Polynitrogen Chemistry: Preparation and Characterization of $(N_5)_2SnF_6$, N_5SnF_5, and $N_5B(CF_3)_4$

William W. Wilson,*[a] Ashwani Vij,[a] Vandana Vij,[a] Eduard Bernhardt,[c] and Karl O. Christe*[a, b]

Abstract: Metathetical processes were used to convert N_5SbF_6 into $N_5[B(CF_3)_4]$ and $(N_5)_2SnF_6$. The latter salt is especially noteworthy because it contains two N_5^+ ions per anion, thus demonstrating that salts with touching polynitrogen cations can be prepared. This constitutes an important milestone towards our ultimate goal of synthesizing a stable, ionic nitrogen allotrope. The stepwise decomposition of $(N_5)_2SnF_6$ yielded N_5SnF_5. Multinuclear NMR spectra show that in HF the SnF_5^- ion exists as a mixture of $Sn_2F_{10}^{2-}$ and $Sn_4F_{20}^{4-}$ ions. Attempts to isolate FN_5 from the thermolysis of $(N_5)_2SnF_6$ were unsuccessful, yielding only the expected decomposition products, FN_3, N_2, *trans*-N_2F_2, NF_3, and N_2.

Keywords: anions · nitrogen · NMR spectroscopy · polynitrogen · vibrational spectroscopy

Introduction

During the past two decades, polynitrogen chemistry has received increasing attention.[1–16] While at the beginning, most of the efforts were devoted to theoretical studies, the recent syntheses of stable salts of the pentanitrogen(+1) cation (N_5^+)[1, 2] have given a strong impetus to experimental studies in this field. So far, the only method for generating N_5^+ compounds has been their direct synthesis from N_2FAsF_6 or N_2FSbF_6 and HN_3 in HF, according to Equation (1).

$$N_2FMF_6 + HN_3 \xrightarrow{HF} N_5MF_6 + HF \qquad (M = As, Sb) \qquad (1)$$

A major goal of this study was to increase the nitrogen content of the N_5^+ salts by combining N_5^+ with multiply charged anions. This presents a significant challenge, because it results in structures with touching polynitrogen ions that will increase both the endothermicity and sensitivity of these compounds.

The general usefulness of the metathetical method is severely restricted by the small number of N_2F^+ salts available. Except for reports on unstable N_2FBF_4[17] and N_2FPF_6[18] salts, no other N_2F^+ compounds have been described in the literature. Therefore, it was desirable to develop a more general method for the syntheses of N_5^+ salts, such as the exchange of SbF_6^- in N_5SbF_6 for other anions. This situation resembles that previously encountered for the syntheses of NF_4^+ salts.[19, 20] Since SbF_5 is among the strongest known Lewis acids,[21] displacement reactions are rarely feasible, and metathetical approaches are required [Eq. (2)].

$$N_5^+SbF_6^- + M^+Y^- \rightarrow N_5^+Y^- + M^+SbF_6^- \downarrow \qquad (2)$$

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.

Results and Discussion

The choices of counterions capable of forming stable N_5^+ salts are limited. For room temperature stability, the strengths of the conjugate Lewis acids should exceed that of AsF_5, because N_5AsF_6 is only marginally stable at room temperature.[1] The stability of the N_5^+ salt might be further enhanced by the use of a weakly coordinating, bulky anion.

[a] Prof. K. O. Christe, Dr. W. W. Wilson, Dr. A. Vij, V. Vij
ERC, Inc. and Space and Missile Propulsion Division
Air Force Research Laboratory (AFRL/PRSP)
10 East Saturn Boulevard, Bldg 8451
Edwards Air Force Base, CA 93524 (USA)
Fax: (+1) 661-275-5471
E-mail: karl.christe@edwards.af.mil
william.wilson@edwards.af.mil

[b] Prof. K. O. Christe
Loker Research Institute
University of Southern California
Los Angeles, CA 90089-1661 (USA)

[c] Dr. E. Bernhardt
FB 6-Anorganische Chemie
Gerhard-Mercator-Universität Duisburg
Lotharstrasse 1, 47048 Duisburg (Germany)

  DOI: 10.1002/chem.200304973 *Chem. Eur. J.* **2003**, *9*, 2840–2844

Several solvents were explored for conducting the reaction given in Equation (2). Anhydrous HF was found to be an excellent choice for the SnF_6^{2-} salt, as shown in Equation (3).

$$2\,N_5SbF_6 + Cs_2SnF_6 \xrightarrow[-78\,^\circ C]{HF} (N_5)_2SnF_6 + 2\,CsSbF_6\downarrow \quad (3)$$

The resulting $(N_5)_2SnF_6$ salt was obtained in high yield with a purity of about 94 wt%. The impurities were about 5 wt% of unreacted $N_5^+SbF_6^-$ and 1 wt% of $CsSbF_6$. The $(N_5)_2SnF_6$ salt is a white, friction sensitive (**caution!**) solid, which is marginally stable at room temperature and decomposes at slightly higher temperature or on storage to N_5SnF_5 with the loss of an "FN_5" equivalent, as shown in Equation (4).

$$(N_5)_2SnF_6 \rightarrow N_5SnF_5 + \text{"}FN_5\text{"} \quad (4)$$

Because "FN_5" is unstable with a predicted life time of nanoseconds,[22] only its primary decomposition products, FN_3 and N_2, and secondary decomposition products, *trans*-N_2F_2, NF_3 and N_2, were observed by checking for noncondensible gas at $-196\,^\circ C$ and FT-IR spectroscopy. The relevant decomposition reactions are shown in Equations (5)–(7).

$$\text{"}FN_5\text{"} \rightarrow N_2 + FN_3 \quad (5)$$

$$2\,FN_3 \rightarrow trans\text{-}N_2F_2 + 2\,N_2 \quad (6)$$

$$3\,FN_3 \rightarrow NF_3 + 4\,N_2 \quad (7)$$

The N_5SnF_5 salt, formed by the controlled thermal decomposition of $(N_5)_2SnF_6$, is a white solid that starts to decompose at about 50–60 °C. The fact that the thermal stabilities of N_5SbF_6, $N_5[B(CF_3)_4]$ (see below), and N_5SnF_5 are all comparable suggests that the thermal stability of the N_5^+ cation is the limiting factor. The thermal decomposition of N_5SnF_5 was studied by its material balance and vibrational spectroscopy and proceeds smoothly according to Equation (8), yielding SnF_4 as the solid nonvolatile residue.

$$N_5SnF_5 \rightarrow SnF_4 + \text{"}FN_5\text{"} \quad (8)$$

The $(N_5)_2SnF_6$ and N_5SnF_5 salts were characterized by vibrational (Tables 1 and 2, and Figure 1) and multinuclear NMR (Table 3 and Figure 2) spectroscopy. The Raman and infrared spectra are in accord with the expectations for N_5^+ and the fluorostannate anions.[1, 2, 23, 24] One remarkable feature in the vibrational spectra of $(N_5)_2SnF_6$ is the fact that the frequencies of all SnF_6^{2-} modes and of the N_5^+ stretching modes are shifted to significantly higher frequencies relative to $(NF_4)_2SnF_6$[23] and the 1:1 salts of N_5^+.[1, 2] In the absence of a crystal structure, we cannot provide a convincing explanation for this unexpected effect. It should also be noted that in mixtures of $(N_5)_2SnF_6$ and N_5SnF_5, generated by partial decomposition of the former, only one set of bands with intermediate frequencies was observed and not two sets with the frequencies of the 2:1 and 1:1 salts. While the bands for SnF_6^{2-} are sharp and narrow, as expected for a monomeric octahedral anion, the bands due to SnF_5^- are broad and poorly defined. This is in accord with the results from the multinuclear NMR study which show SnF_5^- to be present as both a dimer and a cyclic tetramer.

Table 1. Raman and infrared spectra[a] of solid $(N_5)_2SnF_6$ and their assignments.

Obsd frequencies [cm^{-1}] and relative intensities		Assignments (point group)	
Raman	Infrared	N_5^+ (C_{2v})	SnF_6^{2-} (O_h)
2287 (10.0)	2288 m	$\nu_1(A_1)$	
2274 (1.9)			
2227 (1.9)	2228 s	$\nu_7(B_2)$	
2210 (0+)			
2170 (0.2)			
1112 (0+)	1112 s	$\nu_8(B_2)$	
	1083 m	$(\nu_3+\nu_9)(B_2)=1089$	
881 (1.3)	881 w	$\nu_2(A_1)$	
822 (0.1)		$2\nu_9(A_1)=834$	
672 (2.6)		$\nu_3(A_1)$	
	611 vs		$\nu_3(F_{1u})$
600 (6.1)	602 vw		$\nu_1(A_{1g})$
508 (0.4)			$\nu_2(E_g)$
475 (0.2)		$\nu_5(A_2)$	
	417 ms	$\nu_6(B_1)$	
417 (0.5)		$\nu_9(B_2)$	
266 (1.2)			$\nu_5(F_{2g})$
203 (3.0)		$\nu_4(A_1)$	
195 (4.4)			
159 (1.0)			
126 (9.9)		lattice vibration	
119 (4.0)		lattice vibration	
80 (4.0)		lattice vibration	

[a] The following bands due to the SbF_6^- impurity were also observed. Raman: 654 (1.0), ν_1; 572 (0+), ν_2; 282 (0.3), ν_5.

Table 2. Raman and infrared spectra[a] of solid N_5SnF_5 and their assignments.

Obsd frequencies [cm^{-1}] and relative intensities		Assignments (point group)	
Raman	Infrared	N_5^+ (C_{2v})	SnF_5^-
2269 (10.0)	2270 m	$\nu_1(A_1)$	
2209 (2.0)	2212 s	$\nu_7(B_2)$	
	1230 w		combination band
1090 (0+)	1094 ms	$\nu_8(B_2)$	
	1069 m	$(\nu_3+\nu_9)(B_2)=1090$	
	898 w		combination Band
875 (1.0)	878 vw	$\nu_2(A_1)$	
670 (1.8)		$\nu_3(A_1)$	
	670 vs		stretching modes
624 (3.8)	610 s		stretching modes
	590 sh		stretching modes
475 (0.5) vbr	540 sh		stretching modes
	519 m		stretching modes
	421 m	$\nu_6(B_1)$	
420 (0.3)		$\nu_9(B_2)$	
260 sh, br			deformation modes
202 (4.3)		$\nu_4(A_1)$	
120 (4)		lattice vibration	

[a] The following bands due to the SbF_6^- impurity were also observed. Raman: 652 (1.0), ν_1; 575 (0+), ν_2; 280 (0.3), ν_5.

The NMR spectra of N_5SnF_5 in HF were recorded at $-78\,^\circ C$. The ^{14}N spectrum showed a strong resonance at $\delta = -164.7$ ppm and a very broad line at about $\delta = -99.9$ ppm, characteristic for the N_β and the terminal N_α atoms, respectively, of the N_5^+ ion.[1] In addition to the signal due to HF (doublet at $\delta = -189.8$ ppm with $^1J(^1H,^{19}F) = 518.9$ Hz), the

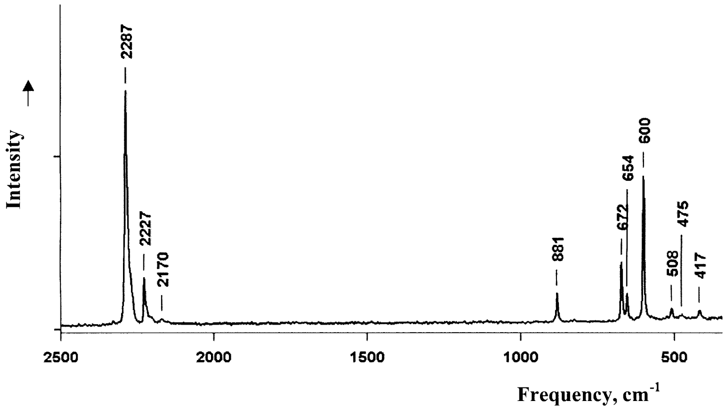

Figure 1. Raman spectrum of solid $(N_5)_2SnF_6$.

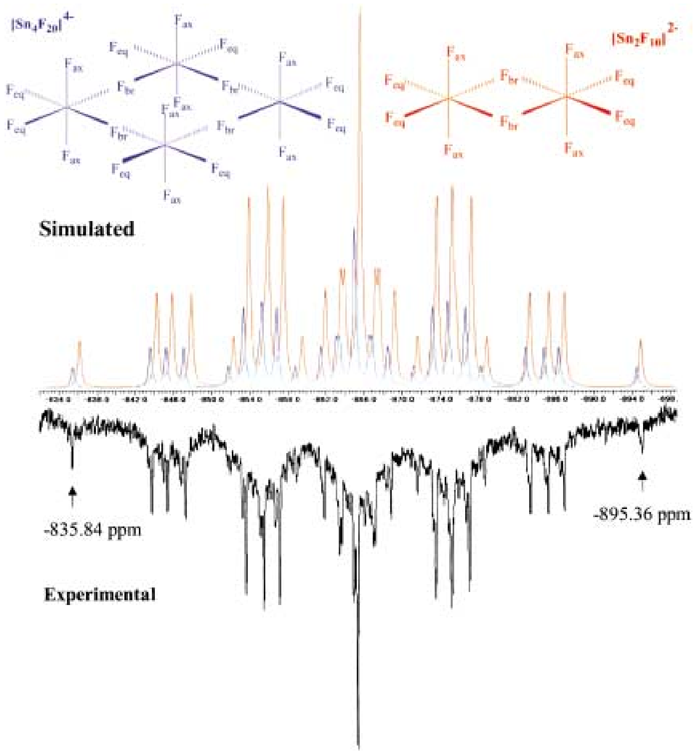

Figure 2. Observed (black trace) and simulated ^{119}Sn NMR spectra of $Sn_2F_{10}^{2-}$ (red trace) and $Sn_4F_{20}^{4-}$ (blue trace) in a 2:1 mole ratio.

^{19}F spectrum showed two very similar sets of signals (Table 3) that varied somewhat in relative intensity from sample to sample and with temperature. The more intense set, with about twice the intensity of the weaker one, is assigned to the dimeric anion, $Sn_2F_{10}^{2-}$. The less intense set has the same area ratios and almost identical shifts and coupling constants and, therefore, must belong to a species with an almost identical molecular structure. The only species that meets these requirements is the cyclic tetramer, $Sn_4F_{20}^{4-}$. Although the ^{19}F NMR spectrum of $Sn_2F_{10}^{2-}$ in SO_2 has been reported previously,[25, 26] its chemical shifts and coupling constants significantly deviate from those recorded in HF. This deviation is probably due to solvent effects, as shown by recording the spectra of Cs_2SnF_6 in HF at −78 and 23 °C (values at this temperature given in parentheses). They showed singlets at $\delta = -160.5$ (-164.5) ppm with $|{}^1J(^{19}F,^{119}Sn)| = 1416$ (1437) Hz and $|{}^1J(^{19}F,^{117}Sn)| = 1355$ (1376) Hz, deviating from the values, $\delta = -139$ ppm and $|{}^1J(^{19}F,^{119}Sn)| = 1604$ Hz,[25] reported for SnF_6^{2-} in SO_2, by about the same amount as found for the $Sn_2F_{10}^{2-}$ signals.[25] The ^{119}Sn spectrum was also recorded and consisted of a complex multiplet (Figure 2). The observed spectrum was successfully simulated assuming first-order triplets of triplets of triplets for both $Sn_2F_{10}^{2-}$ and $Sn_4F_{20}^{4-}$, by using the coupling constants similar to those derived from the tin satellite peaks in the ^{19}F spectra. The ^{119}Sn chemical shifts of $Sn_2F_{10}^{2-}$ and $Sn_4F_{20}^{4-}$ are also almost identical (difference of only 0.4 ppm), thus confirming the close structural relationship of these two anions.

The synthesis of a stable $(N_5)_2SnF_6$ salt is highly significant because it represents the first example of an N_5^+ salt that contains two polynitrogen cations per anion. It demonstrates that salts with touching polynitrogen cations can exist, and that the goal of an ionic nitrogen allotrope might be achievable.

A particularly attractive counterion, $[B(CF_3)_4]^-$, was recently reported by Willner et al.[27] The Lewis acidity of its conjugate parent molecule $B(CF_3)_3CF_2$ (pF^- value of 11.77)[21] exceeds that of SbF_5 (pF^- value of 11.30),[21] and its negative charge is distributed over 12 fluorine atoms, thus rendering it a weakly coordinating anion. For the $[B(CF_3)_4]^-$ salts, HF was a poor solvent choice because the solubility differences between $M[B(CF_3)_4]$ and $MSbF_6$ (M = alkali metal) were found to be too small for an effective metathesis. Although the $M[B(CF_3)_4]$ salts are soluble in water, diethyl ether,

Table 3. Multinuclear NMR spectra[a] of N_5SnF_5 recorded at −78 °C in HF.

Ion	Atom	δ (Multiplicity) (Area ratio)	Coupling constant [Hz]
N_5^+	N_β	−164.7 (s)	
	N_α	−99.9br (s)	
$Sn_2F_{10}^{2-}$	F_{eq}	−173.0 (t) (2)	${}^2J(^{19}F_{eq},^{19}F_{ax}) = 37.1$; $\lvert{}^1J(^{19}F_{eq},^{117}Sn)\rvert = 1671$; $\lvert{}^1J(^{19}F_{eq},^{119}Sn)\rvert = 1744$
	F_{ax}	−165.28 (t) (2)	${}^2J(^{19}F_{eq},^{19}F_{ax}) = 36.8$; $\lvert{}^1J(^{19}F_{ax},^{117}Sn)\rvert = 1406$; $\lvert{}^1J(^{19}F_{ax},^{119}Sn)\rvert = 1468$
	F_{br}	−147.0 (s) (1)	$\lvert{}^1J(^{19}F_{br},^{117/119}Sn)\rvert = 1196$
	Sn[a]	−865.6 (ttt)	$\lvert{}^1J(^{19}F_{eq},^{119}Sn)\rvert = 1740$; $\lvert{}^1J(^{19}F_{ax},^{119}Sn)\rvert = 1440$; $\lvert{}^1J(^{19}F_{br},^{119}Sn)\rvert = 1200$
$Sn_4F_{20}^{4-}$	F_{eq}	−174.2 (t) (2)	${}^2J(^{19}F_{eq},^{19}F_{ax}) = 36.3$; $\lvert{}^1J(^{19}F_{eq},^{117}Sn)\rvert = 1622$; $\lvert{}^1J(^{19}F_{eq},^{119}Sn)\rvert = 1697$
	F_{ax}	−165.33 (t) (2)	${}^2J(^{19}F_{eq},^{19}F_{ax}) = 36$; $\lvert{}^1J(^{19}F_{ax},^{117/119}Sn)\rvert = 1440$
	F_{br}	−145.0 (s) (1)	$\lvert{}^1J(^{19}F_{br},^{117}Sn)\rvert = 1178$; $\lvert{}^1J(^{19}F_{br},^{119}Sn)\rvert = 1230$
	Sn[a]	−865.2 (ttt)	$\lvert{}^1J(^{19}F_{eq},^{119}Sn)\rvert = 1760$; $\lvert{}^1J(^{19}F_{ax},^{119}Sn)\rvert = 1468$; $\lvert{}^1J(^{19}F_{br},^{119}Sn)\rvert = 1230$

[a] Coupling constants derived from simulated spectra.

tetrahydrofuran, acetonitrile, and acetone;[27] the incompatibility of N_5SbF_6 with these solvents precluded their use. Therefore, the metathesis was carried out in SO_2, as shown in Equation (9).

$$N_5SbF_6 + K[B(CF_3)_4] \xrightarrow[-64\,^{\circ}C]{SO_2} N_5[B(CF_3)_4] + KSbF_6\downarrow \quad (9)$$

The precipitate was filtered off and identified by vibrational spectroscopy as $KSbF_6$. The filtrate was taken to dryness, and the residue was characterized by mass balance, and multinuclear NMR and vibrational spectroscopy as 83 wt% $N_5[B(CF_3)_4]$ (Table 4), 14 wt% of $KSbF_6$, and 3 wt% of N_5SbF_6. The impurities are due to the fact that $KSbF_6$ still has an appreciable solubility in SO_2 even at $-64\,^{\circ}C$, and that a very small excess of N_5SbF_6 was used in the reaction. Since the solubility of $CsSbF_6$ in SO_2 is lower than that of $KSbF_6$, the purity of $N_5[B(CF_3)_4]$ could be further improved by using $Cs[B(CF_3)_4]$ in place of $K[B(CF_3)_4]$ in the above-described metathesis reaction. However, attempts to purify the crude product by recrystallization or to grow single crystals of $N_5[B(CF_3)_4]$ from HF have so far been unsuccessful. They resulted in a reverse metathesis in which the $KSbF_6$ impurity reacted with the $N_5[B(CF_3)_4]$ producing $K[B(CF_3)_4]$ and N_5SbF_6.

Table 4. Raman and infrared spectra[a] of solid $N_5[B(CF_3)_4]$ and their assignments.

Obsd frequencies [cm^{-1}] and relative intensities		Assignments (point group)	
Raman	Infrared	N_5^+ (C_{2v})	$B(CF_3)_4^-$ (T)
	3307 w	$(\nu_1+\nu_8)(B_2)=3316$	
	3057 w	$(\nu_2+\nu_7)(B_2)=3060$	
	2662 w	$(\nu_1+\nu_9)(B_2)=2663$	
	2375 w		$(\nu_9+\nu_{10})(F)=2376$
2257 (10.0)	2256 m	$\nu_1(A_1)$	
2200 (2.7)	2197 ms	$\nu_7(B_2)$	
1290 (sh)	1292 sh		$\nu_9(F)$ ^{10}B
1276 (1.6)			$\nu_1(A)$
1270 (sh)	1273 vs		$\nu_9(F)$ ^{11}B
1103 (0.6)(br)	1115 vs, br		$\nu_{10}(F)$
1086 (sh)			$\nu_5(E)$
	1060 sh	$\nu_8(B_2)$	
	929 s		$\nu_{12}(F)$ ^{10}B
	902 vs		$\nu_{12}(F)$ ^{11}B
863 (0.6)		$\nu_2(A_1)$	
728 (6.2)			$\nu_2(A)$
	696 s		$\nu_{13}(F)$
672 (sh)		$\nu_3(A_1)$	
525 (1.8)	521 ms		$\nu_{14}(F)$
525 (1.8)	521 ms		$\nu_{15}(F)$
	489 m	$\nu_5(A_2)$	
	443 w		
	419 m	$\nu_6(B_1)$	
	407 sh	$\nu_9(B_2)$	
319 (2.1)			$\nu_7(E)$
295 (3.3)			$\nu_{16}(F)$
279 (2.7)			$\nu_3(A)$
209 (3.4)		$\nu_4(A_1)$	
110 (0.5)(sh)			$\nu_8(E)$

[a] The following bands due to the SbF_6^- impurity were also observed. Raman: 659 (7.0), ν_1; 574 (0.7), ν_2; 295 (3.3) and 279 (2.7), ν_5; IR: 664 s, br, ν_3.

Multinuclear NMR spectra were recorded for $N_5[B(CF_3)_4]$ in SO_2 at room temperature. In the ^{14}N spectrum, the N_β atom of N_5^+ was observed at $\delta = -163.9$ ppm, in accord with the value of -165.3 ppm reported previously for N_5AsF_6 in HF at $-63\,^{\circ}C$.[1] In the ^{11}B NMR spectrum, a 13 line resonance was observed at $\delta = -18.0$ ppm with $^2J(^{11}B,^{19}F) = 25.7$ Hz, in close agreement with the values previously reported for $K[B(CF_3)_4]$ ($\delta = -18.9$ ppm, $^2J(^{11}B,^{19}F) = 25.9$ Hz) in CD_3CN.[27] In the ^{13}C NMR spectrum, a quartet of quartets at $\delta = 133.75$ ppm with $^1J(^{13}C,^{19}F) = 301.8$ Hz and $^1J(^{11}B,^{13}C) = 72.1$ Hz are in very good agreement with the previously reported values for $K[B(CF_3)_4]$ ($\delta = 132.9$ ppm, $^1J(^{13}C,^{19}F) = 304.3$ Hz and $^1J(^{11}B,^{13}C) = 73.4$ Hz).[27] There was no evidence for any decomposition products, nor any other unidentified species in the solution of $N_5[B(CF_3)_4]$ in SO_2.

The infrared and Raman spectra of solid $N_5[B(CF_3)_4]$ were recorded and are summarized in Table 4. The observed frequencies and intensities are in good agreement with those previously reported for N_5^+ in N_5SbF_6[2] and N_5AsF_6[1] and for $[B(CF_3)_4]^-$ in its alkali metal salts,[27] and establish that $N_5[B(CF_3)_4]$ is the main product of the metathetical reaction of N_5SbF_6 with $K[B(CF_3)_4]$.

The thermal stability of $N_5[B(CF_3)_4]$ was studied by DSC. In all runs, a moderately sized exothermic effect was always observed with an onset at 50 °C and with a maximum at ~66 °C. Additional exotherms were observed at ~93 °C and ~225 °C, but only the first exotherm is due to the decomposition of the $N_5[B(CF_3)_4]$ salt. When the sample was heated to only 75 °C and then cooled back to room temperature before being reheated to 75 °C, the first exotherm was no longer observed, and the residue left in the Al pan no longer exhibited bands for N_5^+ in the IR spectrum, but still showed bands for $[B(CF_3)_4]^-$. The thermal stability of $N_5[B(CF_3)_4]$ is surprisingly high and approaches that of the N_5SbF_6 salt (70 °C). It appears that the thermal stability of the N_5^+ ion itself might be the limiting factor, and that the thermal decomposition of these salts is triggered by the decay of the N_5^+ ion. The thermal stability of the $[B(CF_3)_4]^-$ ion is high; even after being heated to 250 °C, the infrared bands due to the $[B(CF_3)_4]^-$ ion persisted.

In summary, N_5SbF_6 was successfully converted by metathesis into $N_5[B(CF_3)_4]$ and $(N_5)_2SnF_6$. The latter salt is especially noteworthy because it contains two N_5^+ ions per anion, thus demonstrating that salts with touching polynitrogen cations can be prepared. This constitutes an important milestone towards our ultimate goal of synthesizing a stable, ionic nitrogen allotrope. Although the $(N_5)_2SnF_6$ salt is friction sensitive, its stepwise decomposition can be achieved, yielding N_5SnF_5. Multinuclear NMR spectra show that in HF the SnF_5^- ion exists as a mixture of $Sn_2F_{10}^{2-}$ and $Sn_4F_{20}^{4-}$ ions.

Experimental Section

Caution! *N_5SbF_6 is a highly energetic oxidizer. Contact with potential fuels must be avoided. This material should be handled on a small scale, while using appropriate safety precautions such as face shields, leather gloves, and protective clothing. The $(N_5)_2SnF_6$ salt is friction sensitive and must be handled with special caution.*

N_5SbF_6 was prepared from N_2FSbF_6 and HN_3 in HF, as previously described.[2] $K[B(CF_3)_4]$ was prepared from $K[B(CN)_4]$ and ClF_3 according to the literature method.[27] Cs_2SnF_6 was generated by reaction of a 2:1 mixture of CsF and SnF_2 in 48% aqueous HF with a slight excess of 30% aqueous H_2O_2 at 0°C. SO_2 (anhydrous, >99.9%) was supplied by Air Products and was used as received. HF was from Matheson and was dried by storage over BiF_5 before use. Infrared spectra were recorded on a Mattson Galaxy 5030 FTIR spectrometer by using neat powders that were sandwiched between two AgCl windows in a Barnes Engineering Co. mini-press. Raman spectra were recorded on a Bruker Equinox 55 FT-RA spectrometer with a Nd-YAG laser at 1064 nm and neat powders in flamed out Pyrex glass capillaries sealed with Halocarbon wax. Multinuclear NMR spectra were recorded on a Bruker Avance 400 FT-NMR spectrometer in SO_2 or HF and 3 mm i.d. Teflon-FEP tubes (Wilmad Glass), heat-sealed and placed in 5 mm o.d. glass NMR tubes (Wilmad Glass). The thermal stabilities were determined on a DuPont Model 910 differential scanning calorimeter by using 0.5–1.8 mg samples in dry hermetically sealed aluminum pans and a heating rate of $10\,^{\circ}C\,min^{-1}$. The data were analyzed with a DuPont Model 2000 Thermal Analyst.

The metathetical synthesis of $N_5[B(CF_3)_4]$ was carried out by using a stainless-steel/Teflon vacuum line[28] and a double Teflon/FEP U-tube apparatus that consisted of a reaction U-tube, a porous Teflon filter assembly, and a receiver U-tube.[23] The double U-tube was equipped with two stainless-steel valves, and two Teflon-coated magnetic stirring bars, one in each of the two U-tubes. N_5SbF_6 (1.053 mmol) was treated with $K[B(CF_3)_4]$ (1.013 mmol) in anhydrous SO_2 (1.8 mL) in the reaction U-Tube at −64°C. The reaction mixture was stirred at that temperature for 1 h to ensure complete reaction before cooling of the filter assembly to −78°C with powdered dry ice. The mixture was filtered under 1.5 atm N_2 pressure to remove the precipitated $KSbF_6$ from the solution containing the $N_5[B(CF_3)_4]$. The SO_2 was removed in vacuo at −64°C leaving behind a white solid in the receiver U-tube. Based upon the observed mass balance and FT-IR and FT-Raman spectroscopy, the filter cake consisted of 0.2185 g $KSbF_6$ (0.2783 g expected for 1.013 mmol) with only traces of $N_5[B(CF_3)_4]$ from the mother liquor. The filtrate residue consisted of 0.4335 g of 83.37 wt% $N_5[B(CF_3)_4]$, 2.81 wt% N_5SbF_6, and 13.82 wt% $KSbF_6$ (0.3615 g expected for 1.013 mmol $N_5[B(CF_3)_4]$, plus 0.0122 g expected for 0.0399 mmol of excess N_5SbF_6, and 0.0598 g expected for 0.2179 mmol $KSbF_6$).

The synthesis of $(N_5)_2SnF_6$ was carried out metathetically by using the same type of double U-Tube as described above. N_5SbF_6 (0.9430 g, 3.084 mmol) and Cs_2SnF_6 (0.7513 g, 1.507 mmol) were added to the reaction U-tube inside the drybox. HF was condensed into the reaction U-tube at −196°C on the vacuum line. The reaction mixture was warmed to −78°C and stirred for about 10 min to reduce the possibility of localized heating of the reactants as they were initially solvated. Afterwards, the reaction mixture was allowed to slowly warm to room temperature with constant agitation over ~10 min; this was followed by constant stirring for another 30 min to ensure that the metathesis reaction has gone to completion. The reaction U-tube was then cooled to −196°C and checked for noncondensibles; none were found, indicating that there was no decomposition of any N_5^+ salt. The reaction mixture was warmed to room temperature and stirred again for 15 min before the mixture was cooled to −78°C for 15 min in preparation for the low-temperature filtration procedure. At that point the filter assembly was cooled briefly to −78°C with powdered dry ice, and the mixture was filtered under 1.5 atm N_2 pressure to remove the precipitated $CsSbF_6$ from the $(N_5)_2SnF_6$/HF filtrate, which was collected in the receiver U-tube at −78°C. The gaseous N_2 was evacuated from the double U-tube, and the receiver U-tube was warmed to −64°C. The HF was removed in vacuo at −64°C over several hours until only some clear colorless droplets were seen in the receiver U-tube. The −64°C bath was removed, and pumping on the reaction products was continued as they gradually warmed to room temperature. Finally, the white solid $(N_5)_2SnF_6$ product appeared in the receiver U-tube after about 5 minutes; pumping was continued for one additional hour at room temperature to ensure the complete removal of the HF solvent. Based upon mass measurements, and FT-IR and FT-Raman spectroscopy, the filter cake consisted of 1.2267 g of 90.1 wt% $CsSbF_6$, and 9.9 wt% $(N_5)_2SnF_6$ (1.1047 g expected for 2.997 mmol $CsSbF_6$ and 0.1220 g expected for 0.327 mmol $(N_5)_2SnF_6$). Using the same methods of investigation, the reaction products were found to consist of 0.4676 g of 94.0 wt% $(N_5)_2SnF_6$, 4.6 wt% N_5SbF_6, and 1.4 wt% $CsSbF_6$ (0.4398 g expected for 1.180 mmol $(N_5)_2SnF_6$, plus 0.0213 g expected for 0.0697 mmol of excess N_5SbF_6, and 0.0065 g expected for 0.0176 mmol $CsSbF_6$).

Acknowledgement

This work was funded by the Defense Advanced Research Projects Agency, with additional support from the Air Force Office of Scientific Research and the National Science Foundation. We thank Drs. R. Corley, A. Morrish, D. Woodbury, M. Berman, Prof. H. Willner, and M. Finze for their steady support, and Drs. R. Wagner, S. Schneider, T. Schroer, M. Gerken, and R. Haiges for their collaboration and stimulating discussions.

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] G. A. Olah, G. K. S. Prakash, G. Rasul, *J. Am. Chem. Soc.* **2001**, *123*, 3308.
[4] M. T. Nguyen, T. K. Ha, *Chem. Phys. Lett.* **2001**, *335*, 311.
[5] S. Fau, R. J. Bartlett, *J. Phys. Chem. A.* **2001**, *105*, 4096.
[6] R. J. Bartlett, *Chem. Ind.* **2000**, 140, and references therein; a compilation of data for N_2 to N_{10} can be found at http://www.qtb.ufl.edu/~bartlett/polynitrogen.pdf.
[7] G. Chung, M. W. Schmidt, M. S. Gordon, *J. Phys. Chem. A.* **2000**, *104*, 5647, and references therein.
[8] M. N. Glukhovtsev, H. Jiao, P. von R. Schleyer, *Inorg. Chem.* **1996**, *35*, 7124 and references therein.
[9] H. H. Michels, J. A. Montgomery, Jr., K. O. Christe, D. A. Dixon, *J. Phys. Chem.* **1995**, *99*, 187.
[10] G. Schatte, H. Willner, *Z. Naturforsch. Teil. B* **1991**, *46*, 483.
[11] G. Rasul, G. K. S. Prakash, G. A. Olah, *J. Am. Chem. Soc.* **1994**, *116*, 8985.
[12] W. E. Thompson, M. E. Jacox, *J. Chem. Phys.* **1990**, *93*, 3856.
[13] J. P. Zheng, J. Waluk, J. Spanget-Larsen, D. M. Blake, J. G. Radziszewski, *Chem. Phys. Lett.* **2000**, *328*, 227.
[14] T. Ruchti, T. Speck, J. P. Connelly, E. J. Bieske, H. Linnartz, J. P. Maier, *J. Chem. Phys.* **1996**, *105*, 2591.
[15] F. Cacace, G. de Petris, A. Troiani, *Science* **2002**, *295*, 480.
[16] M. I. Eremets, R. J. Hemley, H. Mao, E. Gregoryanz, *Nature* **2001**, *411*, 170.
[17] A. V. Pankratov, N. I. Savenkova, *Russ. J. Inorg. Chem.* **1968**, *13*, 1345.
[18] K. O. Christe, R. D. Wilson, W. W. Wilson, R. Bau, S. Sukumar, D. A. Dixon, *J. Am. Chem. Soc.* **1991**, *113*, 3795.
[19] a) K. O. Christe, J. P. Guertin, A. E. Pavlath, *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 83; b) W. W. Wilson, K. O. Christe, *J. Fluorine Chem.* **1980**, *15*, 83; c) K. O. Christe, W. W. Wilson, R. D. Wilson, *Inorg. Chem.* **1980**, *19*, 1494; d) K. O. Christe, W. W. Wilson, R. D. Wilson, *Inorg. Chem.* **1980**, *19*, 3254; e) W. W. Wilson, K. O. Christe, *J. Fluorine Chem.* **1982**, *19*, 253.
[20] I. V. Nikikitin, V. Ya. Rosolovskii, *Russ. Chem. Rev.* **1985**, *54*, 426.
[21] K. O. Christe, D. A. Dixon, D. McLemore, W. W. Wilson J. A. Sheehy, J. A. Boatz, *J. Fluorine Chem.* **2000**, *101*, 151; K. O. Christe, D. A. Dixon, *Paper 53*, *presented at the 16th ACS Winter Fluorine Conference*, St. Pete Beach, FL, **2003**.
[22] H. M. Netzloff, M. S. Gordon, K. O. Christe, W. W. Wilson, A. Vij, V. Vij, J. A. Boatz, *J. Chem. Phys.*, **2003**, in press.
[23] K. O. Christe, C. J. Schack, R. D. Wilson, *Inorg.Chem.* **1977**, *16*, 849.
[24] K. O. Christe, C. J. Schack, *Inorg.Chem.* **1978**, *17*, 2749.
[25] P. A. W. Dean, *Can. J. Chem.* **1973**, *51*, 4024.
[26] P. A. W. Dean, D. F. Evans, *J. Chem. Soc. A* **1967**, 698.
[27] E. Bernhardt, G. Henkel, H. Willner, G. Pawelke, H. Burger, *Chem. Eur. J.* **2001**, *7*, 4696.
[28] K. O. Christe, R. D. Wilson, C. J. Schack, *Inorg. Synth.* **1986**, *24*, 3.

Received: April 4, 2003 [F4973]

