Defense Threat Reduction Agency
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TECHNICAL REPORT

Organic Perfluorohalogenate Salts; New Energetic Materials

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June 2014

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14. ABSTRACT

The objective of this research project is to develop a new class of energetic materials comprised of an organic fuel (i.e NH_4^+) paired with a strong oxidizing perfluorohalogenate anion (i.e. BrF_4^-). New EM compounds will be synthesized, fully characterized and evaluated for counter-CBW applications.

15. SUBJECT TERMS

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CONVERSION TABLE

Conversion Factors for U.S. Customary to metric (SI) units of measurement.

MULTIPLY ——————————————→ BY ——————————————→ TO GET
TO GET ←—————————————— BY ←—————————————— DIVIDE

angstrom	$1.000\ 000 \times E\ -10$	meters (m)
atmosphere (normal)	$1.013\ 25\ \ \times E\ +2$	kilo pascal (kPa)
bar	$1.000\ 000 \times E\ +2$	kilo pascal (kPa)
barn	$1.000\ 000 \times E\ -28$	meter^2 (m^2)
British thermal unit (thermochemical)	$1.054\ 350 \times E\ +3$	joule (J)
calorie (thermochemical)	$4.184\ 000$	joule (J)
cal (thermochemical/cm^2)	$4.184\ 000 \times E\ -2$	mega joule/m^2 (MJ/m^2)
curie	$3.700\ 000 \times E\ +1$	*giga bacquerel (GBq)
degree (angle)	$1.745\ 329 \times E\ -2$	radian (rad)
degree Fahrenheit	$t_k = (t°f + 459.67)/1.8$	degree kelvin (K)
electron volt	$1.602\ 19\ \ \times E\ -19$	joule (J)
erg	$1.000\ 000 \times E\ -7$	joule (J)
erg/second	$1.000\ 000 \times E\ -7$	watt (W)
foot	$3.048\ 000 \times E\ -1$	meter (m)
foot-pound-force	$1.355\ 818$	joule (J)
gallon (U.S. liquid)	$3.785\ 412 \times E\ -3$	meter^3 (m^3)
inch	$2.540\ 000 \times E\ -2$	meter (m)
jerk	$1.000\ 000 \times E\ +9$	joule (J)
joule/kilogram (J/kg) radiation dose absorbed	$1.000\ 000$	Gray (Gy)
kilotons	4.183	terajoules
kip (1000 lbf)	$4.448\ 222 \times E\ +3$	newton (N)
kip/inch^2 (ksi)	$6.894\ 757 \times E\ +3$	kilo pascal (kPa)
ktap	$1.000\ 000 \times E\ +2$	newton-second/m^2 (N-s/m^2)
micron	$1.000\ 000 \times E\ -6$	meter (m)
mil	$2.540\ 000 \times E\ -5$	meter (m)
mile (international)	$1.609\ 344 \times E\ +3$	meter (m)
ounce	$2.834\ 952 \times E\ -2$	kilogram (kg)
pound-force (lbs avoirdupois)	$4.448\ 222$	newton (N)
pound-force inch	$1.129\ 848 \times E\ -1$	newton-meter (N-m)
pound-force/inch	$1.751\ 268 \times E\ +2$	newton/meter (N/m)
pound-force/foot^2	$4.788\ 026 \times E\ -2$	kilo pascal (kPa)
pound-force/inch^2 (psi)	$6.894\ 757$	kilo pascal (kPa)
pound-mass (lbm avoirdupois)	$4.535\ 924 \times E\ -1$	kilogram (kg)
pound-mass-foot^2 (moment of inertia)	$4.214\ 011 \times E\ -2$	kilogram-meter^2 (kg-m^2)
pound-mass/foot^3	$1.601\ 846 \times E\ +1$	kilogram-meter^3 (kg/m^3)
rad (radiation dose absorbed)	$1.000\ 000 \times E\ -2$	**Gray (Gy)
roentgen	$2.579\ 760 \times E\ -4$	coulomb/kilogram (C/kg)
shake	$1.000\ 000 \times E\ -8$	second (s)
slug	$1.459\ 390 \times E\ +1$	kilogram (kg)
torr (mm Hg, 0^0 C)	$1.333\ 22\ \ \times E\ -1$	kilo pascal (kPa)

*The bacquerel (Bq) is the SI unit of radioactivity; 1 Bq = 1 event/s.
**The Gray (GY) is the SI unit of absorbed radiation.

1.0 EXECUTIVE SUMMARY

A series of new energetic materials (EM) designed to produce primarily reactive gaseous species as detonation products was investigated for counter-CBW (chemical and biological weapons) applications. The goal was to generate reactive gases by replacing the conventional oxidizer moieties such as NO_3^- (nitrate), or ClO_4^- (perchlorate) in ammonium nitrate (AN), or ammonium perchlorate (AP) EM's (energetic materials) with the strong oxidizing perfluorohalogenate anions such as BrF_4^- (tetrafluorobromate), IF_4^- (tetrafluoroiodate), IF_6^- (hexafluoroiodate), and ClF_4^- (tetrafluorochlorate). Thus a series of target compounds included NH_4BrF_4 (ammonium tetrafluorobromate), NH_4IF_4 (ammonium tetrafluoroiodate), NH_4IF_6 (ammonium hexafluoroiodate), and NH_4ClF_4 (ammonium tetrafluorochlorate) as well as salts with other organic cations paired with the perfluorohalogenate ions. These new EM's are predicted to have higher heats of detonation than AP or AN and produce greater than 89wt% of their original mass as reactive detonation products (e.g. hydrofluoric acid and free halogen). Investigations determined that these simple salts were too unstable for the purposed application. The effort was refocused in the second year to include higher solvates or complex ions including the $I_3F_{16}^-$ (triiodohexadecafluoride) ion and $Br_2F_7^-$ (dibromoheptafluoride). New stable tetramethylammonium (Me_4N^+) salts were isolated; $Me_4NI_3F_{16}$ and $Me_4NBr_2F_7$, and characterized using mass balance experiments and Raman spectroscopy. Although spectroscopic data supports the $Me_4NI_3F_{16}$ formulation the assignment could not be confirmed by mass balance experiments due to inconsistent results. Thus the assignment was made solely based on comparison of spectroscopic and thermal data from the literature and needs further confirmation. The formulation of the bromine trifluoride product was unequivocally determined to be $Me_4NBr_2F_7$ by mass balance and spectroscopic methods.   Improved synthesis of the salts was demonstrated substituting Me_4NI (tetramethylammonium iodide) or Me_4NBr (tetramethylammonium bromide) for the hygroscopic Me_4NF (tetramethylammonium fluoride) reagent and oxidizing I^- or Br^- to the neutral halogen in situ with excess interhalogen reagent. The $Me_4NBr_2F_7$ (tetramethylammonium dibromoheptafluoride) was qualitatively determined to be explosive and moderately to very impact sensitive (initiated with a hammer blow) while the $Me_4NI_3F_{16}$ (tetramethylammonium triiodohexadecafluoride) salt was not initiated even with a strong hammer blow. Thus the concept of producing new energetic salts using perfluorohalogente oxidizers has been successfully demonstrated. Due to the unconventional composition and reactivity of the new energetic salts in particular toward water it was not possible to get conventional safety testing data.

2.0 SCOPE

This project: ***Organic Perfluorohalogenate Salts; New Energetic Materials,*** was in support of Basic Research for Combating Weapons of Mass Destruction; Topic E: High Energy-Density Materials with Fast Energy Release. The research was conducted by Dr. Thomas Groshens and Dr. Richard Hollins in the Chemistry and Materials Division at the Naval Air Warfare Center Weapons Division (NAWCWD) China Lake, CA during FY09-FY11.

3.0 BACKGROUND

3.1 General Concept

The capability to counter CBW threats in a preemptive operation is limited by the unique additional requirement placed on current weapons systems to fully neutralize the agents in scenarios they were not designed for. A highly desirable approach to make systems more effective would have the energetic materials function as both a destructive blast agent during detonation and as a neutralizing instrument in a secondary process preventing the wide area dispersal of the harmful CBW agent. This demands consideration of entirely new chemistry unlike that involved in more conventional energetic materials which are designed for maximum blast effect that produce rather benign detonation byproducts (i.e. nitrogen, carbon dioxide and water). With the use of conventional warheads transient thermal effects have minimal destructive impact on CBW agents while the blast has the undesirable effect of airborne dispersal of these materials even in the case of hardened targets. The effort proposed in this program would develop a new class of energetic compounds that provide sufficient blast performance to destroy containers and facilities with the added capability to disperse a high weight percent of byproducts from detonation of the original composition as free halogens and/or halogenated compounds that are highly reactive chemical species and effective biocidal agents. Many of the CW agents likely to pose a threat are phosphorus containing compounds which are susceptible to nucleophilic attack or oxidation processes. Spore forming bacteria represent one of the greatest BW threats where several kill mechanisms are recognized. It is generally agreed that chemical disruption of the outer disulfide rich protein coat allows penetration of oxidants into the core of the spore to destroy it. To neutralize CBW threats where large quantities of material is expected to be present gas phase reactants are very effective agent defeat materials due to their high penetrating and diffusing capability. Thus in sufficiently high concentrations the reactive products from detonation reactions of the proposed new energetics should be capable of chemically altering chemical weapons agents and spore-forming bacteria rendering them harmless.

The first requirement of the proposed multifunctional energetic compounds is that they have reasonable blast performance. Conventional neutral high explosive compounds owe their performance to the close proximity of a fuel supply, generally carbon and hydrogen atoms, to an oxidizing moiety, usually nitro groups, that exist in the same molecule (i.e. nitramine explosives). Energetic salts such as ammonium perchlorate and ammonium nitrate achieve the same molecular scale intimate mixture of fuel and oxidizer with the counterion pairs serving separate fuel/oxidizer roles. This subnanometer scale homogeneous fuel/oxidizer mixture is necessary to obtain true detonation kinetics in energetic materials. The work proposed herein will, as a start, replace the nitrate and perchlorate oxidizing anions in the ammonium salts with strongly oxidizing perfluorohalogenate anions (i.e. BrF_4^-, IF_4^-, IF_6^- or ClF_4^-). These perfluorohalogenate anions are derived from addition of F^- to the neutral interhalogens ClF_3, BrF_3, IF_3, and IF_5 respectively. Only a few examples of salts where an organic cation is paired with a perfluorohalogenate anion have been reported due to their potentially explosive nature.

The highly exothermic heat of reactions for decomposition/detonation of the proposed compounds is the result of the high C-F and H-F bond strengths in the products relative to the halogen-F bonds in the initial compounds. The main challenge in the approach is to select compatible ion pairs that provide stable compounds (i.e. high activation energy) with high

energy output from the decomposition/detonation reactions while maintaining the desired high weight percent output (>85%) of active biocidal products. The fact that the materials proposed in this program are both explosive and produce hazardous byproducts has severely limited their prior investigation. Therefore it is not surprising that this class of compounds has never been explored for ordinance applications.

The neutral interhalogens are an interesting class of hypervalent compounds that have long been recognized as extremely strong oxidizers incompatible with most organic materials. In general the interhalogens react explosively with most organic substances or water. A few Lewis acid-base adducts (e.g. $BrF_5 \cdot$ pyridine) and mixtures of organic solvents with some of the interhalogens (e.g. BrF_5 with acetonitrile) have been reported, however these neutral oxidizer-fuel mixtures were considered less than optimal for the present application.

FIGURE 1 Physical Properties of Neutral Interhalogen Compounds (Rhein and Miles)

➢Relative Reactivity of Fluorohalogen Compounds;

$$ClF_5 = ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5 > BrF > IF_3 > IF$$

➢ Commercially Available Compounds;

	mp °C	bp °C	Mean X-F bond energy
ClF_3	-76.3	11.8	174 kJ mol^{-1}
BrF_3	8.8	125.8	202 kJ mol^{-1}
IF_5	9.4	104.5	269 kJ mol^{-1}

The target ammonium perfluorohalogenate compounds proposed are predicted to be solid salts. A few are either fully oxidized or over oxidized. We expect that the higher melting solid salt products generated using the perfluorohalogenate anions will have a higher activation energy for the decomposition/detonation reactions providing more stable energetic materials than using neutral interhalogen compounds. This is in part due to the reduced oxidizing power of the anion relative to the neutral interhalogen compounds by addition of F$^-$.

FIGURE 2 Proposed Approach to use Perfluorohalogenate Salts for Counter-CBW
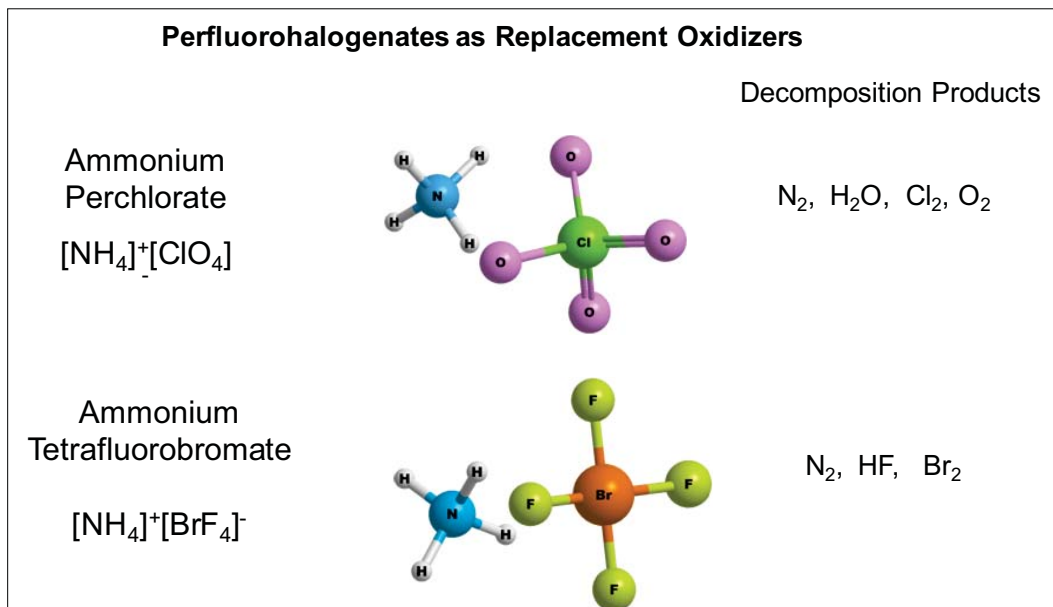
The anions still retain strong oxidizer properties and most of the known inorganic perfluorohalogenate salts liberate free neutral interhalogen compounds by dissociation at high temperature as illustrated by the following reaction (equation 1). The stability constant for a given salt is dependent on the size of the cation and the particular perfluorohalogenate. The thermal stability of the salts increases with cation size where $KBrF_4$ loses 30wt% BrF_3 after 5 minutes at 200°C, the $CsBrF_4$ can be heated to 300°C with no significant loss. Therefore we might expect the dissociation reaction to be unfavorable for the large organic cation salts proposed here-in.

1. $KBrF_4(s)$ $KF(s) + BrF_3(l)$
                                             Heat of dissociation = 34kcal/mol
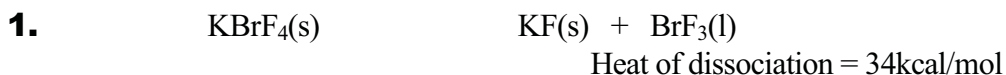
The initial focus of this program was to gain a better understanding the reactivity of these strong oxidizer anions with organic cations and ascertain the identity, chemical and physical properties, and stability of the products. The simplest examples using the approach outlined above would be to prepare ammonium (NH_4^+) salts of ClF_4^-, BrF_4^-, IF_4^-, or IF_6^-. This would provide a series of new energetic analogs to the well characterized ammonium nitrate (NH_4NO_3) and ammonium perchlorate (NH_4ClO_4) oxidizers. Given the high weight percent halogen in the proposed compounds the density should exceed 2.5g/cm^3. Examples of these salts along with their predicted decomposition/detonation reactions are provided in equations 2 and 3 below. For both of these compounds greater than 90 weight percent of reactive species are generated by the reaction (Table 1).

Example 1. Ammonium hexafluoroiodate - 95wt% Biocidal Activity

2. NH_4IF_6 →   HEAT + $4HF + 1/2N_2 + 1/2I_2 + F_2$

Example 2.   Ammonium tetrafluorobromate - 92wt% Biocidal Activity

3. NH_4BrF_4 → $HEAT + 4HF + 1/2N_2 + 1/2Br_2$

Table 1:   Elemental composition of Proposed Compounds

Proposed New Energetic	Formula Weight	Wt% C	Wt% H	Wt% N	Wt% F	Wt% Other Halogen	Wt% Reactive Products
NH_4BrF_4	173.94		2.32	8.05	43.69	45.94	91.95
NH_4IF_4	220.94		1.82	6.34	34.40	57.44	93.66
NH_4IF_6	258.93		1.56	5.41	44.02	49.01	94.59
NH_4ClF_4	129.48		3.11	10.82	58.69	27.38	89.18
$Me_4NI_3F_{16}$	758.83	6.33	1.59	1.85	40.06	50.17	91.82
$Me_4NBr_2F_7$	366.94	13.09	3.30	3.82	36.24	43.55	81.98

Due to the high electronegativity of fluorine, salts of the perfluorohalogenate anions have significant negative enthalpies of formation (-231kcal/mol for $KBrF_4$ versus -64kcal/mol for BrF_3), yet the estimated amount of heat produced from the decomposition/detonation reaction is sufficiently high to expect good explosive performance from these compounds. Using the measured heat of formation of the known $KBrF_4$ and $NaBrF_4$ salts, the heat of formation of ammonium tetrafluorobromate (example 2 above) is estimated to be about -195kcal/mol. The heat of reaction for equation 3 is therefore -61kcal/mol which is higher than the heat of detonation for either ammonium nitrate or ammonium perchlorate (50.16kcal/mol and 57.34kcal/mol respectively).

3.2   Literature Reports of Simple Interhalogenate Ions

Prior studies support the existence of the ammonium salts as stable compounds but no attempt was made to characterize them. In 1964 Whitney *et.al.* at Olin Matheson condensed interhalogen compounds onto dry ammonium fluoride at liquid nitrogen temperature and allowed the mixtures to warm to room temperature (Figure 3). Experiments were conducted with ClF_3, BrF_3, BrF_5 and IF_5. A brief tabulated summary of the results were given but none of the NH_4F-halogenfluoride complexes was further characterized. The ClF_3 reaction mixture exploded below 0°C.

FIGURE 3 Summary of Literature Report on Formation of Proposed Salts

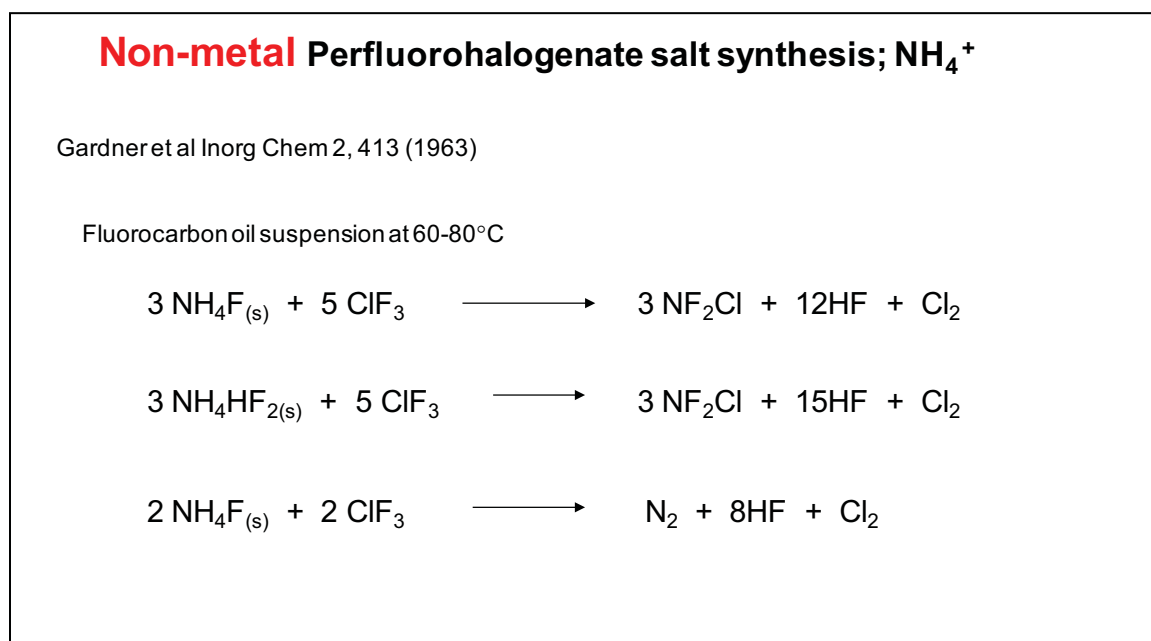Whitney et. al. JACS 86, 2583 (1964)

$$NH_4F + HalF_n \xrightarrow{-196°C} \text{Warm to RT}$$

Presumed Product	Results
NH_4ClF_4	Exploded >0°C
NH_4BrF_6	White Solid dec >0°C
NH_4BrF_4	White Solid
NH_4IF_6	White Solid

Previous studies by Gardner (Figure 4) have shown the primary product from this reaction to be an explosive chlorodifluoroamine if proper conditions were maintained. For the milder interhalogen oxidizers BrF_3, BrF_5, and IF_5 white solids were formed that were thought to be the desired salts.

FIGURE 4 Summary of Relevant Interhalogen Chemistry Literature Report

Non-metal Perfluorohalogenate salt synthesis; NH_4^+

Gardner et al Inorg Chem 2, 413 (1963)

Fluorocarbon oil suspension at 60-80°C

$$3\ NH_4F_{(s)} + 5\ ClF_3 \longrightarrow 3\ NF_2Cl + 12HF + Cl_2$$

$$3\ NH_4HF_{2(s)} + 5\ ClF_3 \longrightarrow 3\ NF_2Cl + 15HF + Cl_2$$

$$2\ NH_4F_{(s)} + 2\ ClF_3 \longrightarrow N_2 + 8HF + Cl_2$$

Whitney speculated the order of stability of the ammonium perfluorohalogenates was probably NH_4BrF_4, $NH_4IF_6 > NH_4BrF_6 > NH_4ClF_4$.

In 1971 Meinert and Gross (Figure 5) reported that the reaction of BrF_5 with tetraethylammonium fluoride or tetramethylammonium fluoride produced the corresponding tetralkylammonium hexafluorobromate salts.

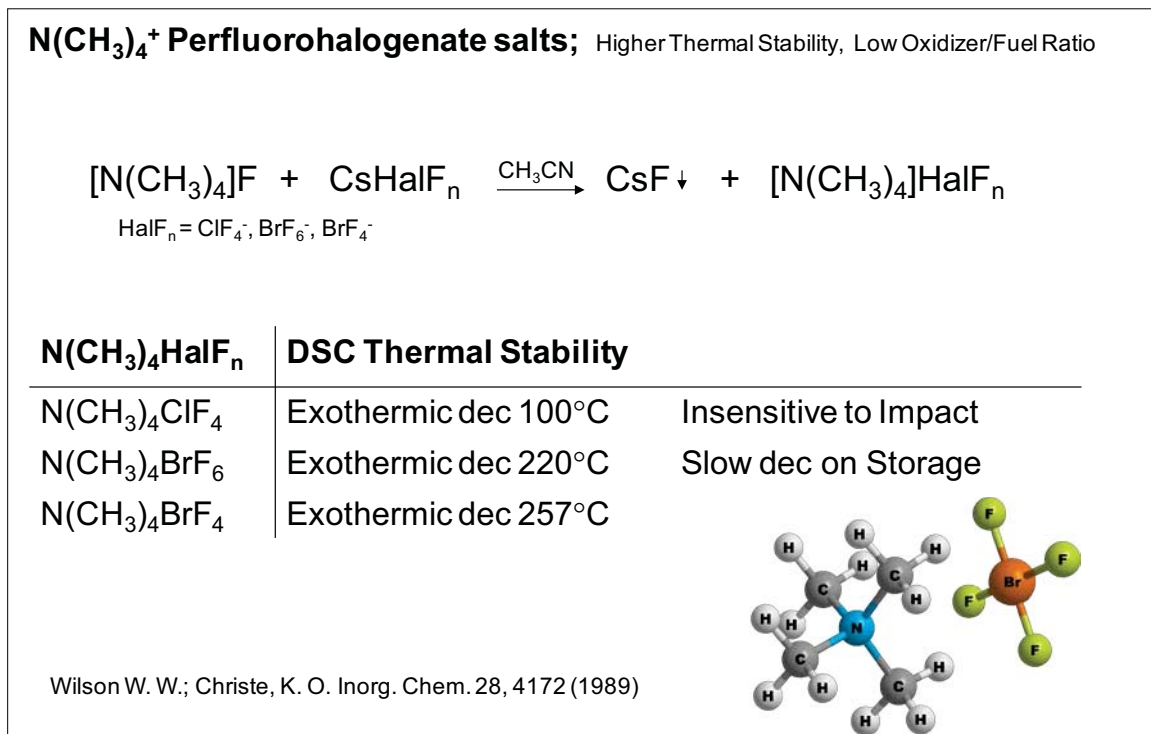**FIGURE 5** Summary of First Isolated Example of Proposed Salts

Meinert, H.; Gross, U. *Z Chem* 11, 469 (1971)

$$[N(CH_3)_4]Cl + AgBrF_6 \xrightarrow{CH_3CN} AgCl \downarrow + [N(CH_3)_4]BrF_6$$

Few details, Also reported $[N(CH_2CH_3)_4]^+$ Salt
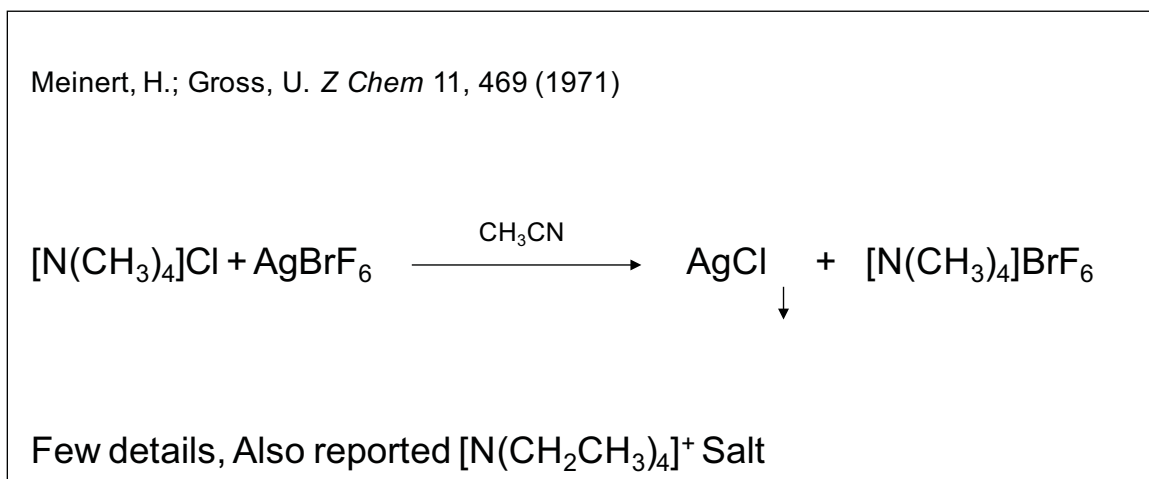
In a follow-up study designed to further characterize these compounds and expand the chemistry to include BrF_4^- and ClF_4^- salts Christe isolated and characterized a series of tetramethyammonium salts of ClF_4^-, BrF_4^-, and BrF_6^- (Figure 6).

All three salts were isolated from the metathetical reactions of tetramethylammonium fluoride with the corresponding ceasium perfluorohalogenate 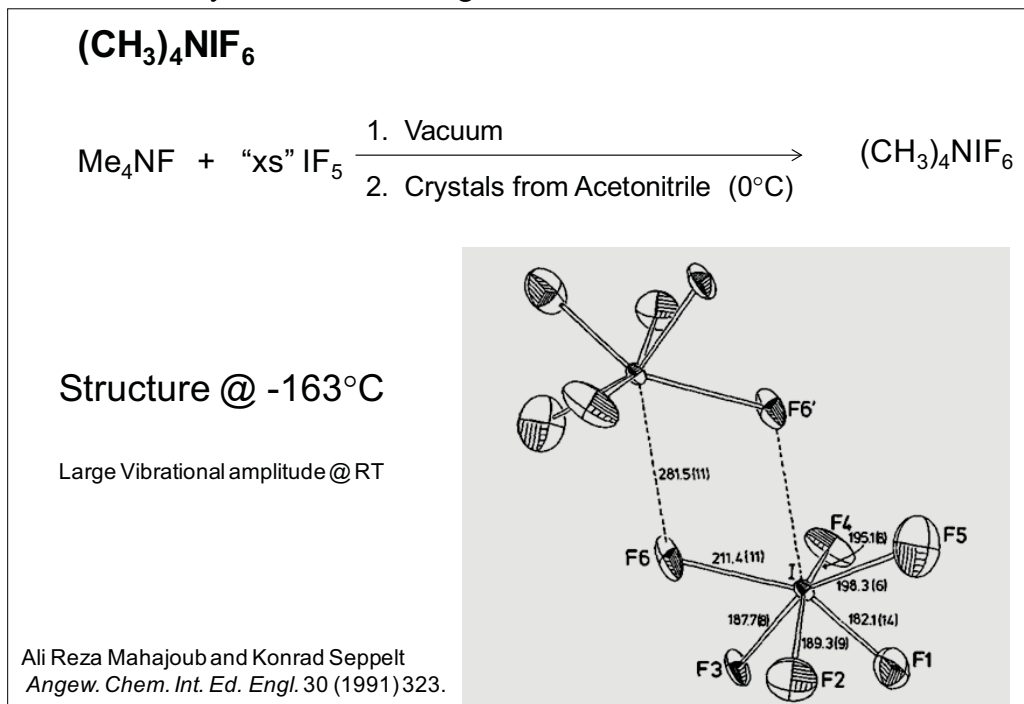salt in acetonitrile (equation 4). Although these compounds are under oxidized with relatively low fluorine content their decomposition reactions still produce an impressively high weight percent yield (62-75wt%) of halogenated products. The colorless stable $[N(CH_3)_4]ClF_4$, $[N(CH_3)_4]BrF_4$, and $[N(CH_3)_4]BrF_6$ solid compounds reportedly underwent highly exothermic decomposition in DSC studies at 100°C, 257°C, and 220°C respectively. The ClF_4^- salt showed no sign of decomposition during storage at 35°C for six months. Full spectroscopic characterization of the compounds was provided as well as some qualitative tests on the sensitivity of $[N(CH_3)_4]ClF_4$ indicating it may be insensitive to impact.

FIGURE 6 Summary of Stable Examples of Perfluorohalogenate Salts

N(CH$_3$)$_4$$^+$ Perfluorohalogenate salts; Higher Thermal Stability, Low Oxidizer/Fuel Ratio

$$[N(CH_3)_4]F \;+\; CsHalF_n \;\xrightarrow{CH_3CN}\; CsF\downarrow \;+\; [N(CH_3)_4]HalF_n$$

HalF$_n$ = ClF$_4^-$, BrF$_6^-$, BrF$_4^-$

N(CH$_3$)$_4$HalF$_n$	DSC Thermal Stability	
N(CH$_3$)$_4$ClF$_4$	Exothermic dec 100°C	Insensitive to Impact
N(CH$_3$)$_4$BrF$_6$	Exothermic dec 220°C	Slow dec on Storage
N(CH$_3$)$_4$BrF$_4$	Exothermic dec 257°C	

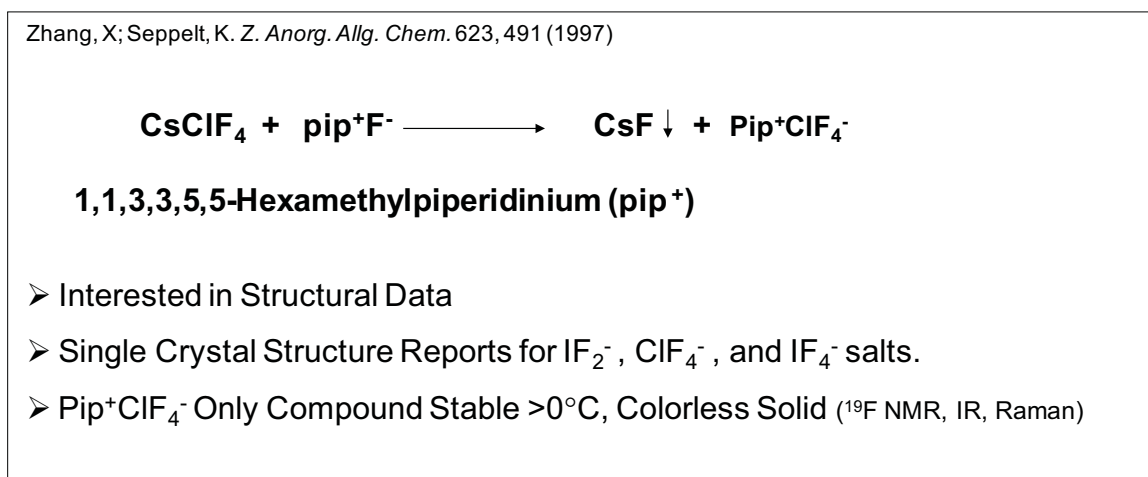Wilson W. W.; Christe, K. O. Inorg. Chem. 28, 4172 (1989)

Suppelt determined the single crystal structure of IF$_6^-$ ion to consist of a dimer with two bridging fluorides between the heptacoordinated Iodine atoms (Figurre 7).

FIGURE 7 Crystal Structure of Organic Hexafluoroiodide Salt

$(CH_3)_4NIF_6$

Me_4NF + "xs" IF_5 →
1. Vacuum
2. Crystals from Acetonitrile (0°C)
→ $(CH_3)_4NIF_6$

Structure @ -163°C

Large Vibrational amplitude @ RT

Ali Reza Mahajoub and Konrad Seppelt
Angew. Chem. Int. Ed. Engl. 30 (1991) 323.

In an effort to determine the structure of other perfluorohalogenate ions Suppelt synthesized a thermally stable ClF_4^- salt using a large bulky hexamethylpiperidinium organic cation and obtained the single crystal x-ray structure (Figure 8).

FIGURE 8 Summary of Stable Organic Tetrafluorochloride Salt

Zhang, X; Seppelt, K. *Z. Anorg. Allg. Chem.* 623, 491 (1997)

$CsClF_4$ + pip^+F^- → $CsF\downarrow$ + $Pip^+ClF_4^-$

1,1,3,3,5,5-Hexamethylpiperidinium (pip$^+$)

➢ Interested in Structural Data

➢ Single Crystal Structure Reports for IF_2^-, ClF_4^-, and IF_4^- salts.

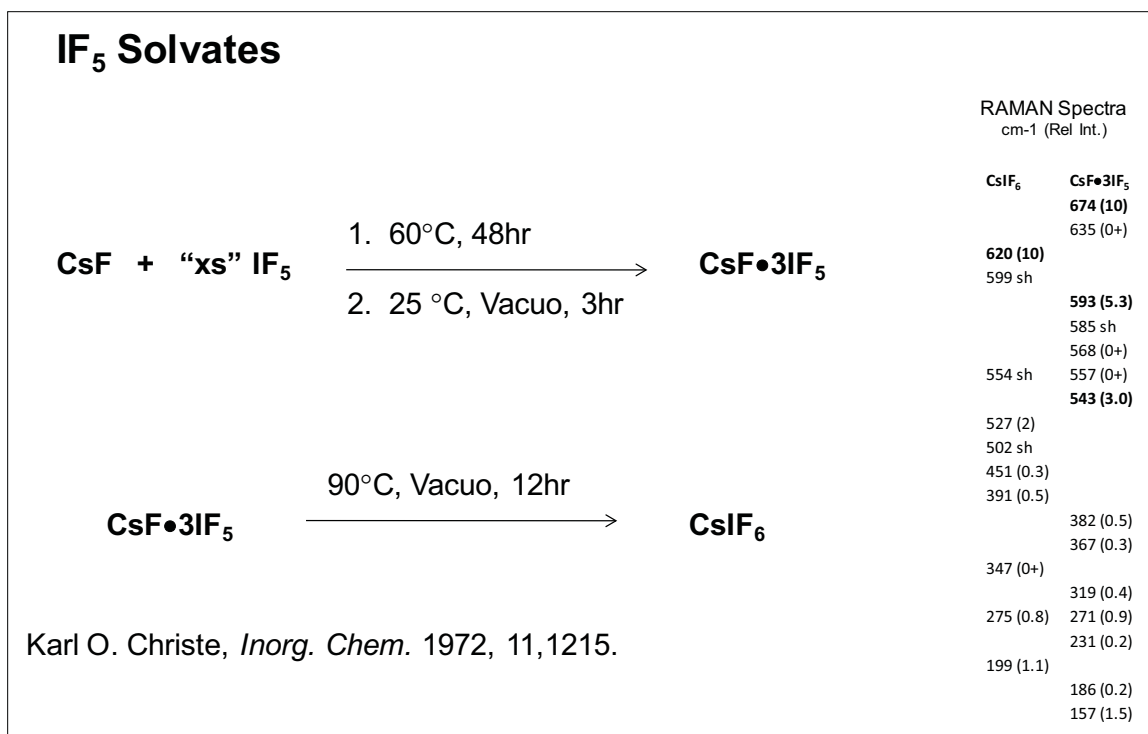➢ $Pip^+ClF_4^-$ Only Compound Stable >0°C, Colorless Solid (¹⁹F NMR, IR, Raman)

3.3 Literature Reports of Complex Interhalogenate Ions

The Lewis Acids iodine pentafluoride and bromine trifluoride are capable of forming complex ions or essentially solvates of the simple perfluorohalogenate. The formation of such complex salts would provide the ability to increase the oxidizer content using the same organic cation by simply adding an excess of the interhalogen. Several examples of complex anion salts of metals and a single example of a tetramethylammonium salt have been published.
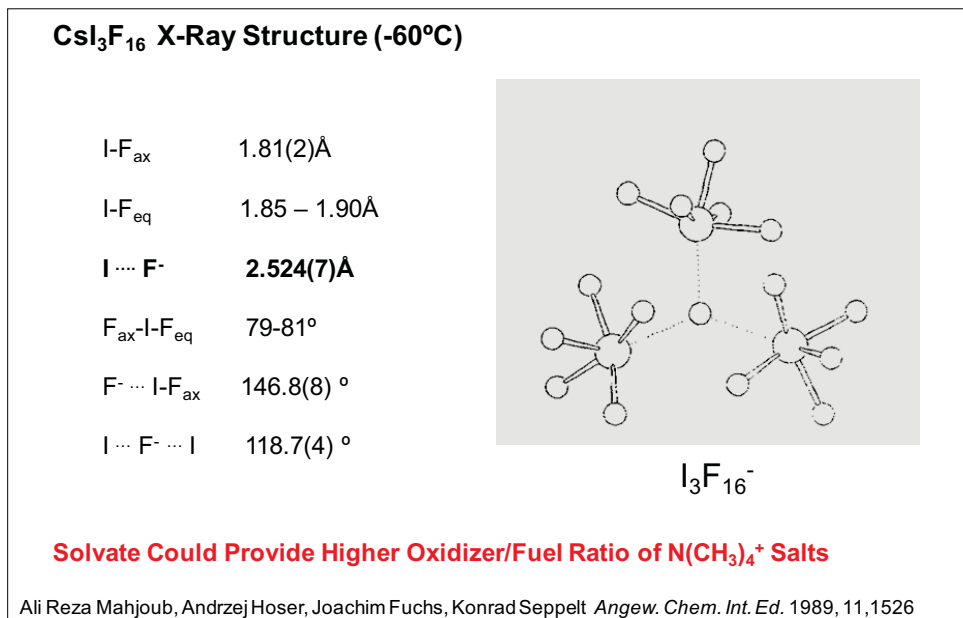
Christe determined that the product from an excess of IF_5 with CsF formed a stable three to one complex that lost two equivalents of IF_5 on heating in a vacuum to form the more thermally stable IF_6^- salt (Figure 9).

FIGURE 9 Synthesis and Characterization of Hexadecafluorotriiodide Ion

IF_5 Solvates

RAMAN Spectra
cm-1 (Rel Int.)

	$CsIF_6$	$CsF \bullet 3IF_5$
		674 (10)
		635 (0+)
	620 (10)	
	599 sh	
		593 (5.3)
		585 sh
		568 (0+)
	554 sh	557 (0+)
		543 (3.0)
	527 (2)	
	502 sh	
	451 (0.3)	
	391 (0.5)	
		382 (0.5)
		367 (0.3)
	347 (0+)	
		319 (0.4)
	275 (0.8)	271 (0.9)
		231 (0.2)
	199 (1.1)	
		186 (0.2)
		157 (1.5)

CsF + "xs" IF_5 → (1. 60°C, 48hr / 2. 25 °C, Vacuo, 3hr) → CsF•3IF_5

CsF•3IF_5 → (90°C, Vacuo, 12hr) → CsIF_6
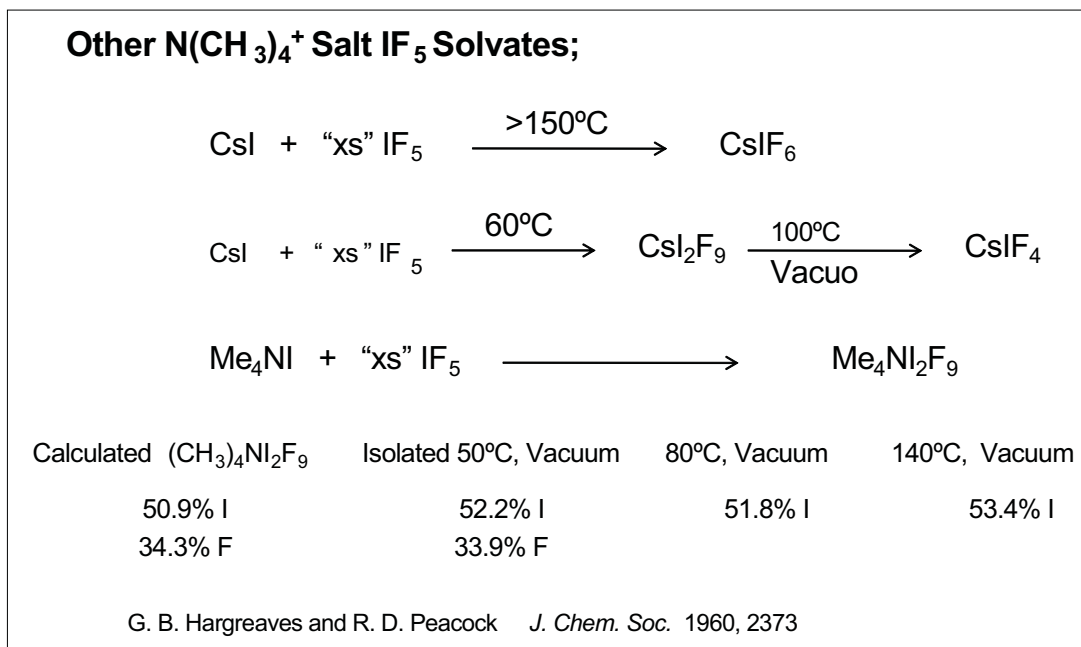
Karl O. Christe, *Inorg. Chem.* 1972, 11,1215.

Subsequently Suppelt was able to isolate suitable crystals of the solvate and determine its structure (Figure 10).

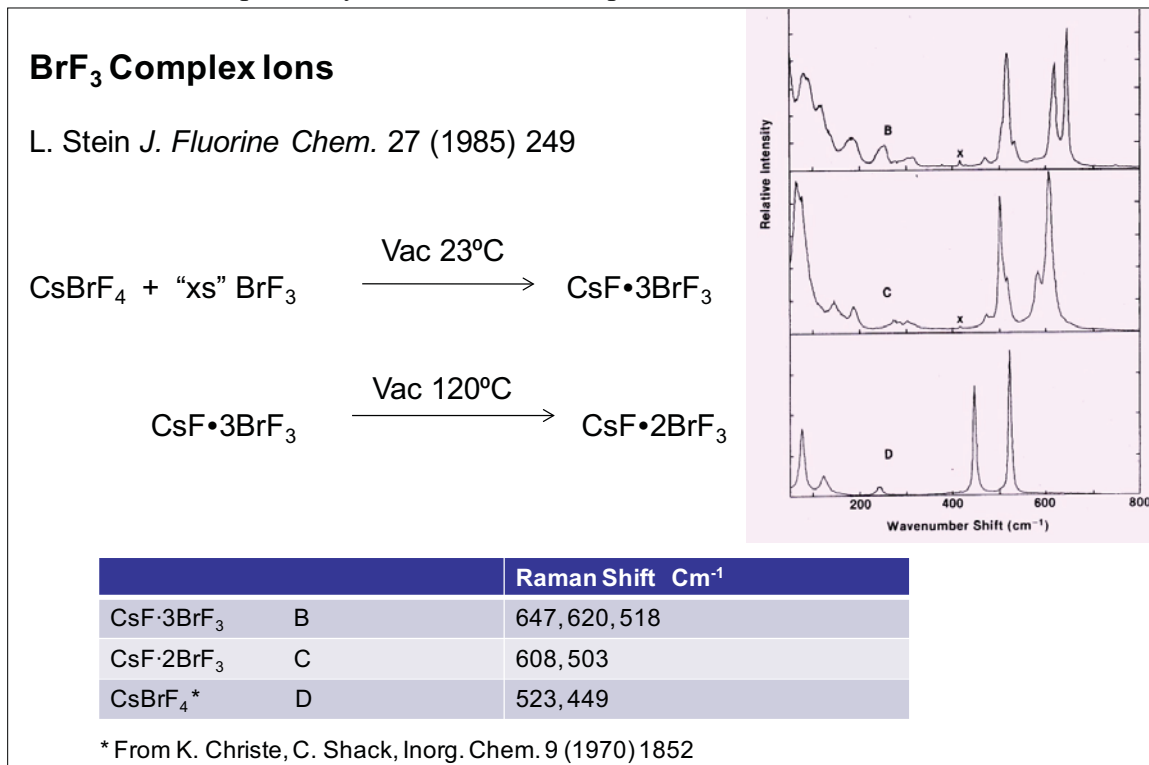**FIGURE 10** Crystal Structure of Cesium Hexadecafluorotriiodide Ion

CsI$_3$F$_{16}$ X-Ray Structure (-60ºC)

I-F$_{ax}$	1.81(2)Å
I-F$_{eq}$	1.85 – 1.90Å
I $\cdots$ F$^-$	**2.524(7)Å**
F$_{ax}$-I-F$_{eq}$	79-81º
F$^-$ $\cdots$ I-F$_{ax}$	146.8(8) º
I $\cdots$ F$^-$ $\cdots$ I	118.7(4) º

I$_3$F$_{16}^-$

Solvate Could Provide Higher Oxidizer/Fuel Ratio of N(CH$_3$)$_4^+$ Salts

Ali Reza Mahjoub, Andrzej Hoser, Joachim Fuchs, Konrad Seppelt *Angew. Chem. Int. Ed.* 1989, 11,1526

In an earlier report Hargreaves reported the results of a study on the reaction of iodide salts with IF$_5$. It is known that the iodide ion I$^-$ is not stable in liquid IF$_5$ and is rapidly oxidized to elemental iodine producing a fluoride ion F$^-$. A series of experiments were carried out under differing conditions and some products were characterized as I$_2$F$_9^-$ salts. The tetramethylammonium salt was determined to be very thermally stable as characterized by elemental analysis (Figure 11).

FIGURE 11 Reported Synthesis of nonafluorodiiodide ion

Other N(CH$_3$)$_4^+$ Salt IF$_5$ Solvates;

$$CsI + \text{"xs" } IF_5 \xrightarrow{>150ºC} CsIF_6$$

$$CsI + \text{"xs" } IF_5 \xrightarrow{60ºC} CsI_2F_9 \xrightarrow[\text{Vacuo}]{100ºC} CsIF_4$$

$$Me_4NI + \text{"xs" } IF_5 \longrightarrow Me_4NI_2F_9$$

Calculated (CH$_3$)$_4$NI$_2$F$_9$	Isolated 50ºC, Vacuum	80ºC, Vacuum	140ºC, Vacuum
50.9% I	52.2% I	51.8% I	53.4% I
34.3% F	33.9% F		

G. B. Hargreaves and R. D. Peacock   *J. Chem. Soc.* 1960, 2373

Stein published results of the complexation of the fluoride ion in excess BrF_3 showing that a rather unstable three to one ion formed that lost one equivalent of BrF_3 rather easily to form a thermally stable $CsBr_2F_7$ salt (Figure 12).

FIGURE 12 Reported Synthesis of BrF_3 Complex Ions/Solvates

BrF₃ Complex Ions

L. Stein *J. Fluorine Chem.* 27 (1985) 249

$$CsBrF_4 + \text{"xs" } BrF_3 \xrightarrow{\text{Vac 23ºC}} CsF \bullet 3BrF_3$$

$$CsF \bullet 3BrF_3 \xrightarrow{\text{Vac 120ºC}} CsF \bullet 2BrF_3$$

		Raman Shift Cm⁻¹
CsF·3BrF₃	B	647, 620, 518
CsF·2BrF₃	C	608, 503
CsBrF₄*	D	523, 449

*From K. Christe, C. Shack, Inorg. Chem. 9 (1970) 1852

4.0   METHODS AND RESULTS

4.1   General

Special apparatus and procedures were required to synthesize, characterize and safely handle the new materials due to the extreme oxidizing ability of the interhalogens and their salts. An all stainless steel and Teflon vacuum line was built in a fume hood and to purify and manipulate volatile compounds for the program. Tanks of brominetrifluoride and iodinepentafluoride reagents were attached to this system. A nitrogen filled drybox was dedicated to the program for the weighing and manipulation of solid reagents and products. A tank of 20% fluorine in nitrogen was also attached to the vacuum line and used to passivate surfaces and oxidize lower valent interhalogen impurities prior to their trap to trap purification.
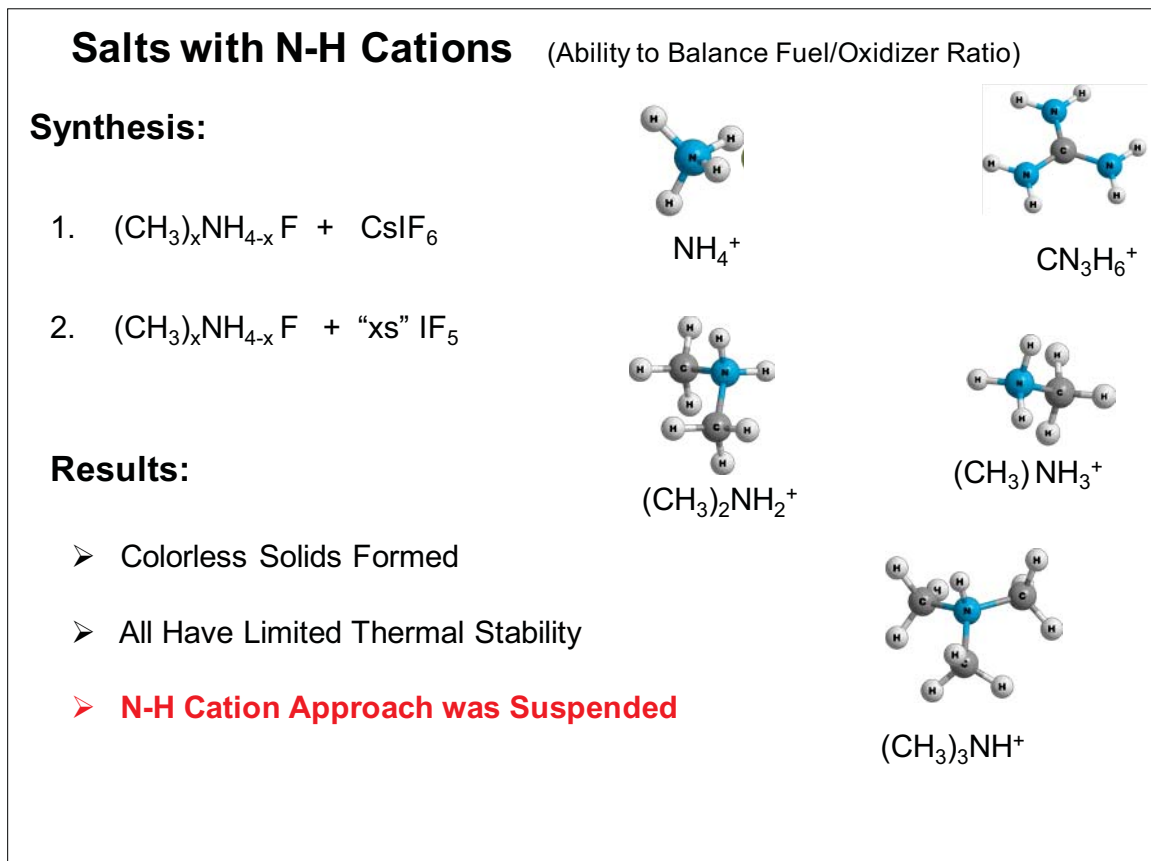
4.2 Salts of Cations with N-H Bonds Paired with Complex Perfluorohalogenate Anions

In the original assessment of the target salts it was decided to initially investigate systems that had a fuel/oxidizer ratio close to 1 such as NH_4BrF_4 which has been mentioned briefly in previously published work without physical characterization. Metathesis and dissolution reactions were investigated to prepare a series of salts containing the IF_6^- anion paired with cations possessing N-H bonds including ammonium, guanidinium, methylammonium, dimethylammonium, and trimethylammonium. Attempts to prepare salts by dissolution of the anhydrous organic fluorides in neat iodine pentafluoride (Reaction 5) or with fluoroform as a solvent as well as methathatical reactions (Reaction 4) with cesium IF_6^- initially produced colorless solids which upon standing at room temperature decomposed. It was concluded from these studies that cations with N-H bonds are unlikely to produce salts with sufficient thermal stability for this program.

The efforts to prepare perfluorohalogenate salts with cations possessing N-H bonds according to reactions 4 and 5 below were abandoned in the first year of the program since all systems investigated produced products with limited thermal stability (Figure 13). For a typical reaction 4, a stoichiometric equivalent of the anhydrous fluoride (prepared from "Olah's Reagent, anhydrous HF/pyridine, and anhydrous amines) was placed in a FEP tube in a nitrogen filled drybox and fitted with a stainless steel valve. The solvent, CF_3H (fluoroform), or acetonitrile was condensed onto the mixture using a liquid nitrogen bath on a stainless steel/FEP vacuum line. The mixture was stirred at ambient temperature for acetonitrile and -78ºC for fluoroform until evidence of reaction ceased. For fluoroform reactions the solvent was removed and the product subsequently dissolved in acetonitrile. In all cases there was some iodine color in the solution isolated by decanting the liquid from the CsF solid. After removing the acetonitrile *in vacuo* the solids were mostly decomposed after standing overnight at ambient temperatures. For reaction 5 a large excess of IF_5 (treated with F_2 to remove the iodine color and trap to trap purified) was condensed on a sample of the anhydrous fluoride in an FEP tube on the vacuum line. The mixture was allowed to warm to ambient temperature and stirred for a period from 1-2 hours before removing the excess iodine pentafluoride *in vacuo* leaving colorless solids that decomposed slowly at room temperature.

4. $(CH_3)_xNH_{4-x} F + CsIF_6 \longrightarrow$

colorless solids with limited thermal stability

5. $(CH_3)_xNH_{4-x} F + IF_5 \longrightarrow$

FIGURE 13 Summary of attempted N-H Cation Salt Synthesis

Salts with N-H Cations (Ability to Balance Fuel/Oxidizer Ratio)

Synthesis:

1. $(CH_3)_x NH_{4-x} F + CsIF_6$

2. $(CH_3)_x NH_{4-x} F + \text{"xs"} IF_5$

Results:

➢ Colorless Solids Formed

➢ All Have Limited Thermal Stability

➢ **N-H Cation Approach was Suspended**

NH_4^+

$CN_3H_6^+$

$(CH_3)_2NH_2^+$

$(CH_3)NH_3^+$

$(CH_3)_3NH^+$

4.3   Salts of Tetramethylammonium Ion Paired with Complex Perfluorohalogenate Anions

4.3.1 Synthesis of Me$_4$NI$_3$F$_{16}$

During our first assessment of target salts for this program the previously reported thermally stable salts of tetramethylammonium with BrF_4^- and IF_6^- were considered less attractive candidates due to their high fuel/oxidizer ratio. Based on examples of stable "solvates" such as $CsF \bullet 3IF_5$, new tetramethylammonium salts were targeted under the program with a higher oxidizer/fuel ratio attained through complexation of the anion with an excess of the interhalogen compound (e.g. IF_5 or BrF_3). Preliminary results supported by Raman spectroscopy indicated that we had isolated examples of this nature containing the tetramethylammonium cation with a more favorable fuel/oxidizer ratio as $I_3F_{16}^-$ or $I_2F_9^-$ complex ion salts (reactions 6 and 7 below).

In a typical experimental procedure 100 to 200mg of the tetramethylammonium fluoride or iodide salt is placed in an FEP tube and a large excess of IF_5 was condensed into the tube using a liquid nitrogen bath. The mixture is allowed to warm to room temperature and at about 10ºC the IF_5 melts and contacts the tetramethylammonium salt in an exothermic reaction. In reaction 4 I_2 formation is immediately apparent as IF_5 is added. The mixture was
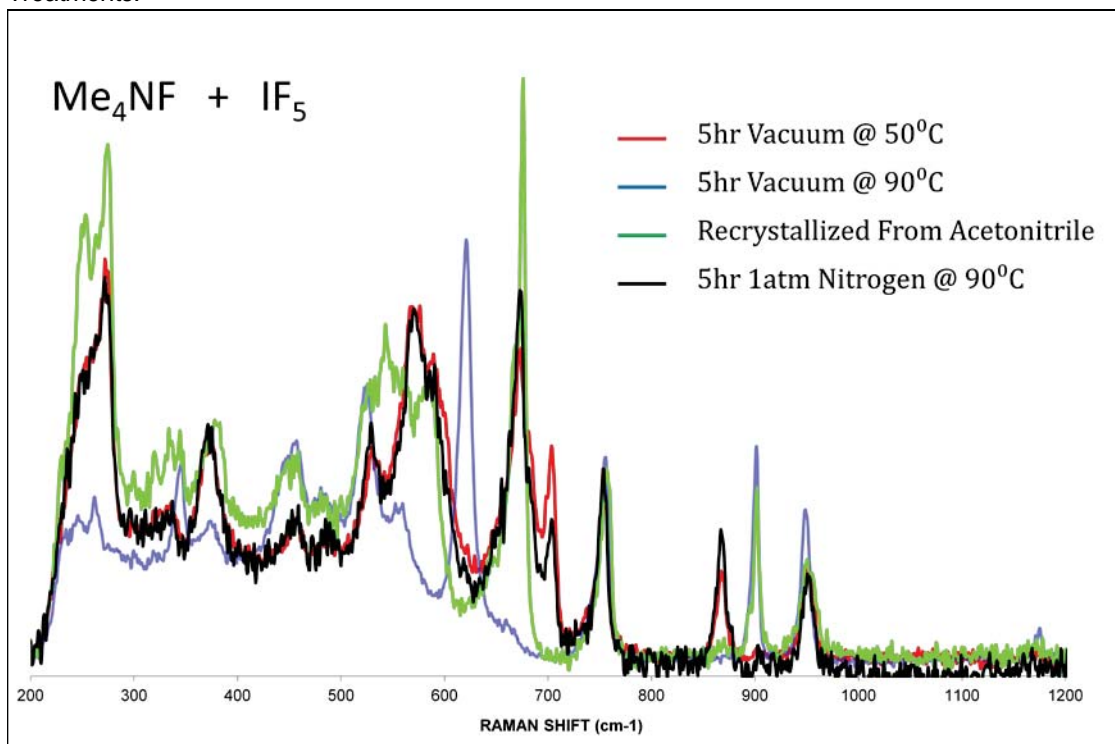
allowed to sit for a period of 12 hours with no apparent further reaction before excess IF_5 and I_2 (if present) were removed *in vacuo* at 50ºC over a 5 hour period.

Samples of the products were submitted for elemental analysis; however, the laboratory was unable to complete the analysis due to the highly reactive nature of the salts. Due to the small scale of the reactions and the large mass of the reaction tubes as well as static charge on samples and FEP tubes in the drybox no quantitative mass balance data could be obtained for these synthesis reactions. In an alternative attempt to confirm the product composition reaction 7 was scaled up to 2 grams in a mass balance experiment. Upon contact of the IF_5 and tetramethylammonium iodide the mixture rapidly heated pressurizing and rupturing the tube. On its release into the open air the mixture erupted in a blue-white flash accompanied by a loud report. No further attempt was made in scale-up due to a delay in a new shipment of IF_5. It is suggested that in future attempts at scaleup controlled addition of liquid IF_5 with stirring in an inert fluorocarbon non-solvent be used to reduce the possibility of thermal runaway.
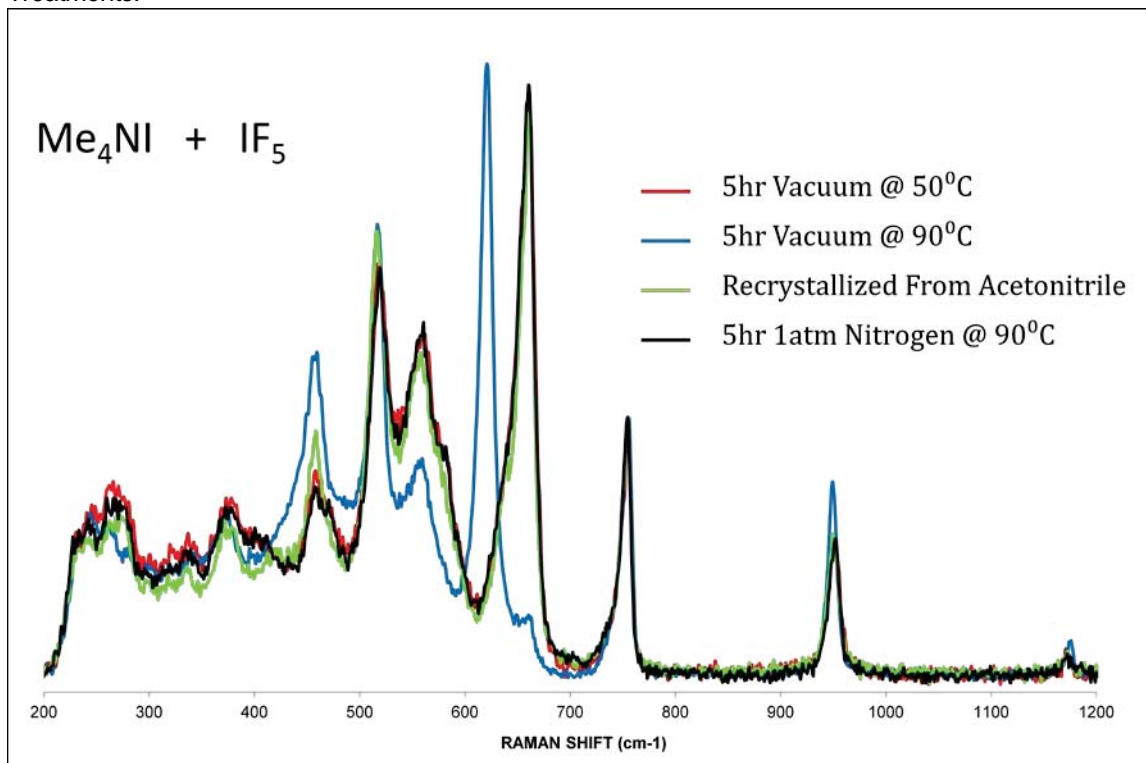

6. $(CH_3)_4NF$ + "xs" IF_5 $\longrightarrow$ $(CH_3)_4NI_3F_{16}$

7. $(CH_3)_4NI$ + "xs" IF_5 $\longrightarrow$ $(CH_3)_4NI_3F_{16}$ + $1/2I_2$

To assess the stability and determine the identity of the $I_3F_{16}^-$ or $I_2F_9^-$ complex ion salt samples were heated to 90ºC for 5 hours at one atmosphere and under vacuum. The Raman spectra of the samples were compared before and after treatment (Figure 14 and 15). By comparison to the published Raman data for $CsIF_6$ (most intense band at 620cm^{-1}) and $CsF\bullet3IF_5$ (bands at 674, 593, and 543cm^{-1}) the products from reactions 6 and 7 are consistent with formation of IF_5 solvates. Bands in Figure 14 at approximately 887 and 907cm^{-1} are thought to be impurity bands from intense I-O modes due to the presence of water impurities introduced at some stage of the preparation since (most likely water in the Me_4NF reagent) these are outside the expected range for the I-F modes. Bands at 750 and 950cm^{-1} are due to tetramethylammonium modes.

The colorless $Me_4NI_3F_{16}$ product had no clear melting point as it began to turn redish at about 130ºC likely from release of IF_5 then show signs of melting about 138ºC. The heat treatment at one atmosphere and 90ºC produced no apparent change in the spectra for either product indicating the "solvate" compounds have sufficient thermal stability for this program.

FIGURE 14 Raman Spectra of the Solvolysis Product from Reaction 6 Before and After Specified Treatments.
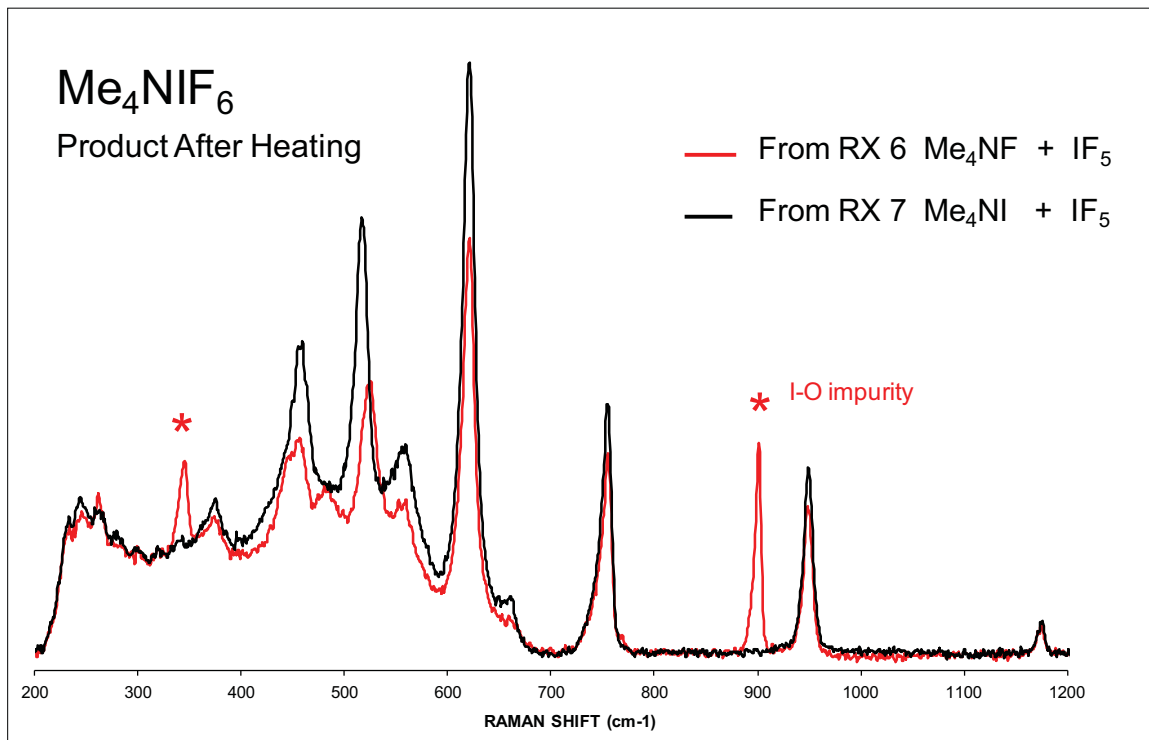

FIGURE 15 Raman Spectra of the Oxidation Product from Reaction 7 Before and after Specified Treatments.
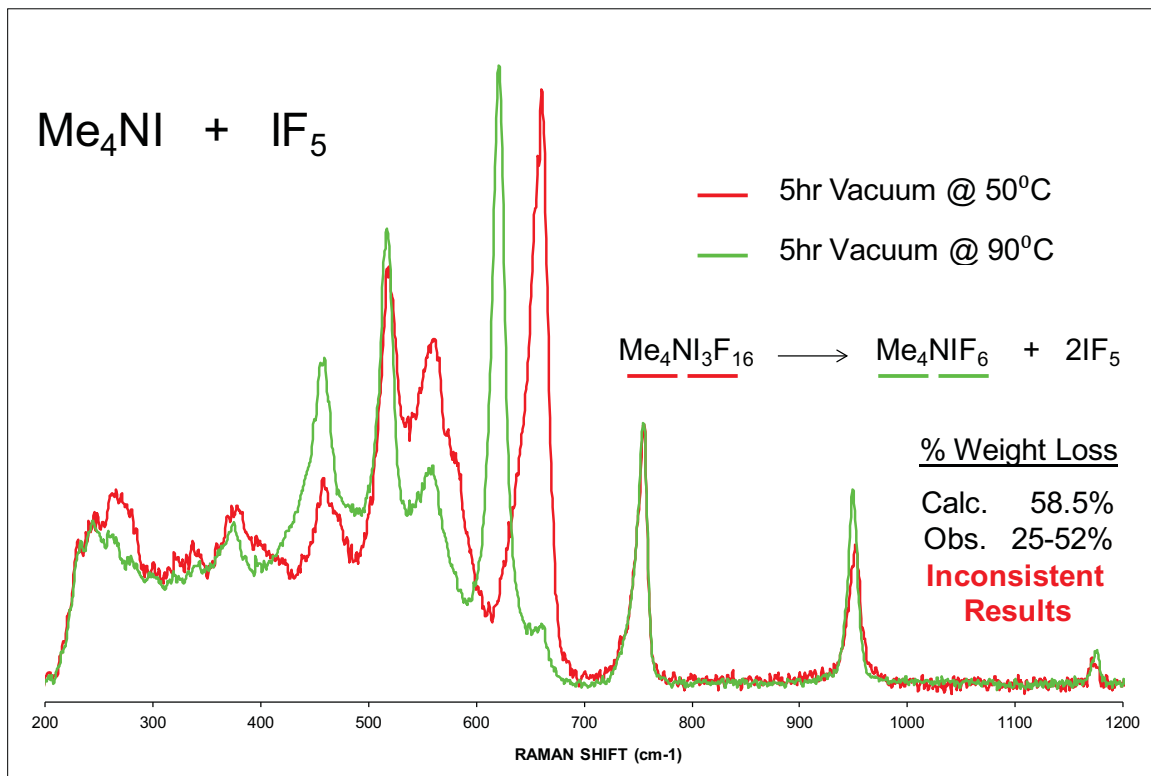
Raman studies on samples from reactions 6 and 7 heated to 90^0C in vacuum were consistent with an initial formulation of $Me_4NI_3F_{16}$ and formation of a common tetramethylammonium hexafluoroiodide product (Figures 16 and 17). Mass balance studies of the thermal treatment were inconsistent with the mass loss varying greatly from 25 to 52 weight percent (Figure 17). This is however not consistent with the previous report by Hargreaves wherein heating the product from reaction 7, formulated as $Me_4NI_2F_9$, resulted in only a minor change in the iodine content as measured by elemental analysis. Exact stoichiometric conditions were not specified in that report and it is possible that IF_3 formed during oxidation of I^- constituted a larger fraction of the mixture than in the present work. It is difficult to identify a reaction where both Me_4NF and Me_4NI would initially produce a common $Me_4NI_2F_9$ product. A more likely scenario is that our product contained varying levels of Me_4NF impurity that was not identifiable in the Raman spectra.
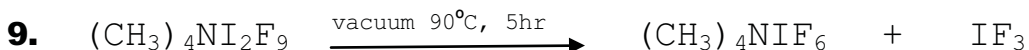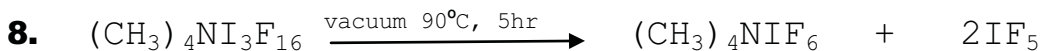
FIGURE 16 Raman spectra of the product from reaction 3 and 4 after heating under vacuum @ 90ºC for 5 hours.
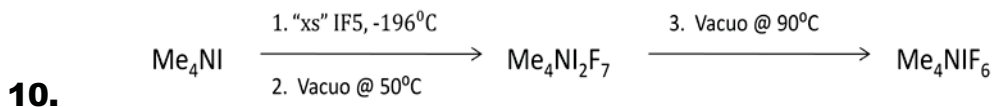
FIGURE 17 Mass Balance Study Supporting Reaction 8

The product from our reactions was assigned as $Me_4NI_3F_{16}$ based on: Mass loss on heating to 90C in vacuuo that is consistent with loss of 2 equivalents of IF_5 (Reaction 8 rather than Reaction 9) and the product being Me_4NIF_6; the thermal stability of our product was inconsistent with the reported data on $Me_4NI_2F_9$; and the close comparison of Raman data to that reported for CsI_3F_{16}.

8. $(CH_3)_4NI_3F_{16} \xrightarrow{\text{vacuum } 90^oC, \ 5hr} (CH_3)_4NIF_6 + 2IF_5$

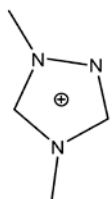**9.** $(CH_3)_4NI_2F_9 \xrightarrow{\text{vacuum } 90^oC, \ 5hr} (CH_3)_4NIF_6 + IF_3$
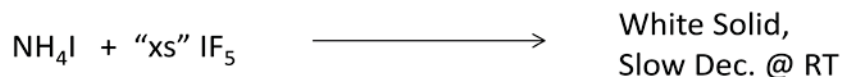
This oxidation chemistry (Reaction 10) provides an improved synthetic method to the tetramethylammonium hexafluoroiodate substituting Iodide reagents for more difficult to prepare anhydrous fluoride reagents.

10. $Me_4NI \xrightarrow[\text{2. Vacuo @ } 50^oC]{\text{1. "xs" IF5, } -196^oC} Me_4NI_2F_7 \xrightarrow{\text{3. Vacuo @ } 90^oC} Me_4NIF_6$

4.3.2 Attempted Synthesis of Other $I_3F_{16}^-$ Salts

Using this oxidation of an organic iodide approach the reactions 11 and 12 below were run to investigate the stability of other $I_3F_{16}^-$ salts. In both examples the products have limited stability.

11.

$$NH_4I \ + \ \text{"xs" IF}_5 \ \longrightarrow \ \text{White Solid, Slow Dec. @ RT}$$

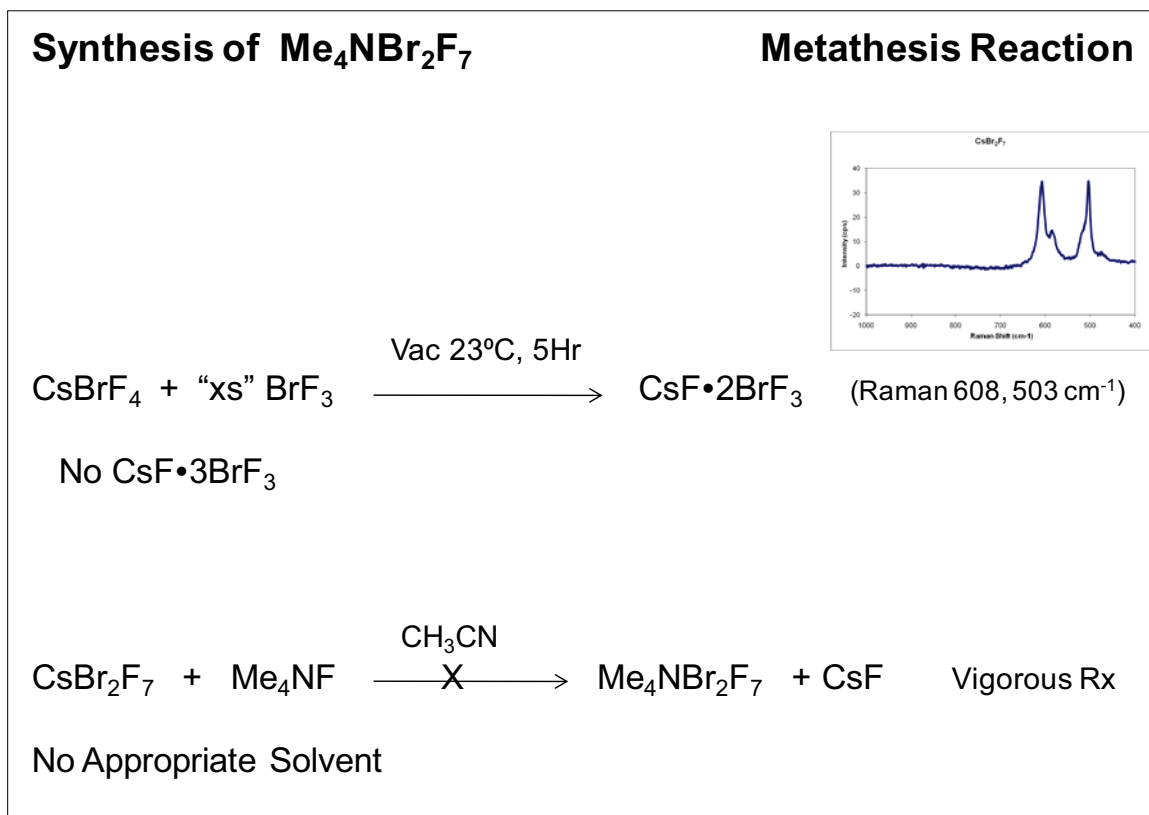$+ \ \text{"xs" IF}_5 \ \longrightarrow \ \text{Liquid Products}$

12.

4.3.3 Synthesis of $Me_4NBr_2F_7$

During the final year of the project efforts were focused on examining the BrF_3 adducts with tetramethylammonium fluoride $(CH_3)_4NF$. There is supporting evidence (see Stein and Wilson results in Figure 12) in the literature to suggest that the oxidizer content in tetramethylammonium salts might be better balanced by incorporating excess bromine trifluoride into the solid in the form of complex anions such as $Br_2F_7^-$ (essentially $F^-\cdot 2BrF_3$) that are thermally stable.
The first synthetic approach considered was a metathesis reaction of the cesium salt of a complex anion with tetramethylammonium fluoride in an appropriate solvent (Figure 18). The reaction of Cesium fluoride with excess bromine trifluoride followed by removal of excess bromine trifluoride in vacuuo for five hours at ambient temperature produced exclusively the one to two adduct as depicted in the first reaction in Figure 18. An attempt was made to prepare the one to two adduct of tetramethylammonium fluoride with bromine trifluoride by metathesis of the cesium salt in acetonitrile (second reaction in Figure 18). A vigorous exothermic reaction occurred possibly due to reaction of the solvent with the complex ion or more likely with free bromine trifluoride generated from the dissociation reaction of the complex ion in solution. In other inert solvents such as 1,1,2-trichloro-2,2,1-trifluoroethane the salts were insoluble and no reaction occurred. This metathesis approach was abandoned due to the lack of an appropriate solvent.
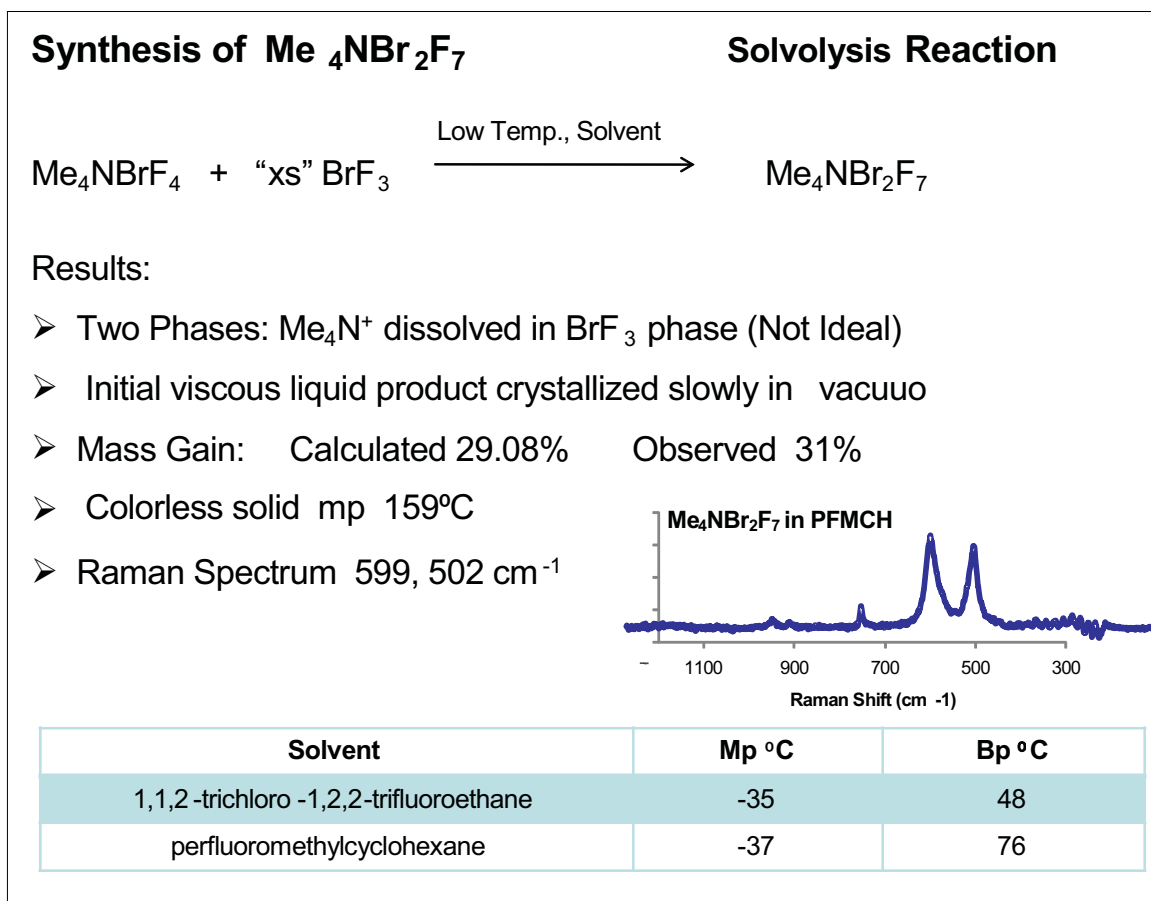
FIGURE 18 Summary of Metathesis Approach Results

Synthesis of Me$_4$NBr$_2$F$_7$ **Metathesis Reaction**

$$CsBrF_4 + \text{"xs" } BrF_3 \xrightarrow{\text{Vac 23}^oC, \text{5Hr}} CsF \cdot 2BrF_3 \quad (\text{Raman } 608, 503 \text{ cm}^{-1})$$

No CsF•3BrF$_3$

$$CsBr_2F_7 + Me_4NF \xrightarrow[\text{X}]{CH_3CN} Me_4NBr_2F_7 + CsF \quad \text{Vigorous Rx}$$

No Appropriate Solvent

Solvolysis reactions were explored as a second synthetic methodology. According to the reaction in Figure 19 an excess of bromine trifluoride was added to tetramethylammonium tetrafluorobromide prepared by the method of Wilson. Due to the anticipated exothermic nature of the reaction an inert solvent was used to dilute the reaction mixture and prevent thermal runaway. In a typical reaction a sample of tetramethylammonium tetrafluorobromide was placed in a FEP reaction tube on the vacuum line and evacuated. The solvent was condensed on the compound using a liquid nitrogen bath. The physical properties of the solvents used, 1,1,2-trichloro-2,2,1-trifluoroethane and perfluoromethylcyclohexane are listed in Figure 19. In the initial experiments the exess bromine trifluoride was condensed on top of the mixture and the tube was allowed to warm slowly to room temperature. In latter experiments the excess brominetrifluoride was slowly added to the tube at -30°C with stirring under a nitrogen blanket using a calibrated Teflon tube and syringe. The second, slow addition, scheme provided the best thermal control of the reaction and was the preferred method. The results were similar in that two liquid phases were formed where it was apparent from NMR experiments that the tetramethylammonium ion is concentrated in the bottom layer with mostly excess brominetrifluoride. This is clearly not the ideal reaction conditions since there is little dilution control of the oxidizer/fuel mixture. On removal of excess bromine trifluoride and solvent a viscous liquid product formed that slowly crystallized on further pumping. Based on mass balance and comparison of Raman data to the cesium salt results the product is assigned as the one to two adduct of tetramethylammoniumfluoride and bromine trifluoride, $(CH_3)_4NF \cdot 2BrF_3$ or $(CH_3)_4NBr_2F_7$.

FIGURE 19 Summary of Solvolysis Reaction Approach

Synthesis of Me$_4$NBr$_2$F$_7$ ## Solvolysis Reaction

$$\text{Me}_4\text{NBrF}_4 \;+\; \text{"xs" BrF}_3 \quad \xrightarrow{\text{Low Temp., Solvent}} \quad \text{Me}_4\text{NBr}_2\text{F}_7$$

Results:

➤ Two Phases: Me$_4$N$^+$ dissolved in BrF$_3$ phase (Not Ideal)

➤ Initial viscous liquid product crystallized slowly in vacuuo

➤ Mass Gain: Calculated 29.08%   Observed 31%

➤ Colorless solid mp 159ºC

➤ Raman Spectrum 599, 502 cm^{-1}

Me$_4$NBr$_2$F$_7$ in PFMCH

Raman Shift (cm^{-1}): 1100, 900, 700, 500, 300

Solvent	Mp ºC	Bp ºC
1,1,2-trichloro-1,2,2-trifluoroethane	-35	48
perfluoromethylcyclohexane	-37	76

The third synthetic approach explored involved the oxidation of the bromide ion in tetramethylammonium bromide to form tetramethylammonium fluoride that is subsequently complexed by excess brominetrifluoride to form the target complex salt (see Figure 20). This has the added advantages of not using anhydrous tetramethylammonium fluoride and avoiding the initial reaction to produce the brominetetrafluoride salt. Bromine was chosen as the solvent since it provided good solubility of the tetramethylammoniumbromide reagent. Again under the conditions explored a two phase mixture was formed. Based on mass balance (Figure 20) and comparison of Raman data (Table 2) to the cesium salt results the product was assigned as the one to two adduct (CH$_3$)$_4$NBr$_2$F$_7$.
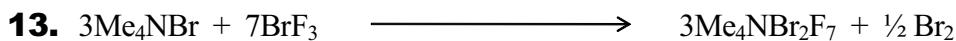
FIGURE 20 Summary of Oxidation Reaction Approach

Synthesis of $Me_4NBr_2F_7$ **Oxidation Reaction**

$$Me_4NBr + 12\ BrF_3 \xrightarrow{\ Br_2\ ,\ 0°C\ } Me_4NBr_2F_7 + 1/2\ Br_2$$

1.5M Me_4NBr in Br_2

Mass Balance

+138.1% (Calc)   +144% (Exp)

Results:

➢ 2 Phase Mixture, Me_4N^+ Partitioned

➢ Initial viscous liquid product crystallized slowly in vacuuo

➢ Raman Spectrum

$Me_4NBr_2F_7$

Bromine: Mp -7.2°C   Bp 58.8°C

Table 2 Raman Data of Bromine Fluoride Salts

$CsBrF_4$	Me_4NBrF_4	$CsBr_2F_7$	$Me_4NBr_2F_7$
448 cm^{-1}	448 cm^{-1}	505 cm^{-1}	504 cm^{-1}
523 cm^{-1}	521 cm^{-1}	609 cm^{-1}	599 cm^{-1}
	746 cm^{-1}		754 cm^{-1}
	949 cm^{-1}		950 cm^{-1}

The preferred conditions for the synthesis of $Me_4NBr_2F_7$ is to use a stoichiometric amount of BrF_3 in bromine solvent at ambient temperature (Reaction 13).

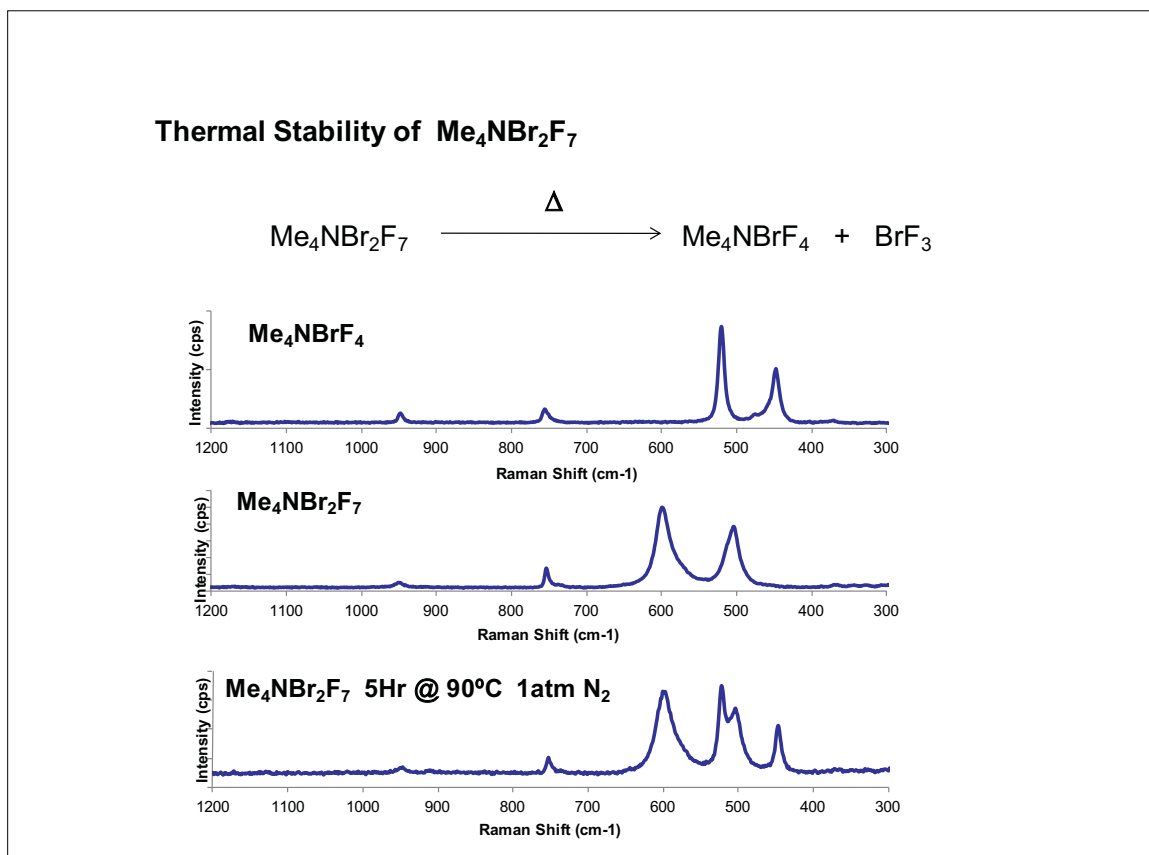**13.** $3Me_4NBr + 7BrF_3 \xrightarrow{\hspace{4cm}} 3Me_4NBr_2F_7 + \frac{1}{2} Br_2$

In a typical experiment a reaction vessel was fashioned by heat sealing a 5/8" FEP tube onto a 25ml FEP bottle that would accommodate a Swagelock fitting. The vessel was attached to a dry nitrogen source and fitted with a magnetic stir bar and 10g (3.6ml) bromine solvent. A 0.935g (6.07mmol) sample of dry Me_4NBr was slowly added with stirring generating heat as the ammonium salt dissolved. The solution was allowed to cool back to ambient temperature then 0.75ml (2.0g, 15.14mmol) of BrF_3 that had been metered out in a long piece of 1/16" FEP tubing attached to a syringe was slowly added with stirring to the solution keeping the temperature below 40ºC. The mixture was stirred overnight under a nitrogen blanket before removing the solvent at ambient temperature under vacuum leaving a colorless crystalline solid. Mass balance confirms formation of the 3:1 adduct $Me_4NBr_2F_7$. The Raman spectra (Figure 21) shows some the presence of some Me_4NBrF_4 in the product.

FIGURE 21 $Me_4NBr_2F_7$ From Stoichiometric Reaction in Br_2 Solvent. (Some Me_4NBr_4 Present)

The thermal stability of the adduct was assessed by placing a small sample in a FEP tube under one atmosphere nitrogen that provided essentially unlimited head space and heating the contents to 90ºC in an oil bath for five hours. Characterization of the resulting solid by Raman spectroscopy showed some loss of bromine trifluoride occurred and the sample contains a mixture of the one to one and one to two adducts (Figure 22). The sample is however expected to be stable enough for consideration in the program. The $(CH_3)_4NBr_2F_7$ solid has a clean melting point of $159ºC$. Samples of the product loosely filling a1/4" to 1/2" of a standard melting point capillary tube were sealed at the end with a small section of tygon tubing placed on a steel block and struck with a hammer. The samples consistently produced a sharp loud report even with a mild blow indicating that the samples were significantly more impact sensitive than RDX under the same conditions.

FIGURE 22   Thermal Stability of $Me_4NBr_2F_7$ Study

Thermal Stability of $Me_4NBr_2F_7$

$$Me_4NBr_2F_7 \xrightarrow{\Delta} Me_4NBrF_4 + BrF_3$$
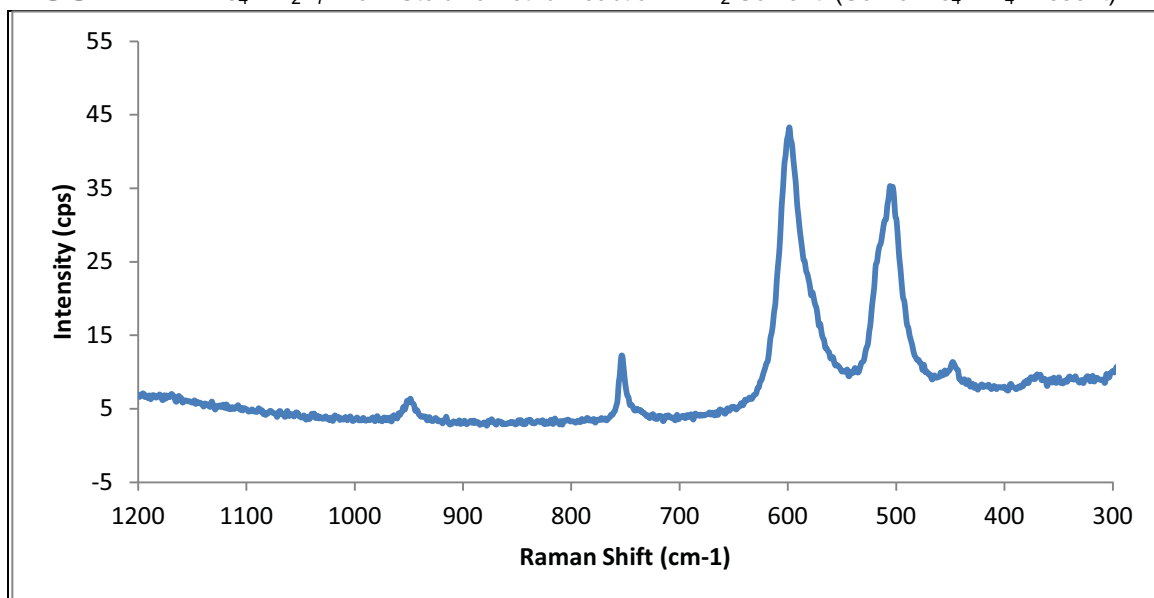
Me_4NBrF_4

$Me_4NBr_2F_7$

$Me_4NBr_2F_7$ 5Hr @ 90°C 1atm N_2

5.0   Discussion/Conclusion

Attempts to synthesize and isolate a series of simple salts of interhalogenates with N-H bonds such as NH_4BrF_4 was abandoned in the second year of the program as they were found to be too unstable for the purposes of this program. The program then focused on the synthesis, isolation and characterization of tetramethylammonium salts with complex interhalogenates. For the IF_5 system the product is spectroscopically consistent with a formulation of $Me_4NI_3F_{16}$. We were unable to conclusively confirm this formulation using mass balance experiments. Improved synthesis was achieved using the Me_4NI rather than the Me_4NF reagent. No suitable solvent was found for this reaction and consequently the best reaction conditions are suggested to run as a heterogenous mixture in an inert non-solvent as a heat sink. The product is a thermally stable (>130°C) colorless solid that did not explode when struck with a strong hammer blow.

With the BrF_3 system the product was determined unambiguously to be $Me_4NBr_2F_7$. A number of synthetic approaches were examined and the best reaction conditions were found to be slow addition of a stoichiometric amount of BrF_3 to a stirred solution of Me_4NBr in Br_2 solvent. The product was a colorless moisture sensitive solid with a melting point of 159°C

andthat was clearly demonstrated to be energetic by consistent initiation with a mild hammer blow.

The moisture sensitivity, reactivity, and unique hazards presented by these new compounds prohibited us from obtaining conventional safety testing data for ESD, Impact and Friction Sensitivity. However the basic concept of substituting more conventional oxidizers with perfluorohalogenate ions was demonstrated by the impact sensitivity of the $Me_4NBr_2F_9$ salt. While the $Me_4NBr_2F_9$ salt may be too impact sensitive for the counter CBW application the $Me_4NI_3F_{16}$ salt may be useful if explosive initiation could be demonstrated.

6.0   REFERENCES

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7.0   PRODUCTS

7.1   Lists of materials synthesized:

One New Energetic Material of the type Proposed $Me_4NBr_2F_7$

7.2   Papers published ---   none

7.3   Students or post-docs funded   ---   None

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