

# Direct syntheses of tetramethylammonium salts of complex fluoroanions <sup>1</sup>

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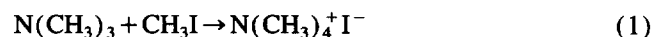
## Abstract

The tetramethylammonium salts of  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{SiF}_5^-$ ,  $\text{SiF}_6^{2-}$ ,  $\text{GeF}_5^-$  and  $\text{GeF}_6^{2-}$  were prepared in high yields by direct synthesis from  $\text{N}(\text{CH}_3)_3$ ,  $\text{CH}_3\text{F}$  and the corresponding Lewis acid at elevated temperature and pressure. Attempts to prepare anhydrous  $\text{N}(\text{CH}_3)_4\text{F}$  directly from  $\text{N}(\text{CH}_3)_3$  and  $\text{CH}_3\text{F}$  at elevated temperature and pressure or by pyrolysis of some of the above tetramethylammonium complex fluoroanion salts were unsuccessful. © 1997 Elsevier Science S.A.

**Keywords:** Hexafluorogermanate; Hexafluorosilicate; Pentafluorogermanate; Pentafluorosilicate; Synthesis; Tetramethylammonium tetrafluoroborate hexafluorophosphate

## 1. Introduction

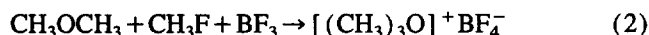
Quaternary ammonium compounds are of significant industrial interest for applications such as surfactants, anti-bacterials, algicides, organo clays and electrolytes [1,2]. The tetramethylammonium salts are of particular interest because they do not possess  $\beta$ -hydrogen atoms. Therefore they are not subject to Hofmann degradation and exhibit increased thermal and chemical stability [3]. Tetramethylammonium salts are generally prepared by quaternizing  $\text{N}(\text{CH}_3)_3$  with a methylating agent, such as  $\text{CH}_3\text{I}$



and converting the resulting iodide to either the hydroxide or other salts using methods such as metathesis or ion exchange [1].

Tetramethylammonium salts containing complex fluoroanions, such as the commercially available  $\text{N}(\text{CH}_3)_4\text{BF}_4$  and  $\text{N}(\text{CH}_3)_4\text{PF}_6$  [4], can be prepared by either neutralizing  $\text{N}(\text{CH}_3)_4\text{OH}$  with the corresponding acid or by displacement reactions between an  $\text{N}(\text{CH}_3)_4^+$  salt of a weaker acid with the corresponding stronger acid. These processes suffer from the general drawbacks of involving numerous steps and relatively expensive starting materials, such as iodides, which must be recovered and recycled.

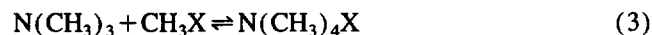
However, for the closely related trimethyloxonium salts, direct syntheses from dimethylether,  $\text{CH}_3\text{F}$  and a Lewis acid, such as  $\text{BF}_3$ ,



are well known [5]. To our knowledge, no analogous direct syntheses of tetramethylammonium salts have been reported. It was therefore of interest to explore direct methods for the synthesis of tetramethylammonium salts containing complex fluoroanions.

## 2. Results and discussion

The known [6] reversibility of the formation and decomposition reactions of tetramethylammonium iodide, bromide and chloride



and the known [3] decomposition path of  $\text{N}(\text{CH}_3)_4\text{F}$

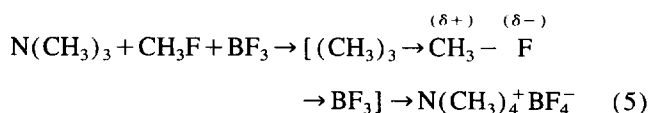


indicate that, under favorable conditions, i.e. elevated temperature and pressure, reaction (4) may also be reversible and thus provide a direct and low cost synthesis of anhydrous  $\text{N}(\text{CH}_3)_4\text{F}$ . However, all our attempts to prepare  $\text{N}(\text{CH}_3)_4\text{F}$  directly from  $\text{N}(\text{CH}_3)_3$  and  $\text{CH}_3\text{F}$  at temperatures up to 350 °C and pressures up to 100 atm were unsuccessful. It therefore appears that the activation energy for the heterolytic fission

<sup>1</sup> Dedicated to Professor Jean'ne Shreeve on the occasion of her 65th birthday.

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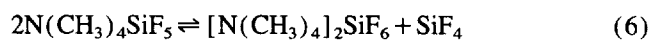
of the C–F bond of  $\text{CH}_3\text{F}$  is too high, but may be lowered by the addition of a strong Lewis acid, as shown in Eq. (5)



In the present study, this approach was successfully demonstrated. It was shown that, in this manner, the  $\text{N}(\text{CH}_3)_4^+$  salts of  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{SiF}_5^-$ ,  $\text{SiF}_6^{2-}$ ,  $\text{GeF}_5^-$  and  $\text{GeF}_6^{2-}$  can be prepared in essentially quantitative yields at temperatures of about 200 °C and under moderate autogenous pressures. Since  $\text{N}(\text{CH}_3)_3$  forms, with these Lewis acids, moderately stable donor–acceptor adducts [7–11], which strongly diminish the effective Lewis acidity of the fluorides, no quaternization takes place until the dissociation temperature of the adducts is reached and the free Lewis acids become available for polarizing  $\text{CH}_3\text{F}$ . The relatively low thermal stability of the  $\text{N}(\text{CH}_3)_3 \cdot \text{SiF}_4$  adduct [8] also explains why  $\text{SiF}_4$ , which is the weakest of the Lewis acids used in this study, surprisingly quaternizes  $\text{N}(\text{CH}_3)_3$  at the lowest temperature, i.e. 100 °C.

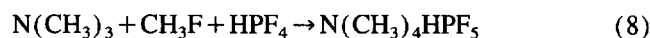
It was also found to be important to use Lewis acids which do not exhibit oxidizing properties. Thus the use of oxidizing Lewis acids, such as  $\text{AsF}_5$  or  $\text{SbF}_5$ , results in charring of the starting materials at temperatures exceeding 100 °C.

In the case of Lewis acids, such as  $\text{SiF}_4$  or  $\text{GeF}_4$ , which can form both monovalent ( $\text{XF}_5^-$ ) and divalent ( $\text{XF}_6^{2-}$ ) anions, the exclusive formation of either type of anion can be achieved by using either the amine or the Lewis acid in sufficient excess. This result is in good agreement with the equilibrium (6)



which was previously established for  $\text{N}(\text{CH}_3)_4\text{SiF}_5$  [12].

Attempts to prepare  $\text{N}(\text{CH}_3)_4\text{PF}_4$  [13] directly from  $\text{N}(\text{CH}_3)_3$ ,  $\text{CH}_3\text{F}$  and  $\text{PF}_3$  were unsuccessful. Although a solid product was formed at 200 °C in moderate yield, it consisted mainly of  $\text{N}(\text{CH}_3)_4\text{HPF}_5$  [14]. Its formation can readily be explained by assuming HF elimination followed by reactions (7) and (8)



The products of all the above reactions were characterized by the observed material balances and their vibrational and multinuclear NMR spectra. Since all the ions and most of the salts have previously been well characterized [3,4,12–22], no individual assignments are given in this paper.

As already mentioned,  $\text{N}(\text{CH}_3)_4\text{F}$  is thermally stable up to about 170 °C [3]. If we can find a relatively labile  $\text{N}(\text{CH}_3)_4^+$  salt of a complex fluoroanion which can conveniently be prepared in anhydrous form by the new direct synthesis method and which decomposes below 170 °C to  $\text{N}(\text{CH}_3)_4\text{F}$  and the corresponding Lewis acid, this will provide a simple synthesis for anhydrous  $\text{N}(\text{CH}_3)_4\text{F}$ . Conse-

quently, the vacuum pyrolyses of these salts were briefly investigated. It was found that  $\text{N}(\text{CH}_3)_4\text{BF}_4$  started to decompose slowly at about 260 °C to  $\text{N}(\text{CH}_3)_3$ ,  $\text{BF}_3$  and  $\text{CH}_3\text{F}$ . In the case of  $\text{N}(\text{CH}_3)_4\text{SiF}_5$ , the thermally least stable of the  $\text{N}(\text{CH}_3)_4$  complex fluoroanion salts studied, decomposition started at about 190 °C. Although the volatile product was the desired  $\text{SiF}_4$ , the  $\text{SiF}_4$  loss was only 50% and the solid residue was  $[\text{N}(\text{CH}_3)_4]_2\text{SiF}_6$  which was stable up to about 300 °C.

In summary, the results of this study show that, by analogy with dimethylether,  $\text{N}(\text{CH}_3)_3$  can also be directly methylated with  $\text{CH}_3\text{F}$  and a Lewis acid, thus providing simple, one-step, high-yield syntheses for tetramethylammonium salts of complex fluoroanions.

### 3. Experimental details

All reactions were carried out in an electrically heated oven using 316 stainless steel cylinders (Hoke) which were closed by stainless steel valves. Volatile materials were handled in a flamed-out Pyrex vacuum line equipped with Kontes Teflon valves and a Heise Bourdon-type pressure gauge. Solid materials were handled in the dry nitrogen atmosphere of a glove box.

Raman spectra were recorded on a Cary model 83 spectrometer using the 488 nm excitation line of an Ar ion laser, a Spex grating pre-monochromator for the elimination of plasma lines and Pyrex melting point capillaries as sample containers. IR spectra were recorded on a Midac FT-IR spectrometer using dry powders pressed as either KBr or AgCl pellets in an Econo press (Barnes Engineering Co.). The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded using a Bruker AM 360 spectrometer at 360.13, 90.56 and 338.81 MHz respectively with tetramethylsilane (TMS) ( $^1\text{H}$  and  $^{13}\text{C}$ ) and  $\text{CCl}_3\text{F}$  ( $^{19}\text{F}$ ) as internal standards.

Commercial  $\text{N}(\text{CH}_3)_3$ ,  $\text{PF}_5$ ,  $\text{BF}_3$ ,  $\text{SiF}_4$  (Matheson),  $\text{AsF}_5$ ,  $\text{PF}_3$ ,  $\text{GeF}_4$  (Ozark Mahoning) and  $\text{CH}_3\text{F}$  (PCR Research Chemicals) were used as received.

#### 3.1. Tetramethylammonium tetrafluoroborate [4,15,16]

In a 100 ml stainless steel cylinder, a mixture of  $\text{N}(\text{CH}_3)_3 \cdot \text{BF}_3$  (29.08 mmol, pre-formed from  $\text{N}(\text{CH}_3)_3$  and a small excess of  $\text{BF}_3$ , followed by removal of the excess  $\text{BF}_3$  in vacuo at 23 °C) and  $\text{CH}_3\text{F}$  (47.83 mmol) was heated under an autogenous pressure of 31 atm to 200 °C. The conversion of the starting materials to  $\text{N}(\text{CH}_3)_4\text{BF}_4$  was periodically checked by removal and measurement of the unreacted  $\text{CH}_3\text{F}$  at ambient temperature and the weight uptake of the cylinder. After 28 and 72 h, the conversions to  $\text{N}(\text{CH}_3)_4\text{BF}_4$  were 90.4% and 97.6% respectively. The unreacted  $\text{N}(\text{CH}_3)_3 \cdot \text{BF}_3$  had sublimated in the form of fine needles to the top of the reactor, whereas the  $\text{N}(\text{CH}_3)_4\text{BF}_4$  had accumulated at the bottom of the reactor, thus allowing for easy product separation. In a separate experiment, a similar mixture, when

heated to 152 °C for 70 h and to 171 °C for an additional 62 h, produced 78.6% and 84.1% respectively of  $N(CH_3)_4BF_4$  which was spectroscopically identified. Ra (solid,  $cm^{-1}$ ): 3037(23), 2990(10), 2955(20), 2912(5), 2809(5), 1474(77), 1414(8), 1290(6), 1179(9), 950(79), 770(100), 754(61), 520(5), 459(12), 350(3). IR (AgCl,  $cm^{-1}$ ): 3040(vw), 1493(s), 1410(w), 1290(w), 1063(vs), 950(s), 923(sh), 769(w), 522(m), 460(vw).  $^1H$  NMR (in  $CD_3CN$ )  $\delta$ : 3.07 (s,  $CH_3$ ).

Ra (solid,  $cm^{-1}$ ) of  $N(CH_3)_3 \cdot BF_3$  adduct: 3020(24), 3010(25), 2958(32), 2922(9), 2867(10), 2794(7), 1475(61), 1470(sh), 1250(5), 1100(5), 989(53), 850(sh), 845(sh), 840(44), 693(100), 544(15), 511(18), 428(8), 346(sh), 338(32), 320(28), 231(13), 220(5), 160(2), 135(sh).

### 3.2. Tetramethylammonium hexafluorophosphate [4,15]

The reaction between  $N(CH_3)_3$ ,  $PF_5$  and  $CH_3F$  was carried out in the same manner as described above for  $N(CH_3)_4BF_4$ . After 48 h at 200 °C, the conversion to  $N(CH_3)_4PF_6$  was 98.2% complete. IR (AgCl,  $cm^{-1}$ ): 3040(vw), 1494(mw), 1416(w), 949(m), 835(s), 779(mw), 743(mw), 562(s), 495(w), 459(w).

### 3.3. Tetramethylammonium pentafluorosilicate [12]

A mixture of  $CH_3F$  (25.0 mmol),  $SiF_4$  (25.0 mmol) and  $N(CH_3)_3$  (20.0 mmol) in a 100 ml stainless steel cylinder, after heating to 240 °C for 112 h, produced  $N(CH_3)_4SiF_5$  in 91.6% yield. In a second experiment, a mixture of  $CH_3F$  (8.0 mmol),  $SiF_4$  (4.0 mmol) and  $N(CH_3)_3$  (4.0 mmol) in a 10 ml stainless steel cylinder, after heating to 100 °C for 48 h, produced  $N(CH_3)_4SiF_5$  in 96.4% yield, based on the limiting reagent  $N(CH_3)_3$ . The product did not contain any detectable amounts of the  $SiF_6^{2-}$  salt. Ra (solid,  $cm^{-1}$ ): 3039(22), 2990(10), 2958(18), 2911(5), 2809(5), 1471(85), 1418(8), 1286(5), 1176(10), 952(80), 757(100), 745(sh), 710(48), 529(3), 459(18), 419(4), 371(25). IR (AgCl,  $cm^{-1}$ ): 3048(w), 1494(m), 1416(mw), 1305(w), 950(ms), 864(vs), 780(vs), 710(w), 481(s), 443(s). NMR (in  $CD_3CN$ , 25 °C):  $^1H$ ,  $\delta$ : 3.06 (s,  $CH_3$ ),  $^{19}F$ ,  $\delta$ : -136.94 (s,  $SiF_5^-$ );  $^{13}C$ ,  $\delta$ : 56.11 (tr,  $^1J(^{13}C-^{14}N) = 4.47$  Hz).

### 3.4. Bis(tetramethylammonium) hexafluorosilicate [16]

A mixture of  $CH_3F$  (12.0 mmol),  $SiF_4$  (2.0 mmol) and  $N(CH_3)_3$  (6.0 mmol) in a 10 ml stainless steel cylinder, after heating to 200 °C for 48 h, produced mainly  $[N(CH_3)_4]_2SiF_6$  containing about 10 mol.%  $N(CH_3)_4SiF_5$ . The conversion of  $SiF_4$  was essentially quantitative. Ra (solid,  $cm^{-1}$ ): 3020(30), 2930(15), 2830(20), 1490(100), 959(70), 758(75), 646(35), 460(10), 381(35). IR (AgCl,  $cm^{-1}$ ), bands marked by an asterisk are due to  $N(CH_3)_4SiF_5$ : 3037(w), 1507(m), 1494\*(w), 965(m), 950\*(w),

876\*(mw), 788\*(mw), 706(vs), 488\*(w), 481(ms), 461(ms), 449\*(w). NMR (in  $CD_3CN$ , 25 °C):  $^1H$ ,  $\delta$ : 3.06 (s,  $CH_3$ );  $^{19}F$ ,  $\delta$ : -137.17 ( $^1J(^{29}Si-^{19}F) = 143.2$  Hz).

### 3.5. Tetramethylammonium pentafluorogermanate

A mixture of  $CH_3F$  (8.0 mmol),  $GeF_4$  (4.0 mmol) and  $N(CH_3)_3$  (2.0 mmol) in a 10 ml stainless steel cylinder, after heating to 200 °C for 48 h, produced  $N(CH_3)_4GeF_5$  in almost quantitative yield based on the limiting reagent  $N(CH_3)_3$ . Ra (solid,  $cm^{-1}$ ): 3025(15), 1468(100), 951(80), 752(90), 674(90), 581(20), 460(10), 371(25), 340(0+, broad), 211(10), 180(5), 135(10). IR (AgCl,  $cm^{-1}$ ): 3040(w), 1497(m), 954(m), 689(vs), 661(vs). NMR (in  $CD_3CN$ , 25 °C),  $^1H$ ,  $\delta$ : 3.06 (s,  $CH_3$ ).

### 3.6. Bis(tetramethylammonium) hexafluorogermanate

A mixture of  $CH_3F$  (12.0 mmol),  $GeF_4$  (2.0 mmol) and  $N(CH_3)_3$  (6.0 mmol) in a 10 ml stainless steel cylinder, after heating to 200 °C for 48 h, produced  $[N(CH_3)_4]_2GeF_6$  in almost quantitative yield based on  $GeF_4$ . Ra (solid,  $cm^{-1}$ ): 1486(100), 956(55), 759(60), 612(80), 318(30). IR (AgCl,  $cm^{-1}$ ): 3037(mw), 1503(m), 961(s), 584(vs), 465(m).

### 3.7. Trimethylamine-germanium tetrafluoride molecular adduct [11]

A mixture of  $CH_3F$  (8.0 mmol),  $GeF_4$  (4.0 mmol) and  $N(CH_3)_3$  (4.0 mmol) was kept in a 10 ml stainless steel cylinder at 100 °C for 48 h. After pumping off the volatile material at room temperature, 4.0 mmol of a molecular  $N(CH_3)_3 \cdot GeF_4$  adduct was left behind. Ra (solid,  $cm^{-1}$ ): 3028(21), 3012(19), 2959(26), 2930(16), 2868(11), 2791(8), 1481(55), 1468(40), 1449(5), 1410(5), 1245(9), 1114(6), 976(32), 821(60), 709(3), 694(11), 669(100), 610(81), 580(7), 536(17), 438(15), 321(14), 289(35), 264(43), 221(22), 115(sh).

### 3.8. The $N(CH_3)_3-CH_3F-PF_3$ system

A mixture of  $CH_3F$  (10.27 mmol),  $PF_3$  (10.27 mmol) and  $N(CH_3)_3$  (8.04 mmol) was heated in a 10 ml stainless steel cylinder to 200 °C for 48 h. After pumping off all volatile material at room temperature, a light brown solid (267 mg) was left behind which consisted mainly of  $N(CH_3)_4^+HPF_5^-$  [14].

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