^+ salts by displacement reactions with Lewis acids stronger than HF was explored by reacting it with PF_5, BF_3 and HSO_3F, [25, 26] resulting in the formation of N_5PF_6, N_5BF_4 and N_5SO_3F, respectively, according to Equations 8 - 10.

$$N_5HF_2 \cdot n HF \ + \ PF_5 \ \xrightarrow[\text{-64°C}]{\text{HF}} \ N_5PF_6 \ + \ (n+1) \, HF \qquad (8)$$

$$N_5HF_2 \cdot n HF \ + \ BF_3 \ \xrightarrow[\text{-64°C}]{\text{HF}} \ N_5BF_4 \ + \ (n+1) \, HF \qquad (9)$$

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$$\text{N}_5\text{HF}_2 \cdot n\text{HF} \ + \ \text{HSO}_3\text{F} \ \xrightarrow[-64°\text{C}]{\text{HF}} \ \text{N}_5\text{SO}_3\text{F} \ + \ (n+2) \ \text{HF} \tag{10}$$

All these new salts are white, marginally stable solids that were characterized by NMR and vibrational spectroscopy. The ^{14}N NMR spectrum of N_5PF_6 was recorded in HF at –40 °C. It showed a strong resonance at δ = -165.1 ppm for the N_β atoms and a very broad line at about δ = -101 ppm for the terminal N_a atoms, and is in good agreement with previously published values for N_5^+ salts.[1-3] In the ^{14}N NMR spectra of N_5BF_4 and $\text{N}_5\text{SO}_3\text{F}$ in HF at –40 °C, the resonances for the N_β atoms were observed at δ = -164.3 ppm and δ = -164.7 ppm, respectively. The experimental vibrational frequencies and assignments of the three salts and, for comparison, of N_5SbF_6 are listed in Table 1. The observed Raman and infrared spectra of N_5PF_6 are shown in Figure 2, and the Raman spectra of N_5BF_4 and $\text{N}_5\text{SO}_3\text{F}$ are shown in Figures 3 and 4, respectively. They establish beyond any doubt the composition of these salts [1-3, 27-29] and their ionic nature.

Whereas the N_5^+ cation is a highly energetic ion with a calculated endothermicity of 351.6 kcal/mol,[22] all of its presently known salts contained non-energetic counter-ions.[1-3] Although a significant advance in potential performance was achieved by successfully doubling the number of polynitrogen ions in a salt by formation of a 2:1 salt $[\text{N}_5^+]_2[\text{SnF}_6]^{2-}$,[3] salts containing energetic counter-ions were still missing. Attempts to combine the N_5^+ cation with the energetic anions, ClO_4^-, NO_3^- and N_3^- by metathetical reactions failed, and a recent theoretical analysis showed that, after inclusion of entropy corrections, N_5^+N_3^- is unstable by 76 kcal/mol with respect to spontaneous decomposition to N_3 and N_2.[22] In spite of these challenges, we have now successfully synthesized two highly energetic N_5^+ salts.

The metathetical reaction between N_5SbF_6 and $NaP(N_3)_6$ in SO_2 proceeded with the expected precipitation of $NaSbF_6$ and the combination of the N_5^+ cation with the energetic anion $P(N_3)_6^-$ [30] to form $N_5P(N_3)_6$ according to Equation 11.

$$N_5SbF_6 \ + \ NaP(N_3)_6 \ \xrightarrow[-64°C]{SO_2} \ N_5P(N_3)_6 \ + \ NaSbF_6\downarrow \qquad (11)$$
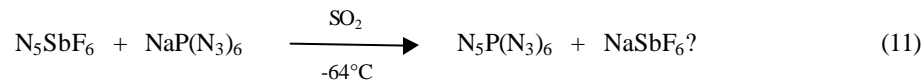
However, the compound is extremely shock sensitive and violently explodes upon the slightest provocation or warm-up towards room temperature (see Figure 5). In addition to its very high energy content, this salt is remarkable for its high energetic-nitrogen content of 91 weight %.

In a similar fashion, $N_5B(N_3)_4$ was prepared from N_5SbF_6 and $NaB(N_3)_4$ [31] according to Equation 12.

$$N_5SbF_6 \ + \ NaB(N_3)_4 \ \xrightarrow[-64°C]{SO_2} \ N_5B(N_3)_4 \ + \ NaSbF_6\downarrow \qquad (12)$$
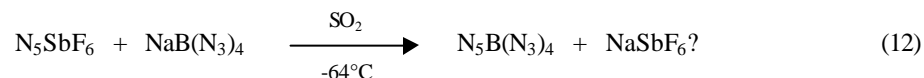
Again, the salt is extremely shock-sensitive and explodes on warm-up towards room temperature. Its energetic-nitrogen content of 95.7 weight % significantly exceeds even that of $N_5P(N_3)_6$. Attempts to carry out these reactions with $CsP(N_3)_6$ and $CsB(N_3)_4$ in HF solution were unsuccessful because HF reacts with the polyazido anions to give PF_6^- and BF_4^-, and lead to the isolation of N_5PF_6 and N_5BF_4, respectively.

Both polyazido salts were identified and characterized by low-temperature Raman spectroscopy. The experimental vibrational frequencies and tentative assignments are given in the experimental section. The observed Raman spectra of $N_5P(N_3)_6$ and $N_5B(N_3)_4$ are shown in

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Figures 6 and 7, respectively. In addition to high energy densities of about 2 kcal/gram and extremely high sensitivities, these compounds exhibit the typical high detonation velocities of covalent azides which render the handling and further characterization of these compounds particularly difficult.

Experimental Section

Caution! *Azides and N_5^+ compounds are highly endothermic and can decompose explosively under various conditions! N_5^+ compounds are highly energetic oxidizers. Contact with potential fuels must be avoided. These materials should be handled only on a scale of less than 2 mmol. The polyazides of this work are extremely shock-sensitive. Because of the high energy content and high detonation velocities of these azides, their explosions are particularly violent and can cause, even on a one mmol scale, significant damage. The use of appropriate safety precautions, such as face shields, heavy leather welding suits, leather gloves, and ear plugs is mandatory. Teflon containers should be used, whenever possible, to avoid hazardous fragmentation. **Ignoring safety precautions can lead to serious injuries!***

Materials and Apparatus: All reactions were carried out in Teflon-FEP or -PFA ampules that were closed by stainless steel valves. Volatile materials were handled in stainless steel/Teflon-FEP or grease-free Pyrex-glass vacuum lines.[32] Non-volatile solids were handled in the dry argon atmosphere of a glove box. All reaction vessels and the stainless steel line were passivated with ClF_3 prior to use.

Infrared spectra were recorded in the range 4000–400 cm^{-1} on a Midac FT-IR model 1720 at a resolution of 1 cm^{-1}. Spectra of solids were obtained by using dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded in the

range 4000–80 cm^{-1} on a Bruker Equinox 55 FT-RA spectrophotometer using a Nd:YAG laser at 1064 nm with power levels of 200 mW or less. Pyrex melting point tubes that were baked out at 300 °C for 48 h at 10 mTorr vacuum or 9 mm o.d. Teflon-FEP tubes with stainless steel valves that were passivated with ClF_3 were used as sample containers. ^{14}N NMR spectra were recorded unlocked at 36.13 MHz on a Bruker AMX 500 spectrometer using solutions of the compounds in DMSO in sealed standard glass tubes. Neat CH_3NO_2 (0.00 ppm) was used as the external reference.

The N_2FSbF_6 starting material was prepared from *cis*-N_2F_2 and SbF_5 in anhydrous HF solution.[19,20,33-36] N_5SbF_6 was prepared from N_2FSbF_6 and HN_3 in HF,[2] $NaP(N_3)_6$ was prepared from PCl_5 and NaN_3,[30] and $NaB(N_3)_4$ from $NaBH_4$ and HN_3.[31] The HF (Matheson Co.) was dried by storage over BiF_5 (Ozark Mahoning).[37] PCl_5 (Aldrich) was purified by sublimation in a dynamic vacuum. The CsF (KBI) was fused in a platinum crucible, transferred while hot to the dry box, and finely powdered. BF_3 (Matheson), PF_5 (Ozark Mahoning), NaN_3 (Aldrich), $NaBH_4$ (Aldrich) and HSO_3F (Aldrich) were used without further purification.

Preparation of $N_5HF_2 \cdot nHF$. A solution of CsF (1.00 mmol) in 2 mL HF was siphoned through a Teflon-FEP tube into a Teflon-FEP ampule containing a solution of N_5SbF_6 (1.00 mmol) in 3 mL HF at –64 °C. Immediately, a white precipitate was formed. The reaction mixture was stirred for 10 minutes to ensure complete reaction. The mixture was allowed to settle, and the supernatant liquid was siphoned into a second Teflon-FEP ampule kept at –64 °C. The $CsSbF_6$ residue was washed twice with about 1 mL of HF. The HF was pumped off from the combined liquids at –64 °C, leaving behind a colorless liquid (0.156 g; weight calculated for 1.00 mmol of $N_5HF_2 \cdot 2.5HF$: 0.159 g).

Preparation of N₅PF₆ and N₅BF₄. Excess PF_5 or BF_3 (2.0 mmol) was condensed at –196 °C into an ampule containing a frozen solution of $N_5HF_2 \cdot nHF$ (1.00 mmol) in 1 mL of HF. The temperature was raised to –64 °C and the reaction mixture kept at this temperature for 1 hour to ensure complete reaction. All volatile material was pumped off at –64 °C, leaving behind a white solid (N_5PF_6: 0.220 g, weight calculated for 1.00 mmol of N_5PF_6: 0.215 g; N_5BF_4: 0.167 g; weight calculated for 1.00 mmol of N_5BF_4: 0.157 g).

Preparation of N₅SO₃F. At –64 °C, a solution of HSO_3F (1.00 mmol) in 2 mL of HF was added to a solution of $N_5HF_2 \cdot nHF$ (1.00 mmol) in 1 mL of HF. The reaction mixture was stirred for 30 minutes at this temperature to ensure complete reaction. All volatiles were pumped off at -64°C leaving behind a white solid (0.175 g; weight calculated for 1.00 mmol of N_5SO_3F: 0.169 g).

Preparation of N₅P(N₃)₆ and N₅B(N₃)₄. At –64 °C, a solution of N_5SbF_6 (0.50 mmol) in 3 mL SO_2 was added to a solution of $NaB(N_3)_4$ or $NaP(N_3)_6$ (0.50 mmol) in 3 mL SO_2, respectively. After the mixture had settled, the liquid phase was transferred into a second Teflon-FEP ampule kept also at –64 °C, and the solid $NaSbF_6$ residue was washed twice with about 1 mL of SO_2. Pumping off all volatile material from the combined liquids at -64°C resulted in a white solid. $N_5P(N_3)_6$: 0.184 g, weight calculated for 0.50 mmol of $N_5P(N_3)_6$: 0.177 g; Raman (50 mW, -80 °C): $\tilde{\nu}$=2266(10.0) (N_5^+ ν_1), 2203(7.5) (N_5^+ ν_7), 2182(5.4)/2074(2.9) ($P(N_3)_6^-$ $\nu_{as}N_3$), 1302(4.7) ($P(N_3)_6^-$ ν_sN_3), 873(3.9) (N_5^+ ν_2), 730(7.4) ($P(N_3)_6^-$ νPN), 666(8.0) (N_5^+ ν_3), 522(5.0) (($P(N_3)_6^-$ δN_3), 483(4.6) (N_5^+ ν_5), 419(4.7) (N_5^+ ν_9), 458(4.7) (($P(N_3)_6^-$ δPNN), 327(4.9) (($P(N_3)_6^-$ δPNN), 203(9.1) (N_5^+ ν_4); $N_5B(N_3)_4$: 0.137 g; weight calculated for 0.50 mmol of $N_5B(N_3)_4$: 0.124 g; Raman (50 mW, -80 °C): $\tilde{\nu}$=2269(1.9) (N_5^+ ν_1), 2207(1.2) (N_5^+ ν_7), 2172(5.4)/2148(2.0) ($B(N_3)_4^-$ $\nu_{as}N_3$), 1371(2.7)/1354(2.6)/1302(2.9) ($B(N_3)_4^-$ ν_sN_3), 875(3.1)

$(N_5^+ \; \nu_2)$, 664(3.6) $(N_5^+ \; \nu_3)$, 581(3.0)/532(4.7) $(B(N_3)_4^-)$, 483(2.3) $(N_5^+ \; \nu_5)$, 421(2.1) $(N_5^+ \; \nu_9)$, 293(2.4) $(B(N_3)_4^-)$, 203(2.6) $(N_5^+ \; \nu_4)$, 189(5.0)/165(6.8)/123(10.0) $(B(N_3)_4^-)$.

References

[1]   K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *Angew. Chem.* **1999**, *111*, 2112; *Angew. Chem. Int. Ed.* **1999**, *38*, 2004.

[2]   A. Vij, W. W. Wilson, V. Vij, F. S. Tham, J. A. Sheehy, K. O. Christe, *J. Am. Chem. Soc.* **2001**, *123*, 6308.

[3]   W. W. Wilson, A. Vij, V. Vij, E. Bernhardt, K. O. Christe, *Chem. Eur. J.* **2003**, *9*, 2840.

[4]   G. A. Olah, G. K. S. Prakash, G. Rasul, *J. Am. Chem. Soc.* **2001**, *123*, 3308.

[5]   M T. Nguyen, T. K. Ha, *Chem. Phys. Lett.* **2001**, *335*, 311.

[6]   S. Fau, R. J. Bartlett, *J. Phys. Chem. A.* **2001**, *105*, 4096.

[7]   R. J. Bartlett, *Chem. Ind.* **2000**, 140, and references therein; a compilation of data for N2 to N10 can be found at http://www.gtb.ufl.edu/~bartlett/polynitrogen.pdf.

[8]   G. Chung, M. W. Schmidt, M. S. Gordon, *J. Phys. Chem. A* **2000**, *104*, 5647, and references therein.

[9]   M. N. Glukhovtsev, H. Jiao, P. von R. Schleyer, *Inorg. Chem.* **1996**, *35*, 7124 and references therein.

[10]   H. H. Michels, J. A. Montgomery, Jr., K. O. Christe, D. A. Dixon, *J. Phys. Chem.* **1995**, *99*, 187.

[11]   G. Schatte, H. Willner, *Z. Naturforsch.* **1991**, *46b*, 483.

[12]   G. Rasul, G. K. S. Prakash, G. A. Olah, *J. Am. Chem. Soc.* **1994**, *116*, 8985.

[13]   W. E. Thompson, M. E. Jacox, *J. Chem. Phys.* **1990**, *93*, 3856.

[14]   J. P. Zheng, J. Waluk, J. Spanget-Larsen, D. M. Blake, J. G. Radziszewski, *Chem. Phys. Lett.* **2000**, *328*, 227.

[15]   T. Ruchti, T. Speck, J. P. Connelly, E. J. Bieske, H. Linnertz, J. P. Maier, *J. Chem. Phys.* **1996**, *105*, 2591.

[16]   F. Cacace, G. de Petris, A. Troiani, *Science* **2002**, *295*, 480.

[17]   M. I. Eremets, R. J. Hemley, H. Mao, E. Gregoryanz, *Nature* **2001**, *411*, 170.

[18]   T. Curtius, *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 3023.

[19]   A. V. Pankratov, N. I. Savenkova, *Russ. J. Inorg. Chem.* **1968**, *13*, 1345.

[20]   K. O. Christe, R. D. Wilson, W. W. Wilson, R. Bau, S. Sukumar, D. A. Dixon, *J. Am. Chem. Soc.* **1991**, *113*, 3795.

[21]   K. O. Christe, D. A. Dixon, D. McLemore, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *J. Fluorine Chem.* **2000**, *101*, 151.

[22]   D. A. Dixon, D. Feller, K. O. Christe, W. W. Wilson, A. Vij, V. Vij, H. D. B. Jenkins, R. M. Olsen, M. S. Gordon, *J. Am. Chem. Soc.* **2004**, *126*, 834.

[23]   H. M. Netzloff, M. S. Gordon, K. O. Christe, W. W. Wilson, A. Vij, V. Vij, J. A. Boatz, *J. Phys. Chem. A* **2003**, *107*, 6638.

[24]   K. O. Christe, W. W. Wilson, R. D. Wilson, *Inorg. Chem.* **1980**, *19*, 1494.

[25]   W. W. Wilson, K. O. Christe, *J. Fluorine Chem.* **1982**, *19*, 253.

[26]   W. W. Wilson, K. O. Christe, *Inorg. Chem.* **1982**, *21*, 2091.

[27]   K. O. Christe, C. J. Schack, R. D. Wilson, *Inorg. Chem.* **1976,** *15,* 1275.

[28]   K. O. Christe, R. D. Wilson, C. J. Schack, *Inorg. Chem.* **1980,** *19,* 3046.

[29]   H. Siebert, *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie, Anorganische und Allgemeine Chemie in Einzeldarstellungen, VII*, Springer, Heidelberg, **1996.**

[30]   a) H. W. Roesky, *Angew. Chem. Int. Ed.* **1967**, *6*, 637; b) P. Volgnandt, A. Schmidt, *Z. Anorg. Allg. Chem.* **1976**, *425*, 189.

[31]   a) E. Wiberg, H. Michaud, *Z. Naturforsch.* **1954**, *96*, 497; b) W. Freank, T. Habereder, A. Hammerl, T. M. Klapötke, B. Krumm, P. Mayer, H. Nöth, M. Warchhold, *Inorg. Chem.* **2001**, *40*, 1334; c) W. Fraenk, H. Nöth, T. M. Klapötke, M. Suter, *Z. Naturforsch.* **2002**, *57b*, 621.

[32]   K. O. Christe, W. W. Wilson, C. J. Schack, R. D. Wilson, *Inorg. Synth.* **1986**, *24*, 39.

[33]   D. Moy, A. R. Young, *J. Am. Chem.Soc.* **1965**, *87*, 1889.

[34]   J. K. Ruff, *Inorg Chem.* **1966**, *5*, 1971.

[35]   H. W. Roesky, O. Glemser, D. Bormann, *Chem. Ber.* **1966**, *99*, 1589.

[36]   K. O. Christe, R. D. Wilson, W. Sawodny, *J. Mol. Struct.* **1971**, *8*, 245.

[37]   K. O. Christe, W. W. Wilson, C. J. Schack, *J. Fluorine Chem.* **1978**, *11*, 71.

Figure 1. Low-temperature Raman spectrum of $N_5HF_2 \cdot n$HF. The bands marked by an asterisk are due to the Teflon-FEP sample tube. Bands marked by ♦ are caused by a trace of SbF_6^- from the starting material.
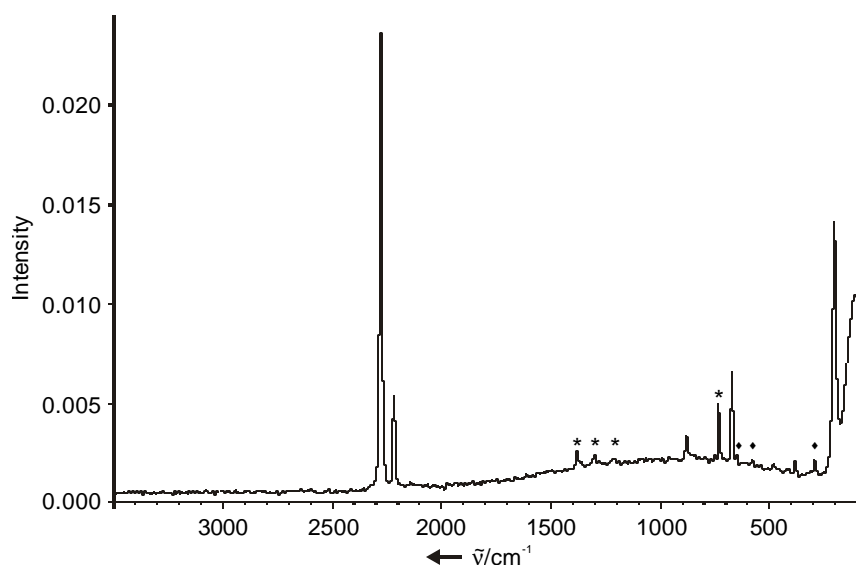
Figure 2. Infrared (upper trace) and Raman (lower trace) spectra of N_5PF_6. The bands marked by an asterisk are due to the Teflon-FEP sample tube.
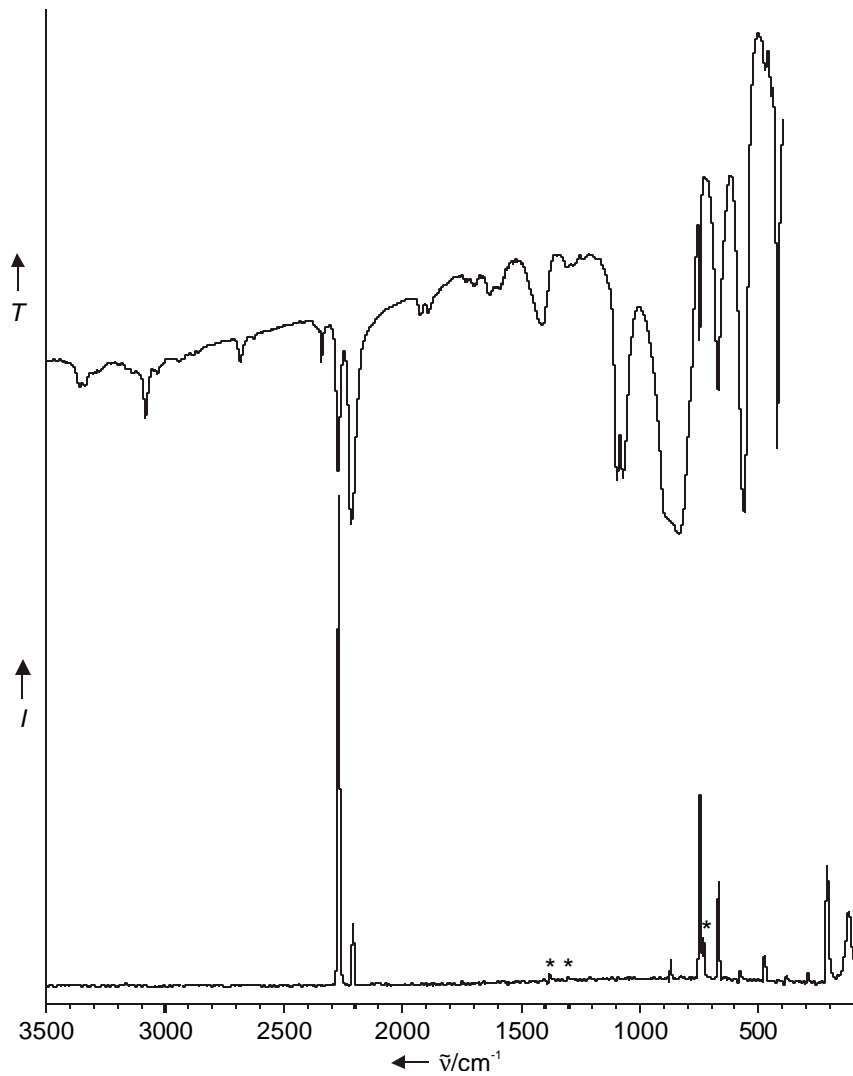
Figure 3. Low-temperature Raman spectrum of N_5BF_4. The bands marked by an asterisk are due to the Teflon-FEP sample tube.
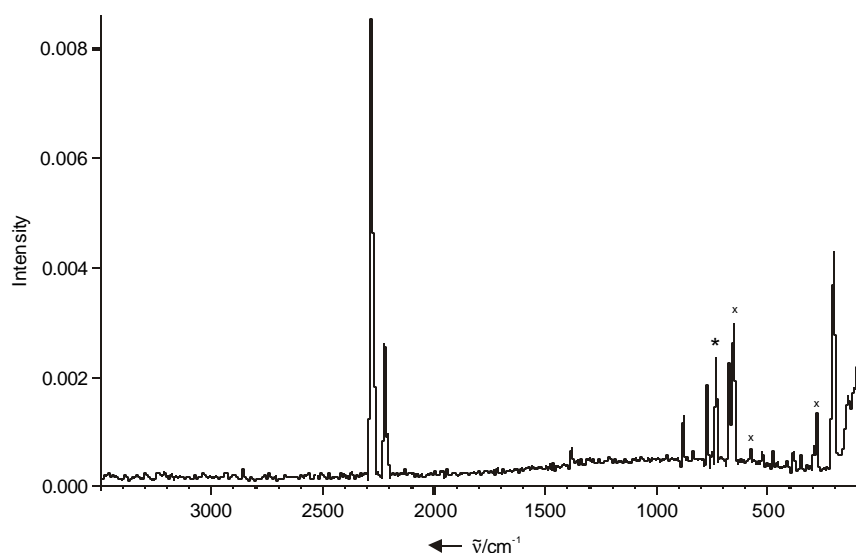
Figure 4. Low-temperature Raman spectrum of N_5SO_3F.
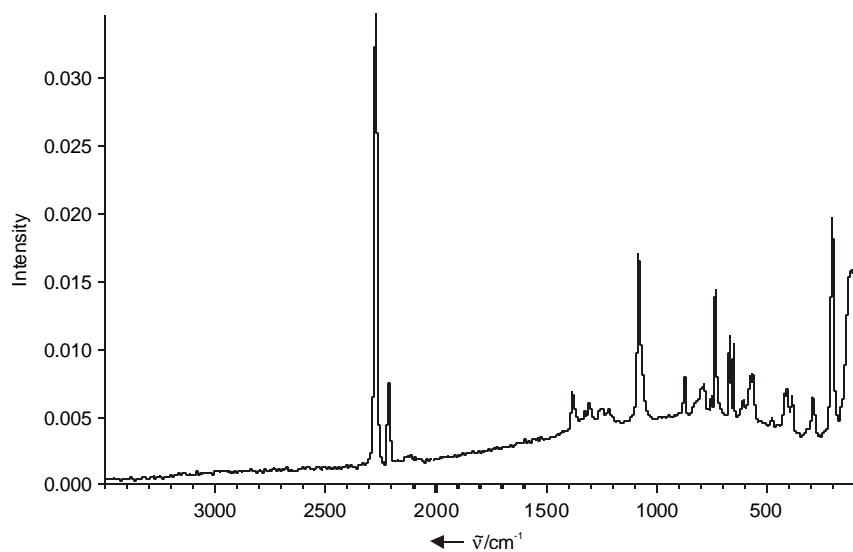

Figure 5: Single-ended 9 mm o.d. Teflon-FEP ampule, used for recording the Raman spectrum, after explosion of less than 500 mg of $N_5^+P(N_3)_6^-$.

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Figure 6. Low-temperature Raman spectrum of $N_5P(N_3)_6$. The bands marked by an asterisk are due to the Teflon-FEP sample tube. The two bands marked with ♦ are caused by the SO_2 solvent.
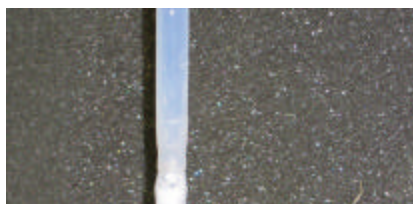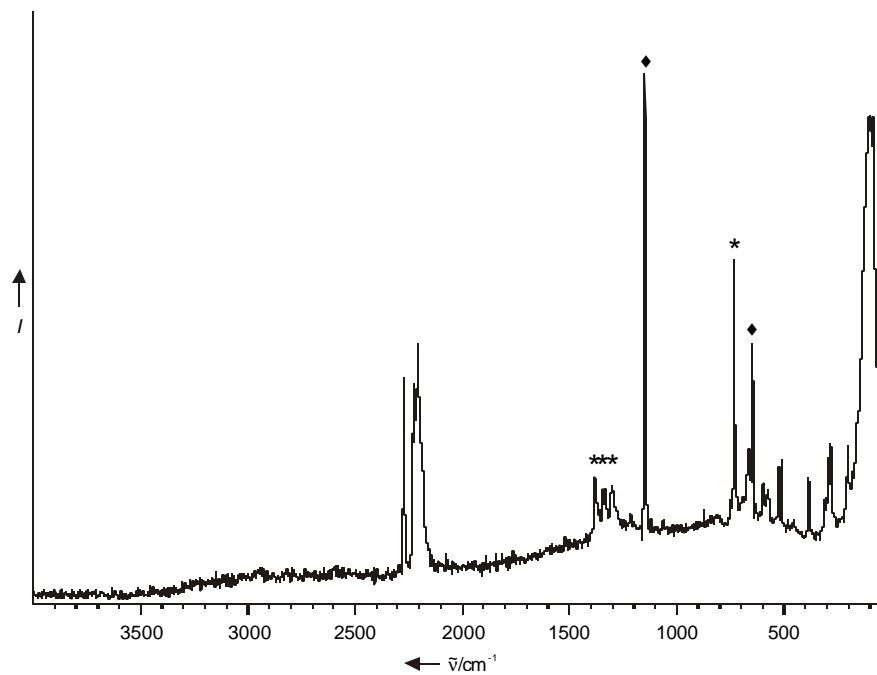
Figure 7. Low-temperature Raman spectrum of $N_5B(N_3)_4$. The bands marked by an asterisk are due to the Teflon-FEP sample tube.
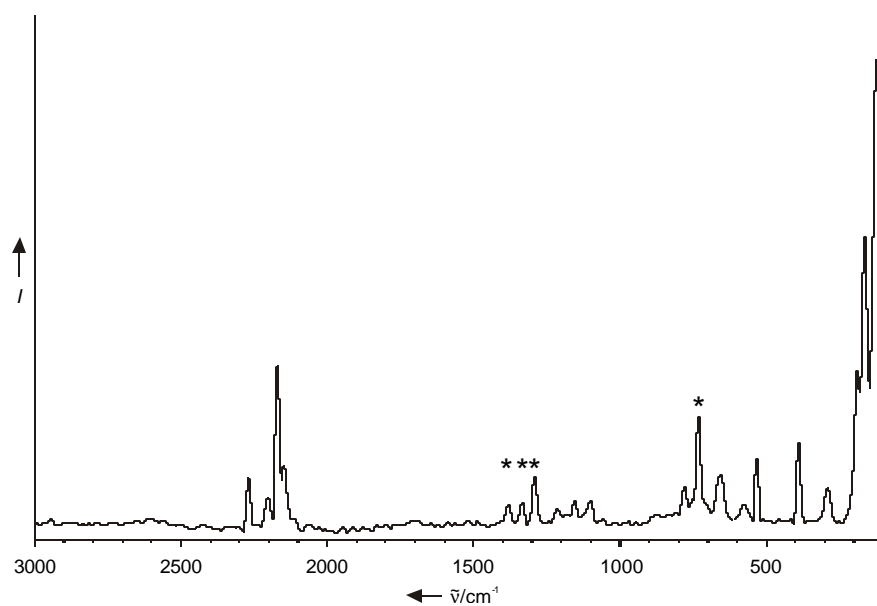
Table 1. Observed vibrational frequencies of $N_5HF_2 \cdot nHF$, N_5SbF_6, N_5PF_6, N_5BF_4 and N_5SO_3F and their assignments

observed frequency (cm^{-1}) and relative intensity							assignments			
$N_5HF_2 \cdot nHF$	N_5SbF_6 [2]		N_5PF_6		N_5BF_4	N_5SO_3F				
Raman	IR	Raman	IR	Raman	Raman	Raman	$N_5^+(C_{2v})$	MF_6^- (O_h)	BF_4^- (T_d)	SO_3F^- (T_d)
	3357 vw		3364 w				$(v_1 + v_3 + v_9)(B_2) = 3358$			
	3334 vw		3337 w				$(v_1 + v_8)(B_2) = 3323$			
	3079 vw		3082 mw				$(v_2 + v_7)(B_2) = 3077$			
	2681 vw		2685 w				$(v_1 + v_9)(B_2) = 2682$			
2279 (10)	2270 m	2268 (9.4)	2273 ms	2269 (10)	2283 (10)	2271 (10)	$v_1(A_1)$			
2218 (2.2)	2205 s	2205 (2.0)	2219 s	2209 (1.3)	2221 (3.0)	2210 (2.2)	$v_7(B_2)$			
	1921 vw		1926 w				$(v_3 + 3v_9)(B_2) = 1914$			
	1891 vw		1891 w				$(v_8 + 2v_9)(B_2) = 1883$			
						1303 (1.7)				$v_4(E)$
	1240 vw							comb. bands		
	1092 ms		1099 s				$(v_3 + v_9)(B_2) = 1086^a$			
						1084 (5.3)				$v_1(A_1)$
	1064 s		1072 s				$v_8(B_2)$			
	902 vvw						$(v_5 + v_6)(B_2) = 903$			
877 (1.3)	871 w	872 (0.6)		869 (0.6)	880 (1.5)	871 (2.3)	$v_2(A_1)$			
840 (0.9)	835 vw	837 (0+)		826 (0+)	837 (0.7)	829 (1.7)	$(2v_9)(A_1) = 828^b$			
						785 (2.1)				$v_2(A_1)$
					771 (2.9)				$v_1(A_1)$	
672 (2.7)		672 (1)	672 s	668 (2.2)	674 (2.7)	669 (3.2)	$v_3(A_1)$			
}	655 vs		881 s					$v_3(F_{1u})$		
			839 vs							
		652 (10)	750 m	747 (3.8)				$v_1(A_{1g})$		
}						574 (2.4)				$v_3(A_1)$
						564 (2.4)				
	582 w	571 (0.8)	563 vs	578 (0.3)				$v_2(E_g)$		
					525 (0.7)				$v_4(F_2)$	
481 (0.7)		478 (0+)	473 w		476 (0.7)	477 (1.4)	$v_5(A_2)$			
	447 w		447 w				?			
422 (0.6)	425 ms				426 (0.4)	420 (1.9)	$v_6(B_1)$			
413 (0.6)	412 mw	416 (0+)		416 (0+)	412 (0.5)	407 (2.0)	$v_9(B_2)$			
	284 vs		563 vs					$v_4(F_{1u})$		
		282 (2.8)	473 w	474 (0.6)				$v_5(F_{2g})$		
					350 (0.6)				$v_2(E)$	
202 (5.8)		204 (5.0)		211 (2.5)	202 (4.8)	203 (5.7)	$v_4(A_1)$			
		107 (5.0)		120 (1.6)	113 (2.0)	111 (4.5)	lattice vibrations			

^{a} In Fermi resonance with $v_8(B_2)$. ^{b} In Fermi resonance with $v_2(A_1)$.

Synopsis

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New High Energy Density Materials. Synthesis and Characterization of $N_5^+P(N_3)_6^-$, $N_5^+B(N_3)_4^-$, $N_5^+HF_2^- \cdot n$HF, $N_5^+BF_4^-$, $N_5^+PF_6^-$, and $N_5^+SO_3F^-$

23 energetic nitrogens and only one phosphorus. The N_5^+ cation was combined for the first time with energetic anions in the form of $N_5^+P(N_3)_6^-$ and $N_5^+B(N_3)_4^-$, containing 91 and 96 weight %, respectively, of energetic nitrogen. Also, the thermally unstable compound $N_5HF_2 \cdot n$HF was prepared by metathesis from N_5SbF_6 and $CsHF_2$ in anhydrous HF. Its usefulness as a general reagent for the synthesis of new N_5^+ salts was demonstrated with the preparation of the new compounds N_5PF_6, N_5BF_4 and N_5SO_3F.