

## Full Paper

Recent Advances in the Chemistry of  $N_5^+$ ,  $N_5^-$  and High-Oxygen Compounds

Karl O. Christe\*

Loker Research Institute, University of Southern California, Los Angeles, CA 90089-1661 (USA)

DOI: 10.1002/prop.200700020

## Abstract


An overview of our work in the areas of polynitrogen and high-nitrogen and high-oxygen chemistry is given. Areas of interest include the synthesis and characterization of novel polynitrogen ions, such as  $N_5^+$  and  $N_5^-$ . Efforts are discussed to combine the  $N_5^+$  cation with energetic counter-ions, such as  $N_3^-$ ,  $NO_3^-$ ,  $ClO_4^-$ ,  $B(N_3)_4^-$  and  $P(N_3)_6^-$ . In the area of high-oxygen carriers, complex nitrate anions were successfully combined with tetrazolium cations to yield CO/H<sub>2</sub>O balanced ionic liquids of interest for liquid monopropellants.

**Keywords:** Polynitrogen, High-Nitrogen Compounds, High-Oxygen Carriers, Oxidizer Balanced Ionic Liquids, Liquid Monopropellants

## 1 Introduction

Polynitrogen chemistry holds a great potential for novel high energy density materials (HEDM). Based on our and others' [1] theoretical predictions, it could provide monopropellants with specific impulses in the 350–500 s range making them comparable to that of the liquid hydrogen/oxygen bipropellant system, but offering significantly higher density impulses and greatly reduced plume signatures. The greatest improvements over the state of the art, however, would be in the area of explosives. Here, a tenfold improvement in detonation pressure over HMX seems possible (Figure 1), assuming that the density of the recently observed [2] high-pressure cubic-gauche form of polynitrogen can be retained under normal conditions.

Where does the energy content of a polynitrogen compound come from and why are polynitrogens so difficult to synthesize and handle? The energy contents of polynitrogen compounds result directly from the large differences in bond dissociation energies between single, double, and triple bonds. Contrary to carbon chemistry, the nitrogen/nitrogen single and double bonds possess much less than 1/3 and 2/3, respectively, of the energy of a triple bond [3]. Therefore, the conversion of N/N single or double bonds to triple bonds is accompanied by a very large energy release (Figure 2). This fact makes the polynitrogens highly endo-

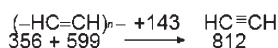
Energetic material	Density (g/cc)	Heat of formation (kJ/mol)	Detonation velocity (mm/μs)	Detonation pressure (GPa)	Energy (HMX=100, V=2.2 V <sub>d</sub> )	Energy (HMX=100, V=40 V <sub>d</sub> )	Impulse (s)	Force (J/g)
								
Reference compounds:								
NC, Nitrocellulose	1.65	-708	7.3	21.2	60	65	226	992
HMX	1.905	74.75	9.1	38.5	105	103	266	1397
CL-20	2.04	393	10	47.8	121	116	273	1380
HEDM:								
$N_5^+ N_5^-$	1.9 *	1239 *	12.1	62	162	156	347	~2000
$N_4(T_d)$	2.3	761	15.5	121	308	288	422	3700
Poly-N	3.9	290	30	660	1060	-	513	-
$N_{50}$	1.97	6780	12.3	65	161	150	331	2296

**Figure 1.** Predicted performance calculations for polynitrogen compounds from [1].

thermic compounds and thermodynamically unstable. They possess only kinetic stability which is determined by the activation energy barrier towards dissociation. Because the weakest bond in a polynitrogen determines the activation energy barrier, it is important to stabilize such bonds through resonance energy which imparts partial double bond character to them. The classic example for resonance stabilization is the azide anion. Figure 3 shows that the azide anion does not possess a single and a triple bond, but two double bonds.

## Carbon bond enthalpies

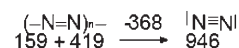
C–C	356 kJ/mol
C=C	599 kJ/mol
C≡C	812 kJ/mol



stable polymers,  
unstable monomers

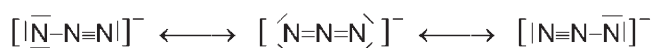
## Nitrogen bond enthalpies

N–N	159 kJ/mol
N=N	419 kJ/mol
N≡N	946 kJ/mol



unstable polymers,  
stable monomer

**Figure 2.** Comparison of the single, double, and triple bond energies of nitrogen-nitrogen and carbon-carbon bonds.



**Figure 3.** Resonance stabilization of the single bonds in the azide anion.

\* Corresponding author; e-mail: kchriste@usc.edu

The difficulties in synthesizing and handling polynitrogen are a direct consequence of their high endothermicities because, in general, sensitivity increases with endothermicity. A further complication is an almost complete absence of methodology for preparing such compounds. Possible synthetic approaches require the use of starting materials which contain already most or all of the desired energy, combined with exothermic coupling reactions which permit to combine energetic fragments in a controllable and facile fashion at low temperatures. The use of a suitable solvent is highly desirable to absorb any liberated reaction energy and to protect the desired product against thermal decomposition. In view of these great experimental challenges, it is not surprising that by 1999 only one stable polynitrogen species, the azide anion, had been prepared in bulk. It was discovered by Curtius in 1890 [4].

A second area of great interest to us is the search for a higher performing non-toxic replacement for the state of the art liquid monopropellant hydrazine. The major drawbacks of hydrazine are its relatively low performance of 236 s  $I_{sp}$  and its vapor toxicity. Hydrazine is a carcinogen and requires special handling. In this brief review, recent progress will be described which was made in our laboratory in both areas.

## 2 Results and Discussion

### 2.1 Historical Note

In the course of the high energy density matter (HEDM) program, which was initiated in 1986 by the Air Force [5], the potential of polynitrogen compounds for HEDM was recognized by numerous theoretical studies [6]. However, no systematic efforts were undertaken to synthesize any of the potential candidates predicted by the theoreticians. This changed in 1998, when Dr. Oestmark from the Swedish Defense Research Agency proposed to DARPA an experimental study to prepare tetrahedral  $N_4$ . In response to this proposal and upon urging from the Air Force Research Laboratory, DARPA issued a broad agency solicitation for experimental efforts and funded eight programs in the polynitrogen area. One of these programs was our effort at the Air Force Research Laboratory at Edwards Air Force Base. This effort was initiated and led by Karl Christe, who was also a Research Professor at the Loker Research Institute of the University of Southern California in Los Angeles. The AFRL effort was expanded one year later to include a program at USC. Because of the overlap and close cooperation between these two programs, the results from both laboratories have been combined for this account. The following scientists were associated with this program:

Responsible Scientist (PI): Karl O. Christe

Senior Investigators at AFRL: William W. Wilson, Ashwani Vij, Vandana Vij, Jerry Boatz (Computational Chemistry), Jeff Sheehy (Computational Chemistry)

Senior Investigators at USC: Ross Wagner, Thorsten Schroer, Stefan Schneider, Michael Gerken, Ralf Haiges, CJ Bigler Jones

Collaborators: David Dixon (PNNL), David Feller (PNNL), Mark Gordon (ISU, Ames), Heather Netzloff (ISU, Ames), Ryan Olson (ISU Ames), Fook Tham (UC Riverside), James Pavlovich (UC Santa Barbara), Robert Bau (USC), Irena Tsyba (USC), Eduard Bernhardt (University Duisburg, Germany), Don Jenkins (University of Warwick, UK).

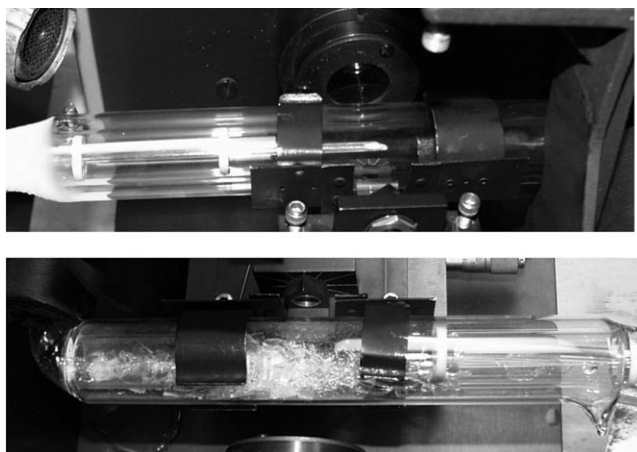
### 2.2 Synthesis and Characterization of $N_5^+$ Salts

The experimental work at the Air Force Research Laboratory in Edwards had begun with Bill Wilson in the fall of 1998 and used the general strategy which was already presented in Section 1. Furthermore, the synthesis of a polynitrogen cation also had to incorporate the use of one cation in the starting materials because the first ionization potentials of nitrogen compounds are around 1255 kJ/mol. Final prerequisites were that the starting materials had to be readily accessible and that the desired product had to be resonance stabilized and could not contain any weak N–N single bonds. After some deliberation, the following system was chosen for the first experiment (Eq. (1)):



Both the starting materials were known compounds, and some  $N_2F^+AsF_6^-$  was still on hand from previous work [7]. With considerable luck, the reaction succeeded at the first attempt, and a white solid was obtained that was marginally stable at room temperature and, most encouragingly, reacted explosively with water or organic materials. It was characterized by low-temperature Raman spectroscopy. The observed spectrum was in qualitative accordance with the expectations for a V-shaped  $N_5^+$  cation, and ab initio calculations of the frequencies and intensities proved beyond doubt that  $N_5^+AsF_6^-$  had indeed been prepared. This was further confirmed by  $^{15}N$  substitution experiments which showed the correct  $^{14}N$ – $^{15}N$  isotopic shifts. Final proof for the presence of  $N_5^+$  was obtained at Christmas time 1998 by low-temperature nitrogen NMR spectroscopy which showed the predicted chemical shifts. A theoretical calculation for  $N_5^+$  had been published by Pyykkoe and Runeberg [8] in 1991 as part of a systematic study of the isoelectronic dicyanamide series, but little emphasis was given to  $N_5^+$  as a promising new species and, therefore, their paper had vanished from our memories.

The successful synthesis of  $N_5^+AsF_6^-$  was reported in January 1999 at the 14th ACS Winter Fluorine Conference in St. Petersburg, FL [9], and was an instant sensation because it was only the second stable polynitrogen ever made. Furthermore, a mishap during the low-temperature Raman characterization, in which a few milligram of material destroyed the recording apparatus (Figure 4), caught the public's eye. Within one week, our discovery

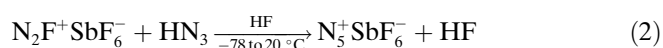


**Figure 4.** Raman apparatus before (upper picture) and after (lower picture) the mishap.

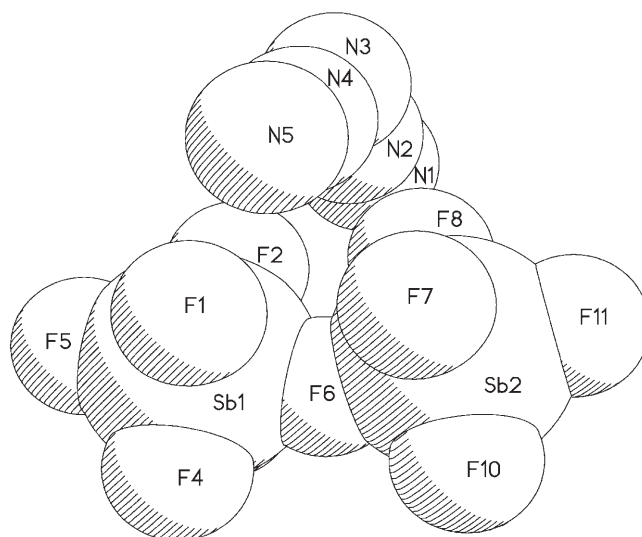
was highlighted in Chemical & Engineering News [10], and from there it spread like wildfire around the world. It was covered in the New York Times, the London Times, the New Scientist, the Hindu, Chemistry in Britain, the CPIA Bulletin, Nature, Aviation Week, Popular Mechanics, Chemistry & Industry, the Rheinische Post, etc. It was also selected by Chemical & Engineering News as one of Chemistry's five top achievements in 1999 [11]. The full scientific paper on  $N_5AsF_6$  was published in the July 1999 issue of *Angewandte Chemie* [3] and highlighted on its cover. Our discovery was also covered by a US Patent in 2001 [12].

The successful synthesis of  $N_5AsF_6$  prompted DARPA to increase our support. Two new colleagues, Dr. Ashwani Vij and his wife Vandana Vij, were hired at AFRL, and a second laboratory was set up at the University of Southern California in Los Angeles. With DARPA support, two old laboratories, which the late Professor Anton Burg had generously made available to us, were completely rebuilt and equipped for polynitrogen and HEDM work. Dr. Ross Wagner, a retired former colleague from Rocketdyne, and four young German scientists, Drs. Thorsten Schroer, Stefan Schneider, Michael Gerken, and Ralf Haiges, who had come to USC as post-docs, joined the program.

The next major goal of the program was the synthesis of a more stable  $N_5^+$  salt and the development of a scalable process for its safe production. These goals were accomplished at Edwards by the synthesis of  $N_5^+SbF_6^-$  according to Eq. (2).



Because  $SbF_5$  is a stronger Lewis acid than  $AsF_5$  [13],  $N_5SbF_6$  is considerably more stable than  $N_5AsF_6$ . It is stable up to about  $60^\circ C$  and, surprisingly, is insensitive to mechanical shock (negative drop weight tests at 29.4 J). It was thoroughly characterized [14], and the crystal structure of  $N_5Sb_2F_{11}$  was determined (Figure 5). The experimental



**Figure 5.** Crystal structure of  $N_5^+Sb_2F_{11}^-$  shown as a space-filling model.

structure was in excellent agreement with our earlier structure predictions which were based on the good match between calculated and observed spectroscopic properties [3].

The synthesis of  $N_5SbF_6$  was successfully scaled up to the 5 g level. During this scale-up, the handling of large amounts of shock-sensitive pure  $HN_3$ , generated from  $NaN_3$  and stearic acid, had led to numerous explosions with significant damage to our equipment. This problem was overcome by the generation of  $HN_3$  from  $NaN_3$  and a large excess of anhydrous HF and co-distillation of the  $HN_3$  and HF, thus avoiding the handling of pure  $HN_3$ . This approach provided a very safe and scalable synthesis for  $N_5SbF_6$ .

The preparation of the  $N_2F^+SbF_6^-$  precursor was a time-consuming, multi-step synthesis and involved the following individual reactions:

- Reduction of  $N_2F_4$  to  $N_2F_2$   
 $Graphite + AsF_5 \rightarrow C_{12}AsF_5$   
 $C_{12}AsF_5 + N_2F_4 \rightarrow 2C_{12}AsF_6^- + trans-N_2F_2$
- *trans*–*cis* isomerization of  $N_2F_2$ :  
 $trans-N_2F_2 + AsF_5 \xrightarrow{T/P} N_2F^+AsF_6^-$   
 $N_2F^+AsF_6^- + NaF \xrightarrow{HF} NaAsF_6 + cis-N_2F_2$
- Formation of  $N_2F^+SbF_6^-$ :  
 $cis-N_2F_2 + SbF_5 \xrightarrow{HF} N_2F^+SbF_6^-$
- If  $N_2F_4$  is not available, add:  
 $H_2NCONH_2 \rightarrow F_2NCONH_2 \rightarrow NHF_2 \rightarrow N_2F_4$

These steps were significantly improved by replacing the originally used, expensive, highly oriented pyrolytic graphite (HOPG) by cheap mineral graphite flakes and by replacing stoichiometric amounts of expensive  $AsF_5$  in the tricky *trans*–*cis* isomerization of  $N_2F_2$  by catalytic amounts of reusable solid  $AlF_3$ . The latter improvement also

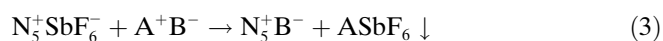
eliminated the previously required displacement step between  $N_2F^+AsF_6^-$  and NaF. Using these improvements, the cost and time required for the synthesis of  $N_2F^+SbF_6^-$  were greatly reduced. Much of this process research was carried out at AFRL by Vandana Vij in fulfillment of the requirements for her Master's Thesis from the University of Idaho in Moscow, ID, under the direction of Karl Christe.

The availability of sufficient amounts of stable  $N_5SbF_6$  made it possible to study its reaction chemistry and to develop methods for converting it into other  $N_5^+$  salts. For example, its electron affinity was experimentally determined using bracketing methods and substrates with known first ionization potentials [14]. In this manner, we were able to show that  $N_5^+$  is capable of oxidizing NO,  $NO_2$ , and  $Br_2$  to  $NO^+$ ,  $NO_2^+$ , and  $Br_2^+$ , respectively, but not  $Cl_2$ ,  $O_2$ , or Xe. Therefore, the electron affinity of  $N_5^+$  must fall between 10.52 and 11.48 eV. This result is in excellent agreement with our theoretical calculations [15] which gave a value of 10.55 eV (1018.5 kJ/mol) for the adiabatic electron affinity of  $N_5^+$ .

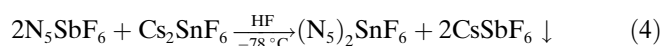
#### First IP of substrate (eV)

$N_5^+SbF_6^- + NO \rightarrow NO^+SbF_6^- + 2.5N_2$	9.26
$N_5^+SbF_6^- + NO_2 \rightarrow NO_2^+SbF_6^- + 2.5N_2$	9.75
$N_5^+SbF_6^- + Br_2 \rightarrow Br_2^+SbF_6^- + 2.5N_2$	10.52
$N_5^+SbF_6^- + Cl_2 \rightarrow Cl_2^+SbF_6^- + 2.5N_2$	11.48
$N_5^+SbF_6^- + O_2 \rightarrow O_2^+SbF_6^- + 2.5N_2$	12.07
$N_5^+SbF_6^- + 2Xe \rightarrow 2Xe^+SbF_6^- + 2.5N_2$	12.13

For the conversion of  $N_5SbF_6$  into other  $N_5^+$  salts, metathetical approaches were chosen, that were similar to those used by us in the past to prepare many novel  $NF_4^+$  salts [16]. In this approach, the ions in two salts are exchanged. It requires a compatible solvent in which both starting materials are soluble, and one of the products is soluble while the other one is insoluble, as shown schematically in Eq. (3).

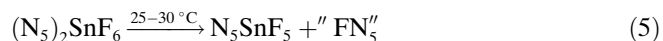


Because  $CsSbF_6$  has a low solubility in anhydrous HF, and  $NaSbF_6$  has a low solubility in  $SO_2$  solution, these two solvents were studied extensively. It was found that HF works well in the cases where the  $B^-$  anion is derived from an acid stronger than HF, and HF does not displace  $B^-$  from its salt. In this manner, the novel  $(N_5^+)_2SnF_6^{2-}$  salt was successfully prepared (Eq. (4)) and characterized [17].



This salt is a white solid that is marginally stable at room temperature and is somewhat friction sensitive. The successful isolation of this compound was particularly note-

worthy because it demonstrated that salts with touching polynitrogen ions can be isolated. This achievement justifies hope for the eventual synthesis of an ionic solid consisting exclusively of polynitrogen ions. Normally, large inert counterions, which can serve as spacers, are required to separate highly energetic ions and, thus suppress propagation and spontaneous explosive decomposition. Another interesting aspect of this compound was its thermal decomposition. Under carefully controlled conditions, this compound could be decomposed stepwise producing  $N_5^+SnF_5^-$  (Eq. (5)).



The  $N_5SnF_5$  salt is a white solid and has a thermal stability comparable to that of  $N_5SbF_6$  (50–60 °C). The structure of the  $SnF_5^-$  anion in this compound is interesting and was shown by  $^{119}Sn$  NMR spectroscopy to be a mixture of tetrameric and dimeric polyanions [17].

Attempts were made to detect the expected " $FN_5$ " by-product through dynamic FT-IR spectroscopy; however, only its expected decomposition products,  $FN_3$ ,  $N_2F_2$ , and  $NF_3$  were observed. Therefore, a theoretical study on the stability and lifetime of  $FN_5$  was carried out in collaboration with Mark Gordon's group [18]. This study identified at least six vibrationally stable isomers of  $FN_5$  but, in accordance with the experimental results [17], the predicted lifetimes of these species are in the nanosecond range.

Another  $N_5^+$  salt,  $N_5^+B(CF_3)_4^-$ , was prepared by the metathetical route [17]. For the synthesis of this compound, the use of anhydrous HF did not result in a good separation of the products because their solubilities in HF were too similar. Therefore,  $SO_2$  was used as a solvent (Eq. (6)) and good product separation was achieved.

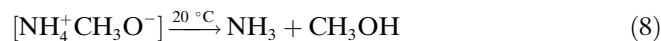
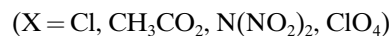
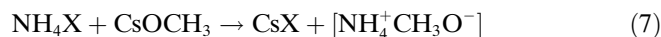


The resulting  $N_5B(CF_3)_4$  salt is a white stable solid which also decomposes between 50 and 66 °C. It appears that the thermal stabilities of most of these  $N_5^+$  salts are similar and are governed by the stability of the  $N_5^+$  cation itself.

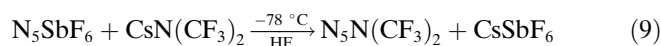
In the course of working with the azide ion in  $SO_2$  solution, an interesting observation was made. When colorless azide ions are dissolved in colorless liquid  $SO_2$ , bright yellow solutions are formed. To clarify this startling observation, the  $SO_2$ /azide system was thoroughly characterized. It was found that  $SO_2$  forms well defined 2:1 and 1:1 adducts with the  $N_3^-$  anion [19, 20]. In addition, the crystal structure of the  $SO_3N_3^-$  anion was also determined [19].

The thermal instability of these  $SO_2/N_3^-$  adducts and their facile decomposition to  $CsN_3$  and  $SO_2$  were exploited for the development of an improved synthesis of pure anhydrous  $CsN_3$  [21]. Furthermore, the requirement for anhydrous cesium salts in metathetical reactions prompted us to develop a general method for the syntheses of anhydrous cesium salts. It is based on the fact that  $NH_4^+$  salts are usually non-hygroscopic and are readily available, whereas the corresponding cesium salts are highly hygroscopic and

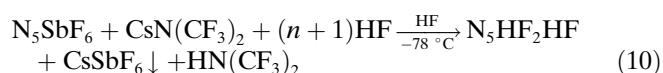
difficult to come by. Using a clever metathesis, in which the undesired by-product is thermally unstable and decomposes to volatile compounds, anhydrous cesium salts free of any impurities can be easily prepared [22]. The process is exemplified by the generic Eqs. (7) and (8).



In the course of an attempt to prepare  $\text{N}_5^+\text{N}(\text{CF}_3)_2^-$  according to Eq. (9)



an unexpected result was obtained [23]. After the removal of all volatile products at  $-64^\circ\text{C}$ , a clear colorless liquid was isolated. Its low-temperature Raman spectrum seemingly exhibited only bands due to  $\text{N}_5^+$ . This situation was reminiscent of  $\text{NF}_4^+\text{HF}_2^-n\text{HF}$  [24] and, indeed, the counterion in this case was also polybifluoride. It is formed because a large excess of HF can displace  $\text{N}(\text{CF}_3)_2^-$  from its salts with the formation of  $\text{HN}(\text{CF}_3)_2$  (Eq. (10)).



On warming up to room temperature, the  $\text{N}_5^+\text{HF}_2^-n\text{HF}$  salt decomposes; however, like  $\text{NF}_4^+\text{HF}_2^-n\text{HF}$ , it is an extremely useful reagent for the synthesis of other salts derived from Lewis acids stronger than HF. This principle was demonstrated for the syntheses of  $\text{N}_5^+\text{BF}_4^-$ ,  $\text{N}_5^+\text{PF}_6^-$ , and  $\text{N}_5^+\text{SO}_3\text{F}^-$  (Eq. 11).



All these new  $\text{N}_5^+$  salts are white, marginally stable solids that were characterized by vibrational and NMR spectroscopy [23].

### 2.3 The Pentazolate Anion, cyclo- $\text{N}_5^-$

One of the drawbacks of the  $\text{N}_3^-$  anion is its low first ionization potential of 256.2 kJ/mol (2.66 eV), making it highly vulnerable to electron loss when combined with a powerful oxidizer, such as  $\text{N}_5^+$  (electron affinity of 1018.5 kJ/mol) [14]. It was, therefore, of interest to pursue the synthesis of alternate polynitrogen anions that might possess higher ionization potentials. A promising candidate, cyclo- $\text{N}_5^-$ , (Figure 6) had been identified by numerous theoretical calculations, some of them dating back to the last century [6b, 6c, 25–33]. This anion is isoelectronic with the cyclopentadienide anion,  $\text{C}_5\text{H}_5^-$ , and possesses a highly aromatic ring system. Its barrier towards decomposition to  $\text{N}_3^- + \text{N}_2$  is predicted to be 117 kJ/mol (Figure 7).

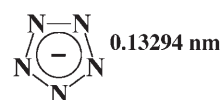


Figure 6. The calculated structure of the pentazolate anion.

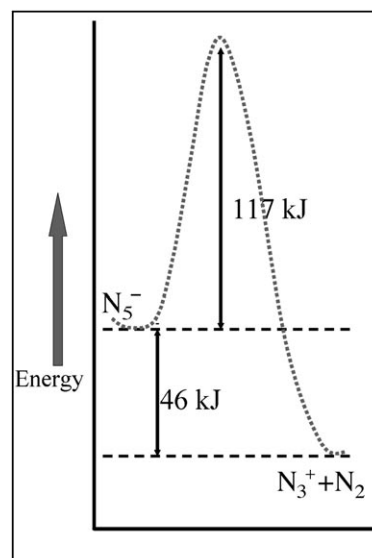


Figure 7. Energy profile for the decomposition of  $\text{N}_5^-$  to  $\text{N}_3^- + \text{N}_2$  along the reaction coordinate, showing a predicted barrier of 117 kJ/mol and an exothermicity of 46 kJ/mol.

Although the existence and stability of substituted pentazole ring compounds had been demonstrated successfully more than 40 years ago by Huisgen and Ugi [34–37] and substituted pentazoles had been well characterized [38–44], attempts to prepare either the parent  $\text{HN}_5$  molecule or its anion,  $\text{N}_5^-$  [37, 45], had been unsuccessful. In our pursuit of the  $\text{N}_5^-$  anion, the following strategy was employed: (i) the use of Ugi-Huisgen-type, substituted phenylpentazoles as starting materials; (ii) the transfer of maximum negative charge to the pentazole ring by the use of highly electron donating substituents on the phenyl ring in para-position to the pentazolyl substituent to increase the aromaticity and stability of the pentazole ring, while at the same time weakening the connecting C–N bond; (iii) the selective cleavage of the C–N bond while keeping the N–N bonds of the pentazole ring intact; and (iv) the use of an analytical method that is ideally suited for the generation and detection of anions. Similar approaches had been described in the literature, but attempts to cleave the C–N bond by ozonolysis had been unsuccessful [37, 45]. Therefore, the well-known para-oxophenyl-pentazolate anion [35, 45] and para-dimethylaminopentazole [35, 36, 38, 39] were chosen as starting materials and negative ion electrospray ionization mass spectrometry (ESI-MS) [46–49] as the analytical tool.

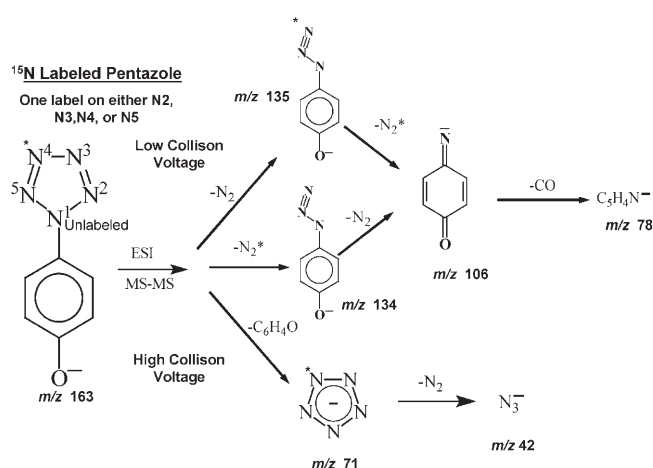
The arylpentazoles and the corresponding diazonium salt precursors were prepared using literature methods [35, 36, 38, 39, 45, 50] and characterized by multinuclear NMR



spectroscopy [38–43]. The ESI-MS cleavage experiments were carried out at UC Santa Barbara. For these experiments, the pentazoles were dissolved in strongly polar solvents, such as  $CH_3CN$  or a mixture of  $CH_3OH$  and  $CH_2Cl_2$ . The desired negative ion peaks were mass-selected and subjected to product ion mass analysis following collision induced dissociation (CID) at variable collision voltages using  $N_2$  or Ar as the collision gases.

The best results were obtained with pyridinium para-pentazolylphenolate in  $CH_3CN$  solution, and unambiguous proof for the formation of cyclo- $N_5^-$  anions was obtained using normal and  $^{15}N$  substituted starting materials (Figure 8). Our results were published in *Angewandte Chemie* [51] and prompted numerous theoretical studies on all kinds of adducts, analogous to the well-known ferrocene-type compounds, and also reports by other groups that had independently pursued the same problem. For example, one year after our report, the Swedish group of Oestmark and coworkers published a paper on the detection of cyclo- $N_5^-$  by laser desorption ionization (LDI) time-of-flight (TOF) mass spectroscopy of solid p-dimethylaminophenylpentazole [52] in which they quoted a previous report from their group at a meeting [53] dealing with an ESI-MS and LDI-TOF study of the same system. However, the results presented in that report had been inconclusive.

Attempts to prepare cyclo- $N_5^-$  salts in bulk by either the oxidative cleavage of the C–N bond using ozone [37, 45] or the reductive one using alkali metals in liquid ammonia [37], had been unsuccessful. There was only one claim for the preparation of the cyclo- $N_5^-$  anion in solution and its identification by  $^{15}N$  NMR spectroscopy [54]. Using  $(NH_4)_2Ce(IV)(NO_3)_6$  (CAN) in aqueous methanol at  $-40^\circ C$ , the para-methoxyphenyl group in para-methoxyphenylpentazole was oxidized to para-benzoquinone, supposedly yielding the zinc salt of the pentazolate anion as coproduct. The following  $^{15}N$  NMR evidence was presented [54] for the formation of  $N_5^-$ : (i) the observation of a signal at  $-10 \pm 2$  ppm which is close to the value predicted [54, 55]



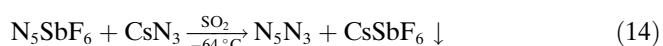
**Figure 8.** ESI-MS fragmentation observed for the mass-selected  $^{15}N$  singly labeled 4-pentazolyl-phenolate anion at low and high collision voltages.

for  $N_5^-$ ; and (ii) the observation of two signals at  $-283$  and  $-147$  ppm which were attributed to the terminal and central nitrogen atoms, respectively, of  $N_3^-$ , the expected decomposition products of  $N_5^-$  [15]. Because the synthesis of the arylpentazole starting material was carried out with azide which was singly  $^{15}N$ -labeled only in the terminal position, the appearance of the  $^{15}N$ -label in all positions of the azide decomposition product would be strong evidence for the formation of an intermediate  $N_5^-$  anion in which all nitrogens have become equivalent (Eq. (2)).

The work of Butler's group was repeated in our laboratory. It was shown [56] that the previous claim [54] for the first observation of the pentazolate anion in the condensed phase is insufficiently supported. The peak in the previously published [54] spectra at  $-10 \pm 2$  ppm is due to the nitrate anion, while the peak at  $-147.2$  ppm belongs to  $N_\gamma$  of the decomposition product 4-MeOC $_6$ H $_4$ N $_3$ . Neither the pentazolate anion nor the crucial decomposition product, an azide anion with a  $^{15}N$ -label at the central nitrogen atom, was observed. Therefore, Butler's claim for a bulk synthesis of cyclo- $N_5^-$  should be discredited [56].

## 2.4 $N_5^+$ Salts with Energetic Counter-Ions

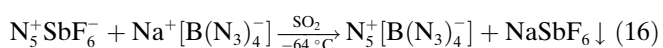
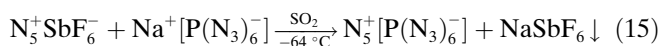
Whereas the  $N_5^+$  cation is a highly energetic ion with a calculated endothermicity of  $1471.8$  kJ/mol [3], all of the counterions described in Section 2.2 were non-energetic. Although the use of a doubly charged anion in  $(N_5)_2SnF_6$  had allowed the doubling of the  $N_5^+$  and energy content [17], an energetic anion would be required for a true HEDM. For this reason, the possibilities were investigated to combine the  $N_5^+$  cation with energetic anions, such as  $ClO_4^-$ ,  $NO_3^-$ ,  $N_3^-$ , and  $P(N_3)_6^-$ , by metathetical reactions in solvents, such as HF,  $SO_2$ ,  $CHF_3$ , or  $CH_3CN$  (typical desired reactions are shown in Eqs. (12)–(14)).



The  $CsNO_3$  reaction did not proceed as desired because  $CsNO_3$  is less soluble in  $SO_2$  than  $CsSbF_6$ . Furthermore, there is not sufficient lattice energy available to stabilize the salt. Born-Haber cycle calculations show that stabilization would require  $645$  kJ/mol, while our estimate for the lattice energy of  $N_5^+NO_3^-$  is only  $540$  kJ/mol. In the case of the perchlorate salt, the reaction proceeded but  $NO^+ClO_4^-$  and  $N_2$  were formed, and again the available lattice energy would be insufficient (by  $54$  kJ/mol) to stabilize the salt. In the case of the azide ion, many reactions were carried out under different conditions, but only explosive decompositions were observed upon melting of the solvent containing the frozen reactants. The lattice energy deficit in this case was estimated to be  $222$  kJ/mol. A more thorough theoretical analysis, carried out in collaboration with Dave Dixon,

Dave Feller, Don Jenkins, and Mark Gordon, showed that after the inclusion of entropy corrections,  $N_5^+N_3^-$  is unstable by 318 kJ/mol with respect to spontaneous decomposition to  $N_3$  and  $N_2$  and that any experimental efforts in this direction are unrewarding [15].

Although the perchlorate, nitrate, and azide salts of  $N_5^+$  could not be prepared, two extremely energetic  $N_5^+$  salts,  $N_5^+[P(N_3)_6]^-$  (Eq. (15)) and  $N_5^+[B(N_3)_4]^-$  (Eq. (16)) were successfully prepared and characterized by low-temperature Raman spectroscopy [23].



Both salts, however, are extremely shock and temperature sensitive and explode in response to the slightest provocation with great violence (Figure 9). In addition to its high energy content,  $N_5^+[B(N_3)_4]^-$  is remarkable for its high content (95.7 wt.%) of energetic nitrogen, setting a new world record for a solid [23].

The synthesis of the tetrazolate salt,  $N_5^+CHN_4^-$ , from both the  $Cs^+$  salt in HF solution and the  $Na^+$  salt in  $SO_2$  solution was also attempted. In HF solution, the tetrazolate anion was displaced with evolution of the free tetrazole, while in  $SO_2$  solution the solubilities were unfavorable for a metathesis. Similar attempts to prepare  $N_5^+$  salts with halogen fluoride anions were also unsuccessful. These findings are in accordance with theoretical calculations on the stabilities of azolypentazoles [57].

An important question which needed a conclusive answer was whether  $N_5^-$ , if available in bulk, would offer an opportunity to prepare a stable  $N_5^+N_5^-$  salt. While we were actively pursuing the actual syntheses of  $N_5^+$  and  $N_5^-$ , Bartlett and coworkers [33] and Gagliardi and coworkers [31] published theoretical papers on this subject, implying that  $N_5^+N_5^-$  might exist as a stable compound. Their

conclusions are in stark contrast to the results from our own studies which were carried out in collaboration with David Dixon, David Feller, and Mark Gordon [15]. It was shown that in the cases where the formed radicals are not vibrationally stable, the use of vertical instead of adiabatic ionization potentials and electron affinities can cause very large errors in stability predictions. As a result,  $N_5^+N_5^-$  was predicted to be unstable by about 368 kJ/mol with respect to the decomposition to  $N_3$  radicals and  $N_2$  and that this decomposition does not involve a significant activation energy barrier [15]. In spite of our predicted instability of  $N_5^+N_5^-$ , the bulk syntheses of other  $N_5^-$  salts remain a very desirable goal because of the many potential uses one could foresee for this interesting new class of compounds.

## 2.5 CO/H<sub>2</sub>O Balanced Ionic Liquids for Liquid Monopropellant Applications

Energetic Ionic Liquids (EIL) are of great interest for liquid monopropellant applications and, particularly, as a non-toxic replacement for the presently used, carcinogenic hydrazine [58–60]. The EILs offer enhanced stability, higher densities, no vapor pressure and, hence, no vapor toxicity. For environmental reasons, it is also desirable to avoid halogen-containing ingredients, such as perchlorates.

The previously known EIL exhibited serious shortcomings. They consisted of small oxidizing anions, such as  $ClO_4^-$ ,  $NO_3^-$ , or  $N(NO_2)_2^-$ , and large fuel cations containing quaternary nitrogen heterocycles with long asymmetric, poorly packing side-chains. The most serious problem with these EILs was that they were underoxidized. The small anions did not carry sufficient oxygen for a complete oxidation of the large fuel cations to carbon monoxide, resulting in poor performance.

In 1998, the author proposed the concept of oxidizer-balanced EIL. It was reduced to practice by the preparation of 1-ethyl-3-methylimidazolium tetranitratoborate [61]. It was shown that this compound was indeed an ionic liquid with a freezing point of  $-25^\circ C$ , however, its energy content and thermal stability were marginal. Subsequently, a significantly improved compound was prepared using the tetranitratoaluminate anion as a thermally more stable high-oxygen carrier and the 1-ethyl-4,5-dimethyl-tetrazolium cation as a more energetic counterion [62]. These compounds are the first examples of single component, CO-balanced, EILs. Although an example of an oxygen balanced tetrazolium salt, 5-amino-tetrazolium nitrate, had previously been reported [63], its melting point of  $173^\circ C$  did not classify it as an ionic liquid.

Polynitratoaluminates were first studied in the 1960s in the US [64] and, subsequently, during the 1970s in the USSR [65–75]. Several examples of alkali metal [65–73],  $NO_2^+$  [74, 75] and ethylammonium salts [76] of tetra-, penta-, and hexanitratoaluminate anions are known. The tetranitratoaluminate anion contains 12 oxygen atoms; of these, 10.5 are available to oxidize a fuel cation, a binder, and a metal additive.



**Figure 9.** Typical damages caused by the explosions of about 0.5 mmol of  $N_5^+P(N_3)_6^-$ . In the left picture, the explosion destroyed the heavy ceramic plate of a stirring plate. The right picture shows the close-up of an exploded, originally straight Teflon reaction tube.

Alkylated tetrazolium cations were used in our study because of their large positive heats of formation and their potential to form ionic liquids. Ionic salts of the tetranitratatoaluminate anion were prepared in essentially quantitative yields in one-pot reactions in nitromethane solution. The starting materials were the chloride salt of the cation, aluminum trichloride, and dinitrogen tetroxide. The synthesis of 1-ethyl-4,5-dimethyl-tetrazolium tetranitratatoaluminate is shown in Scheme 1. 1-Ethyl-4,5-dimethyl-tetrazolium chloride (**1**) was prepared by alkylation of 1,5-dimethyl-tetrazole with ethyl iodide, followed by anion exchange of iodide for chloride using an anion exchange resin. The alkylation places the ethyl group primarily into the 1 position, but 16% is also found at the 2 position of the tetrazolium cation. The percentage of the minor isomer was reduced to 6% by recrystallization from ethanol and could be reduced further by additional recrystallizations. This relatively small isomeric impurity was not removed from the product. It offers the benefit of lowering the melting point of the salt without altering its energetic or chemical properties. The reaction of the tetrazolium chloride, in nitromethane solution, with one equivalent of anhydrous aluminum trichloride gave the tetrachloroaluminate salt **2** which is a viscous ionic liquid. This intermediate was then reacted directly with an excess of  $N_2O_4$  in nitromethane solution. Compound **3** was obtained as a clear, nearly colorless, viscous liquid by pumping off the volatile compounds,  $NOCl$ ,  $CH_3NO_2$ , and excess  $N_2O_4$ , at ambient temperature. It is stable in dry air, hydrolyzes in water, and is soluble in  $CH_3NO_2$  and moderately soluble in  $CH_2Cl_2$ . The identity and purity of the product was established by Raman, infrared,  $^1H$ ,  $^{14}N$ ,  $^{15}N$ , and  $^{13}C$  NMR spectroscopy and the observed material balance. The tetranitratatoaluminate anion contains two monodentate and two bidentate nitrato ligands, as shown by the crystal structure of  $[N(CH_3)_4]^+ [Al(NO_3)_4]^-$  [77]. In this pseudo-octahedral structure, the two monodentate ligands are in cis position to each other.

For energetic materials, stability and physical properties are very important. The thermal stability of **3** was investigated with TGA and DSC. The DSC showed a glass transition temperature,  $T_g$ , at  $-46^\circ C$  and a strongly exothermic decomposition with a maximum at  $217^\circ C$  and an onset at  $183^\circ C$ . In accordance with the DSC data, the TGA showed catastrophic weight loss to start at  $183^\circ C$ ;

however, very slow weight loss also occurred at much lower temperatures, but the exact onset was difficult to ascertain. When a sample of **3** was held isothermally in the TGA apparatus at  $75^\circ C$  for 4 h, a 10.4% weight loss was observed. The slow weight loss observed at the lower temperatures is attributed to the loss of  $NO_2$  and oxygen, accompanied by the formation of  $Al-O-Al$  bridges. Similar observations were previously reported by Shirokova and Rosolovskii [66] for the cesium polynitratatoaluminates.

Ignition of EIL often presents major problems. The ignition of compound **3** and self-sustained burning were readily achieved by either thermal heating of **3** to about  $200^\circ C$  or by the use of a hot 40 gauge Ni/Cr wire wrapped around the sample container, a glass melting point capillary. The capillary was filled to the top with the sample, and a DC current passed through the wire. After a few seconds, compound **3** ignited quite spectacularly, giving off flames and light fluffy alumina.

The theoretical performance of 1-ethyl-4,5-dimethyl-tetrazolium  $[Al(NO_3)_4]^-$  as a propellant was estimated from the calculated heats of formation of the free gaseous cation (836 kJ/mol) and anion ( $-1486$  kJ/mol), calculated at the MP2/6-311 + G(d) level of theory, an estimate [78] of the Coulomb energy of the ions in the liquid of about 419 kJ/mol, using publicly available performance calculation codes [79]. Based on these estimates, the performance of this system significantly exceeds those of state of the art materials, such as hydrazine [80].

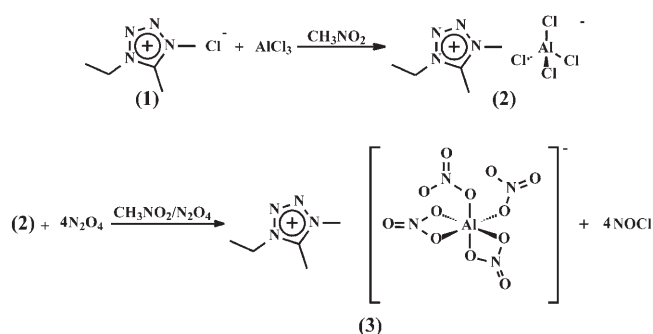
### 3 Summary of Results

The novel polynitrogen ions  $N_5^+$  and  $N_5^-$  have been prepared, and 13 novel  $N_5^+$  salts have been isolated and characterized. The  $N_5^+SbF_6^-$  salt is, surprisingly, thermally stable to  $70^\circ C$  and is not shock-sensitive. The feasibility of preparing  $N_5^+$  salts with touching  $N_5^+$  cations was demonstrated for  $[N_5^+]_2[SnF_6]^{2-}$ , and the possibility of combining the  $N_5^+$  cation with highly energetic anions was demonstrated for  $[N_5^+][P(N_3)_6]^-$  and  $[N_5^+][B(N_3)_4]^-$ . Although the latter salts are much too sensitive for practical use, they nevertheless demonstrate that such approaches are feasible and worthy of pursuit.

A new concept of using complex anions with a high content of oxygen for the synthesis of oxidizer balanced energetic ionic liquids has successfully been demonstrated.

### 4 Conclusions

Polynitrogen compounds hold great promise for HEDM applications and, particularly, for explosives. The feasibility of preparing such compounds has been demonstrated successfully for  $N_5^+$  and  $N_5^-$ . However, the synthesis of pure polynitrogens presents many challenges due to their high sensitivity and the scarcity of useful synthetic methods and starting materials. Therefore, this research falls into the



Scheme 1.



high risk/high pay-off category, but definitely merits further exploration.

The successful synthesis of oxidizer balanced energetic ionic liquids and their use as liquid monopropellants represents a major breakthrough. They offer the potential for significantly higher performance while at the same time eliminating the vapor toxicity of the presently used carcinogenic hydrazine.

## 5 References

- [1] H. Östmark, Personal communication, based on paper 06 presented at the *Polynitrogen Workshop*, Los Angeles, CA, United States, September 15, **2006**.
- [2] M. I. Eremets, A. G. Gavriliuk, I. A. Trojan, D. A. Dzivenko, R. Boehler, Single-Bonded Cubic Form of Nitrogen, *Nat. Mater.* **2004**, 3, 558.
- [3] K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz,  $N_5^+$ : A Novel Homoleptic Polynitrogen Ion as a High Energy Density Material, *Angew. Chem., Int. Ed.* **1999**, 38, 2004.
- [4] T. Curtius, The Azide Ion, *Ber. Dtsch. Chem. Ges.* **1890**, 23, 3023.
- [5] W. J. Lauderdale, W. A. Sowell, *Proceedings of the High Energy Density Matter (HEDM) Conference*, Air Force Astronautics Laboratory, Report AFAL CP-87-002, September, **1987**, and subsequent reports.
- [6] In view of the many publications in this area, only a few selected references are listed here which contain many of the pertinent references: a) W. J. Lauderdale, J. F. Stanton, R. J. Bartlett, Stability and Energetics of Metastable Molecules: Tetraazatetrahydrene ( $N_4$ ), Hexaazabenzene ( $N_6$ ), and Octaazacubane ( $N_8$ ), *J. Phys. Chem.* **1992**, 96, 1173; b) M. N. Glukhovtsev, H. Jiao, P. v. R. Schleyer, Besides  $N_2$ , what is the Most Stable Molecule Composed Only of Nitrogen Atoms? *Inorg. Chem.* **1996**, 35, 7124; c) M. T. Nguyen, Polynitrogen Compounds: 1. Structure and Stability of  $N_4$  and  $N_5$  Systems, *Coord. Chem. Rev.* **2003**, 244, 93.
- [7] K. O. Christe, R. D. Wilson, W. W. Wilson, R. Bau, S. Sukumar, D. A. Dixon, The  $N_2F^+$  Cation. An Unusual Ion Containing the Shortest Presently Known Nitrogen-Nitrogen and Nitrogen-Fluorine Bonds, *J. Am. Chem. Soc.* **1991**, 113, 1991.
- [8] P. Pykkö, N. Runeberg, Ab initio Studies of Bonding Trends, *J. Mol. Struct. (Theochem.)* **1991**, 234, 279.
- [9] The results on  $N_5^+$  were presented as a surprise part of Paper 22, K. O. Christe, D. A. Dixon, A Quantitative Scale for the Strength of Lewis Acids, at the *ACS 14th Winter Fluorine Conference*, St. Petersburg, FL, January 17–22, **1999**.
- [10] R. Rawls, News of the Week,  $N_5^+$  Cation Makes Explosive Debut, *Chem. Eng. News* **1999**, 77(4), 7.
- [11] P. Zurer, Chemistry's Top Five Achievements in 1999, *Chem. Eng. News* **1999**, 77(48), 38.
- [12] K. O. Christe, W. W. Wilson, *Pentanitrogen(I+) Cation and Salt Containing the Same*, U.S. Patent 6,224,696, May 1, **2001**.
- [13] K. O. Christe, D. A. Dixon, D. McLemore, W. W. Wilson, J. A. Sheehy, J. A. Boatz, On a Quantitative Scale for Lewis Acidity and Recent Progress in Polynitrogen Chemistry, *J. Fluor. Chem.* **2000**, 101, 151.
- [14] A. Vij, W. W. Wilson, V. Vij, F. S. Tham, J. A. Sheehy, K. O. Christe, Polynitrogen Chemistry. Synthesis, Characterization, and Crystal Structure of Surprisingly Stable Fluoroantimonate Salts of  $N_5^+$ , *J. Am. Chem. Soc.* **2001**, 123, 6308.
- [15] D. A. Dixon, D. Feller, K. O. Christe, W. W. Wilson, A. Vij, V. Vij, H. D. B. Jenkins, R. M. Olson, M. S. Gordon, Enthalpies of Formation of Gas Phase  $N_3$ ,  $N_3^-$ ,  $N_5^+$ , and  $N_5^-$  from ab initio Molecular Orbital Theory, Stability Predictions for  $N_5^+N_3^-$  and  $N_5^+N_5^-$ , and Experimental Evidence for the Instability of  $N_5^+N_3^-$ , *J. Am. Chem. Soc.* **2004**, 126, 834.
- [16] a) K. O. Christe, J. P. Guertin, A. E. Pavlath, The Tetrafluoronitronium (V) Cation,  $NF_4^+$ , *Inorg. Nucl. Chem. Lett.* **1966**, 2, 83; b) W. W. Wilson, K. O. Christe, Simplified Synthesis of  $NF_4^+SbF_6^-$ , *J. Fluor. Chem.* **1980**, 15, 83; c) K. O. Christe, W. W. Wilson, R. D. Wilson, Synthesis and Characterization of  $(NF_4)_2MnF_6$ , *Inorg. Chem.* **1980**, 19, 3254; d) W. W. Wilson, K. O. Christe, Synthesis and Properties of  $(NF_4)_2SiF_6$  and Interaction of  $SiF_4$  with Anhydrous HF and  $CsHF_2$ , *J. Fluor. Chem.* **1982**, 19, 253.
- [17] W. W. Wilson, A. Vij, V. Vij, E. Bernhardt, K. O. Christe, Polynitrogen Chemistry: Preparation and Characterization of  $(N_5)_2SnF_6$ ,  $N_5SnF_5$ , and  $N_5B(CF_3)_4$ , *Chem.-Eur. J.* **2003**, 9, 2840.
- [18] H. M. Netzloff, M. S. Gordon, K. O. Christe, W. W. Wilson, A. Vij, V. Vij, J. A. Boatz, On the Existence of  $FN_5$ , A Theoretical and Experimental Study, *J. Phys. Chem. A* **2003**, 107, 6638.
- [19] K. O. Christe, J. A. Boatz, M. Gerken, R. Haiges, S. Schneider, T. Schroer, F. S. Tham, A. Vij, V. Vij, R. I. Wagner, W. Wilson, Synthesis and Characterization of the  $SO_2N_3^-$ ,  $(SO_2)_2N_3^-$ , and  $SO_3N_3^-$  Anions, *Inorg. Chem.* **2002**, 41, 4275.
- [20] K. O. Christe, M. Gerken, R. Haiges, S. Schneider, T. Schroer, I. Tsyba, R. Bau, The  $(SO_2)_2N_3^-$  Anion, *Inorg. Chem.* **2003**, 42, 416.
- [21] M. Gerken, S. Schneider, T. Schroer, R. Haiges, K. O. Christe, Improved Synthesis of  $CsN_3$ , *Z. Anorg. Allg. Chem.* **2002**, 628, 909.
- [22] R. Haiges, K. O. Christe, An Improved Method for Product Separation in Metathetical Reactions and its Demonstration for the Synthesis of Anhydrous Cesium Salts, *Z. Anorg. Allg. Chem.* **2002**, 628, 1717.
- [23] R. Haiges, S. Schneider, T. Schroer, K. O. Christe, 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  $N_5^+SO_3F^-$ , *Angew. Chem., Int. Ed.* **2004**, 43, 4919.
- [24] K. O. Christe, W. W. Wilson, R. D. Wilson, Synthesis and Properties of  $NF_4^+ClO_4^-$  and  $NF_4^+HF_2^- \cdot nHF$  and Some Reaction Chemistry of  $NF_4^+$  Salts, *Inorg. Chem.* **1980**, 19, 1494.
- [25] M. T. Nguyen, M. Sana, G. Leroy, J. Elguero, Etude theorique de la structure et de la reactivite de l'anion du pentazole, *Can. J. Chem.* **1983**, 61, 1435.
- [26] M. T. Nguyen, M. A. McGinn, A. F. Hegarty, J. Elguero, Can the Pentazole Anion ( $N_5^-$ ) be Isolated and/or Trapped in Metal Complexes?, *Polyhedron* **1985**, 4, 1721.
- [27] M. N. Glukhovtsev, P. v. R. Schleyer, C. Maerker, Pentaaza- and Pentaphosphacyclopentadienide Anions and their Lithium and Sodium Derivatives: Structures and Stabilities, *J. Phys. Chem.* **1993**, 97, 8200.
- [28] V. A. Ostrovskii, G. B. Erusalimskii, M. B. Shcherbinin, Quantum-Chemical Study of Five-Membered Nitrogen-Containing Heterocycles. II. Structure and Aromaticity of Azoles, *Russ. J. Org. Chem.* **1995**, 31, 1284.
- [29] R. J. Bartlett, Exploding the Mysteries of Nitrogen, *Chem. Ind. (London, U.K.)* **2000**, 4, 140, and references cited therein.
- [30] M. T. Nguyen, T. K. Ha, Decomposition Mechanism of the Polynitrogen  $N_5$  and  $N_6$  Clusters and their Ions, *Chem. Phys. Lett.* **2001**, 335, 311.
- [31] L. Gagliardi, G. Orlandi, S. Evangelisti, B. O. Ross, A Theoretical Study of the Nitrogen Clusters Formed from the Ions  $N_3^-$ ,  $N_5^+$  and  $N_5^-$ , *J. Chem. Phys.* **2001**, 114, 10733.
- [32] M. Lein, J. Frunzke, A. Timoskin, G. Frenking, Iron Bispentazole  $Fe(\eta^5-N_5)_2$ , a Theoretically Predicted High-Energy Compound: Structure, Bonding Analysis, Metal-Ligand Bond Strength and a Comparison with the Isoelectronic Ferrocene, *Chem.-Eur. J.* **2001**, 7, 4155.
- [33] S. Fau, K. J. Wilson, R. J. Bartlett, On the Stability of  $N_5^+N_5^-$ , *J. Phys. Chem. A* **2002**, 106, 4639.
- [34] R. Huisgen, I. Ugi, Die Lösung eines klassischen Problems der organischen Stickstoffchemie, *Angew. Chem.* **1956**, 68, 705; *Chem. Ber.* **1957**, 90, 2914.
- [35] I. Ugi, R. Huisgen, Die Zerfallsgeschwindigkeit der Arylpentazole, *Chem. Ber.* **1958**, 91, 531.

- [36] I. Ugi, H. Perlinger, L. Behringer, Kristallisierte Arylpentazole, *Chem. Ber.* **1958**, *91*, 2324.
- [37] I. Ugi, Pentazole, *Angew. Chem.* **1961**, *73*, 172.
- [38] J. D. Wallis, J. D. Dunitz, An All-Nitrogen Aromatic Ring-System-Structural Study of 4-Dimethyl Aminophenylpentazole, *J. Chem. Soc., Chem. Commun.* **1983**, *16*, 910.
- [39] M. Witanowski, L. Stefaniak, H. Januszewski, K. Bahadur, G. A. Webb, Nitrogen-14 NMR Evidence for the Pentazole Ring Structure, *J. Cryst. Mol. Struct.* **1975**, *5*, 137.
- [40] R. Müller, J. D. Wallis, W. v. Philipsborn, Direct Structural Proof for the Pentazole Ring System in Solution by  $^{15}\text{N}$  NMR Spectroscopy, *Angew. Chem.* **1985**, *97*, 515; *Angew. Chem., Int. Ed.* **1985**, *24*, 513.
- [41] R. N. Butler, S. Collier, A. F. M. Fleming, Pentazoles: Proton and Carbon-13 NMR Spectra of Some 1-Arylpentazoles: Kinetics and Mechanism of Degradation of the Arylpentazole System, *J. Chem. Soc., Perkin Trans. 2* **1996**, 801.
- [42] a) R. N. Butler, A. Fox, S. Collier, L. A. Burke, Pentazole Chemistry: The Mechanism of the Reaction of Aryldiazonium Chlorides with Azide Ion at  $-80^\circ\text{C}$ : Concerted versus Stepwise Formation of Arylpentazoles, Detection of a Pentazene Intermediate, A Combined  $^1\text{H}$  and  $^{15}\text{N}$  NMR Experimental and ab initio Theoretical Study, *J. Chem. Soc., Perkin Trans. 2* **1998**, 2243; b) L. A. Burke, R. N. Butler, J. C. Stephens, Theoretical Characterization of Pentazole Anion with Metal Counter Ions. Calculated and Experimental  $^{15}\text{N}$  Shifts of Aryldiazonium, -Azide and -Pentazole systems, *J. Chem. Soc., Perkin Trans. 2* **2001**, 1679.
- [43] A. Hammerl, T. M. Klapötke, Tetrazolypentazoles: Nitrogen-Rich Compounds, *Inorg. Chem.* **2002**, *41*, 906.
- [44] F. Biesemeier, U. Müller, W. Massa, Die Kristallstruktur von Phenylpentazol,  $\text{C}_6\text{H}_5\text{N}_5$ , *Z. Anorg. Allg. Chem.* **2002**, *628*, 1933.
- [45] V. Benin, P. Kaszynski, J. G. Radziszewski, Arylpentazoles Revisited: Experimental and Theoretical Studies of 4-Hydroxyphenylpentazole and 4-Oxophenylpentazole Anion, *J. Org. Chem.* **2002**, *67*, 1354.
- [46] M. Yamashita, J. B. Fenn, Electrospray Ion Source. Another Variation on the Free-jet Theme, *J. Phys. Chem.* **1984**, *88*, 4451.
- [47] C. M. Whitehouse, R. N. Dreyer, M. Yamashita, J. B. Fenn, Electrospray Interface for Liquid Chromatographs and Mass Spectrometers, *Anal. Chem.* **1985**, *57*, 675.
- [48] R. B. Cole (Ed.), *Electrospray Ionization Mass Spectrometry*, Wiley-Interscience, New York **1997**.
- [49] B. H. Lipshutz, K. L. Stevens, B. James, J. G. Pavlovich, J. P. Snyder, Analyses of Anionic Cu(I) Complexes via Electrospray Mass Spectrometry, *J. Am. Chem. Soc.* **1996**, *118*, 6796.
- [50] C. Colas, M. Goeldner, An Efficient Procedure for the Synthesis of Crystalline Aryldiazonium Trifluoroacetates – Synthetic Applications, *Eur. J. Org. Chem.* **1999**, 1357.
- [51] A. Vij, J. G. Pavlovich, W. Wilson, V. Vij, K. O. Christe, Experimental Detection of the Pentaazacyclopentadienide (Pentazolate) Anion,  $\text{cyclo-N}_5^-$ , *Angew. Chem., Int. Ed.* **2002**, *41*, 3051.
- [52] H. Östmark, S. Wallin, T. Brinck, P. Carlqvist, R. Claridge, E. Hedlund, L. Yudina, Detection of Pentazolate Anion ( $\text{cyclo-N}_5^-$ ) from Laser Ionization and Decomposition of Solid *p*-Dimethylaminophenylpentazole, *Chem. Phys. Lett.* **2003**, *379*, 539.
- [53] A. Hahma, E. Holmberg, N. Hore, R. Tryman, S. Wallin, H. Oestmark, Synthesis and Characterization of Phenylpentazoles, *33rd Int. Annual Conference of ICT*, Karlsruhe, Germany, June 25–28, **2002**, p. 62/1.
- [54] R. N. Butler, J. C. Stephens, L. A. Burke, First Generation of Pentazole ( $\text{HN}_5$ , Pentazolic Acid), the Final Azole, and a Zinc Pentazole Salt in Solution: A New *N*-Dearylation of 1-(*p*-methoxyphenyl) Pyrazoles, A 2-(*p*-Methoxyphenyl) Tetrazole and Application of the Methodology to 1-(*p*-Methoxyphenyl) Pentazole, *Chem. Commun. (Cambridge, U. K.)* **2003**, 1016.
- [55] L. A. Burke, R. N. Butler, J. C. Stephens, Theoretical Characterization of Pentazole Anion with Metal Counter Ions. Calculated and Experimental  $^{15}\text{N}$  Shifts of Aryldiazonium, -Azide and -Pentazole Systems, *J. Chem. Soc., Perkin Trans. 2* **2001**, 1679.
- [56] T. Schroer, R. Haiges, S. Schneider, K. O. Christe, The Race for the First Generation of the Pentazolate Anion in Solution is Far from Over, *Chem. Commun. (Cambridge, U. K.)* **2005**, 1607.
- [57] A. Hammerl, T. M. Klapötke, P. Schwerdtfeger, Azolypentazoles as High-Energy Materials: A Computational Study, *Chem – A Eur. J.* **2003**, *9*, 5511.
- [58] M. W. Schmidt, M. S. Gordon, J. A. Boatz, Triazolium-Based Energetic Ionic Liquids, *J. Phys. Chem. A* **2005**, *109*, 7285.
- [59] K. E. Gutowski, J. D. Holbrey, R. D. Rogers, D. A. Dixon, Prediction of the Formation and Stabilities of Energetic Salts and Ionic Liquids Based on ab Initio Electronic Structure Calculations, *J. Phys. Chem. B* **2005**, *109*, 23196.
- [60] a) L. Courtheoux, D. Amariei, S. Rossignol, C. Kappenstein, Facile Catalytic Decomposition at Low Temperature of Energetic Ionic Liquid as Hydrazine Substitute, *Eur. J. Inorg. Chem.* **2005**, 2293; b) L. Courtheoux, E. Gautron, S. Rossignol, C. Kappenstein, Transformation of Platinum Supported on Silicon-Doped Alumina During the Catalytic Decomposition of Energetic Ionic Liquid, *J. Catal.* **2005**, *232*, 10.
- [61] K. O. Christe, G. Drake, *Energetic Ionic Liquids*, Provisional US Patent Application 60/416,418, filed October 7, **2002**, through the US Air Force.
- [62] C. Bigler Jones, R. Haiges, T. Schroer, K. O. Christe, Oxygen-Balanced Energetic Ionic Liquid, *Angew. Chem., Int. Ed.* **2006**, *45*, 4981.
- [63] M. Denffer, T. M. Klapötke, G. Kramer, G. Spieß, J. M. Welch, G. Heeb, Improved Synthesis and X-Ray Structure of 5-Aminotetrazolium Nitrate, *Propellants, Explos., Pyrotech.* **2005**, *30*, 191.
- [64] Work done by Callery Chemical Company, from 1961–1966, for the US Air Force and Office of Naval Research.
- [65] G. N. Shirokova, V. Ya. Rosolovskii, A Thermographic Study of Caesium Nitratealuminates, *Russ. J. Inorg. Chem.* **1971**, *16*, 808.
- [66] G. N. Shirokova, V. Ya. Rosolovskii, Caesium Nitratealuminates, *Russ. J. Inorg. Chem.* **1971**, *16*, 1106.
- [67] a) N. V. Krivtsov, G. N. Shirokova, V. Ya. Rosolovskii, Enthalpies of Formation of Caesium Nitratealuminates, *Russ. J. Inorg. Chem.*, **1973**, *18*, 503; b) G. N. Shirokova, S. Ya. Zhuk, V. Ya. Rosolovskii, Enthalpy of Formation of Rubidium Nitratealuminates, *Russ. J. Inorg. Chem.* **1975**, *12*, 1868.
- [68] G. N. Shirokova, S. Ya. Zhuk, V. Ya. Rosolovskii, Rubidium Nitratealuminates, *Russ. J. Inorg. Chem.* **1975**, *20*, 856.
- [69] a) O. A. D'yachenko, L. O. Atovmyan, G. N. Shirokova, V. Ya. Rosolovskii, X-Ray Crystal Structure of the Pentanitratealuminate Anion, *J. Chem. Soc., Chem. Commun.* **1973**, 595; b) O. A. D'yachenko, L. O. Atovmyan, S. M. Aldoshin, K. V. Titova, V. Ya. Rosolovskii, Crystal and Molecular Structure of the Tetraethylammonium Tetranitratoborate, *Doklady Akad. Nauk SSSR*, **1978**, *238*, 1132.
- [70] G. N. Shirokova, S. Ya. Zhuk, V. Ya. Rosolovskii, Potassium Nitratealuminates  $\text{K}_2[\text{Al}(\text{NO}_3)_5]$  and  $\text{K}_3[\text{Al}(\text{NO}_3)_6]$ , *Russ. J. Inorg. Chem.* **1976**, *21*, 527.
- [71] N. V. Krivtsov, G. N. Shirokova, S. Ya. Zhuk, V. Ya. Rosolovskii, Enthalpy of Formation of Potassium Nitratealuminates, *Russ. J. Inorg. Chem.* **1976**, *21*, 1409.
- [72] G. N. Shirokova, S. Ya. Zhuk, V. Ya. Rosolovskii, Rubidium Hexanitratealuminate, *Russ. J. Inorg. Chem.* **1976**, *21*, 1459.
- [73] G. N. Shirokova, S. Ya. Zhuk, V. Ya. Rosolovskii, Thermal Changes of Potassium Nitratealuminates, *Russ. J. Inorg. Chem.* **1976**, *21*, 1557.
- [74] N. V. Krivtsov, V. Ya. Rosolovskii, G. N. Shirokova, Enthalpy of Formation of Nitryl Tetranitratealuminate and of the  $\text{Al}^{3+}\text{aq}$  Ion, *Russ. J. Inorg. Chem.* **1971**, *16*, 1402.

- [75] G. N. Shirokova, V. Ya. Rosolovskii, Preparation and Properties of Nitryl Tetranitratoaluminate, *Russ. J. Inorg. Chem.* **1971**, 16, 1699.
- [76] C. C. Addison, P. M. Boorman, N. Logan, Anhydrous Aluminum Nitrate, and the Nitronium and Alkylammonium Tetranitratoaluminates, *J. Chem. Soc. A* **1966**, 10, 1434.
- [77] C. Bigler Jones, R. Haiges, K. O. Christe, in press.
- [78] The method used for the estimation of the Coulomb energy from molecular volume based lattice energy estimates by the Glasser and Jenkins method and sublimation enthalpy estimates has been described in Ref. [58].
- [79] S. Gordon, B. J. McBride, *Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications. I. Analysis and II. User's Manual and Program Description*, Reference Publication No. NASA/RP-1311, Lewis Research Center, Cleveland OH, June 1996.
- [80] E. W. Schmidt, *Hydrazine and its Derivatives*, John Wiley & Sons, New York, **1984**.

### Acknowledgements

We gratefully acknowledge financial support of this work by the Air Force Office of Scientific Research, DARPA, the Office of Naval Research, the Lawrence Livermore National Laboratory, and the National Science Foundation. Key contributors to this effort include Drs. William Wilson, Ralf Haiges, Stefan Schneider, Thorsten Schroer, Ross Wagner, Jerry Boatz, Jeff Sheehy, David Dixon, Greg Drake, Ross Wagner, and Ashwani Vij and Mr. CJ Bigler Jones and Mrs. Vandana Vij.

(Received November 29, 2006; Ms 2006/051)

# Life's Simple Pleasures!



No need to waste precious time looking for the right information – Register now for the free **Wiley-VCH Alerting Service**.

**It's simple – and it's fast.**

To receive regular news per e-mail tailored precisely to your needs and interests, just fill in the registration form at [www.wiley-vch.de/home/pas/](http://www.wiley-vch.de/home/pas/)

