aluminum oxide crystals with both iron and chromium ions, and it should be possible to extend the doping to all other transition metal ions, as long as the corresponding fluoride is available. Also, it is possible that this reaction may be modified by substituting aluminum fluoride with the various metal fluorides to give the corresponding metal oxides.

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Formation of Complex Fluoroborate Anions

BY J. J. HARRIS

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Complex fluorometallates or fluorometallate anions formed by sharing of fluorine atoms at a corner, edge, or face of a polyhedron containing the metal are well known. For example, AlF_4^- salts are formed by sharing of fluorine atoms at the edge of chains of the octahedra containing aluminum while AlF_5^- salts are formed by the sharing of a fluorine atom at the corners of long chains of the octahedra containing aluminum atoms.[1] Aluminum has been similarly reported to form anions of the type $Al_2Cl_7^-$ by sharing a chlorine atom.[2,3] Complex anions of similar types have not been reported involving boron trifluoride and the tetrafluoroborate anion,[3a] although complex borohydride anions including $B_2H_7^-$ are, of course, well-established.[4] Complex acids or salts of fluoroboric acid, *e.g.*, $K_4B_4F_{10}$, have been reported, but these salts are ill-defined and their existence is questionable.[5]

The boron trifluoride complexes of argon containing greater than 4 moles of boron trifluoride per mole of argon have been said to result from the addition of boron trifluoride molecules to fluorine atoms of the boron trifluoride molecules attached directly to the argon atom.[6] The strongly nucleophilic boron trifluoride molecule might also be expected to add to the negatively charged tetrafluoroborate anion giving a new species, $B_2F_7^-$. Further addition of boron trifluoride would give higher species such as $B_3F_{10}^-$ and $B_4F_{13}^-$. The absence of reports of adducts of this type indicates the tetrafluoroborate anion to be a very weak coordinating group, at least in its common environments.

We have found that certain amine tetrafluoroborate salts will absorb boron trifluoride to give the previously unreported $B_2F_7^-$ anion. The absorbed boron trifluoride can be removed quantitatively at reduced pressure with recovery of the original amine tetrafluoroborate salt. The amine salts investigated and the results at atmospheric pressure and 0° are shown in Table I.

TABLE I
ABSORPTION OF BORON TRIFLUORIDE BY AMINE TETRAFLUOROBORATE SALTS

Absorption	No absorption
$(C_2H_5)_3NH^+BF_4^-$	$C_2H_5NH_3^+BF_4^-$
$(i\text{-}C_3H_7)_2C_2H_5NH^+BF_4^-$	$sec\text{-}(C_4H_9)_2NH_2^+BF_4^-$
$(n\text{-}C_4H_9)_4N^+BF_4^-$	$(py)H^+BF_4^-$
	$(CH_3)_4N^+BF_4^-$

It is apparent from Table I that amine salts which will absorb boron trifluoride (at least at atmospheric pressure and 0°) contain relatively bulky cations. Thus the tetramethylammonium tetrafluoroborate salt gave no absorption of boron trifluoride while tetra-*n*-butylammonium tetrafluoroborate gave good boron trifluoride absorption. The tetrafluoroborate salts of bulky tertiary ammonium ions from triethylamine and diisopropylethylamine gave absorption of boron trifluoride, but the salt from the unhindered pyridinium cation gave no absorption of boron trifluoride. The critical factor is probably the distance between the tetrafluoroborate anion and the center of positive charge in the cation. When bulky cations are present the distance between the charged centers is increased to such an extent that the interaction of the cation and the tetrafluoroborate anion becomes relatively weak. The coordinating power of the tetrafluoroborate anion toward a nucleophile thus approaches its maximum potential value and it is able to coordinate with a free boron trifluoride molecule.

The mole ratio of absorbed boron trifluoride to salt is shown as a function of temperature in Table II.

TABLE II
MOLE RATIO OF ABSORBED BORON TRIFLUORIDE TO SALT

	Temp, °C				
Salt	0	25	50	75	100
$(i\text{-}C_3H_7)_2C_2H_5NH^+BF_4^-$	0.883	0.754	0.095	0.02	. . .
$(C_2H_5)_3NH^+BF_4^-$	0.891	0.712	0.542	0.369	0.236
$(n\text{-}C_4H_9)_4N^+BF_4^-$	1.01	1.00	1.00	0.772	0.699

In all instances the tetrafluoroborate salt was recovered quantitatively by placing the sample under reduced pressure at room temperature. It seems probable that at higher pressures and lower temperature further addition of boron trifluoride to the $B_2F_7^-$ anion to form species such as $B_3F_{10}^-$, etc., might occur.

The absorption of boron trifluoride causes several changes in the physical properties of the salt. These are as follows.

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(1) A. G. Sharpe, "Fluorine Containing Complex Salts and Acids," Vol. II, "Fluorine Compounds," J. H. Simons, Ed., Academic Press Inc., New York, N. Y., 1954, p 9.

(2) L. Ambroz and Z. Zlamal, *J. Polymer Sci.*, **30**, 381 (1958).

(3) V. A. Koptyug, V. G. Shubina, and A. I. Rezvukhim, *Izv. Akad. Nauk SSS, Ser. Khim.*, 201 (1965).

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(5) H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949.

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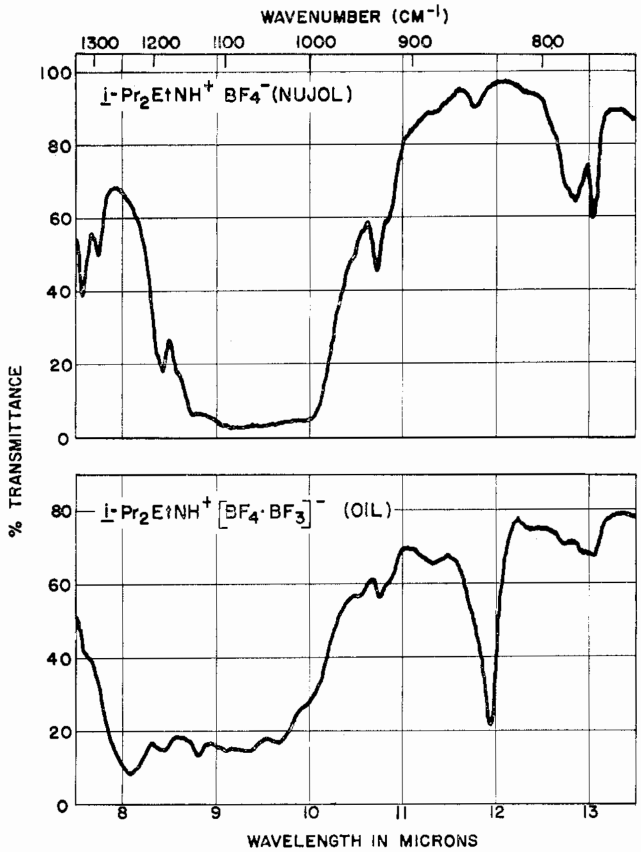

Figure 1.—Infrared absorption spectra of $(i\text{-}C_3H_7)_2C_2H_5NH^+$-$BF_4^-$ (Nujol) and $(i\text{-}C_3H_7)_2C_2H_5NH^+[BF_4\cdot BF_3]^-$ (oil).

(1) The meltng point of the salt is lowered. Thu diisopropylethylammonium tetrafluoroborate (mp 214° and triethylammonium tetrafluoroborate (mp 107° each become liquid at 0° when allowed to react with boron trifluoride. Tetra-*n*-butylammonium tetrafluoroborate (mp 161°) is liquid at 80° after absorbing boron trifluoride.

(2) The infrared spectra are changed in the bands characteristic of the tetrafluoroborate anion. The intense tetrafluoroborate band[7] at 1150–1000 cm^{-1} is weakened while a new band centered at 1220 cm^{-1} is formed. Further, the tetrafluoroborate band[7] at 763 cm^{-1} is replaced by a much stronger, relatively sharp band at 833 cm^{-1}. The spectrum of diisopropylethylammonium tetrafluoroborate is shown in Figure 1 between 1335 and 741 cm^{-1} before and after absorption of boron trifluoride. The spectrum of the other $B_2F_7^-$ adducts is quite similar in this region.

(3) The F^{19} nmr spectrum of a benzene solution of diisopropylethylammonium tetrafluoroborate boron trifluoride adduct (exact ratio not known since BF_3 was lost during sampling) has a single sharp line 144.2 ppm upfield from $CFCl_3$. This is intermediate between boron trifluoride, 132.6 ppm upfield from $CFCl_3$, and tetrafluoroborate anion, 149.4 ppm upfield from $CFCl_3$.[8,9] Rapid equilibration of the species apparently causes all the fluorine atoms to become equivalent even though the sample prepared at 25° had less than equimolar quantities of boron trifluoride.

(4) The benzene-insoluble salts $(i\text{-}C_3H_7)_2C_2H_5NH^+$-$BF_4^-$, $(C_2H_5)_3NH^+BF_4^-$, and $(n\text{-}C_4H_9)_4N^+BF_4^-$, after absorbing boron trifluoride, become miscible with a limited quantity of benzene. Addition of larger quantities of benzene gives a two-layer system. For example, an oil from 4.172 g (0.0221 mole) of triethylammonium tetrafluoroborate and 0.960 g (0.0142 mole) of boron trifluoride absorbs 3.383 g of benzene before formation of two layers occurs.

It may be possible for tetrafluoroborate salts to complex other Lewis acids; however no reaction was noted between diisopropylethylammonium tetrafluoroborate and one other Lewis acid, phosphorus pentafluoride.

Experimental Section

Reagents.—Tetramethylammonium tetrafluoroborate from Ozark Mahoning Co. was recrystallized from water–methanol. Tetra-*n*-butylammonium tetrafluoroborate was prepared in 80% yield from the reaction of tetra-*n*-butylammonium bromide and boron trifluoride etherate,[11] then recrystallized from benzene. Diisopropylethylammonium tetrafluoroborate and di-*sec*-butylammonium fluoroborate were by-products of previously reported investigations.[12] Pyridinium tetrafluoroborate and triethylammonium tetrafluoroborate were prepared from the reaction of the amine and boron trifluoride etherate in methanol.[13] Ethylammonium tetrafluoroborate was prepared from the reaction of ethylamine and fluoroboric acid. All salts were analyzed with the nitron reagent.[14] The results and melting points are given in Table III.

Table III

Analysis and Melting Points of Salts

Salt	BF_4 Found	BF_4 Theory	Melting point, °C Found	Melting point, °C Reported
$C_2H_5NH_3^+BF_4^-$	65.17	65.33	147–149	
sec-$(C_4H_9)_2NH_2^+BF_4^-$	39.76	40.10	142–144	
$(C_2H_5)_3NH^+BF_4^-$	45.81	45.93	106–108	106.5–108[a]
$(i\text{-}C_3H_7)_2C_2H_5NH^+BF_4^-$	40.00	40.10	213–215	
$(py)H^+BF_4^-$	51.92	52.01	216–222	217[b]
$(CH_3)_4N^+BF_4^-$	53.74	53.94	>400	417–419[c]
n-$(C_4H_9)_4N^+BF_4^-$	26.15	26.37	160–161.5	161.8[d]

[a] E. Mueller and H. Huber-Emden, *Ann.*, **649**, 70 (1961). [b] I. G. Ryss and S. L. Idel's, *Zh. Neorgan. Khim.*, **2**, 2270 (1957). [c] C. M. Wheeler and R. A. Sandstedt, *J. Am. Chem. Soc.*, **77**, 2025 (1955). [d] C. R. Witschonke and C. A. Kraus, *ibid.*, **69**, 2472 (1947).

All salts were dried by azeotroping in benzene and had no trace of OH bands in the infrared spectra when very concentrated samples were run. Any residual moisture in the sample would cause formation of $BF_3\cdot H_2O$. Thus residual moisture would be indicated by failure of the $B_2F_7^-$ salt to return to its original weight when placed under reduced pressure. Solvents were dried over calcium hydride.

Procedure.—The salts were placed in a 50-ml flask fitted with a two-way stopcock connected to a vacuum supply and a boron trifluoride source and any net absorption noted. Quantitative measurements were made by introducing a chloroform solution

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[7] G. L. Cote and H. W. Thompson, *Proc. Roy. Soc.* (London), **A210**, 217 (1951).

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[11] C. M. Wheeler and R. A. Sandstedt, *J. Am. Chem. Soc.*, **77**, 2024 (1955).

[12] J. J. Harris and B. Rudner, Abstracts of Papers, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 251.

[13] P. A. van der Meulen and H. A. Heller, *J. Am. Chem. Soc.*, **54**, 4404 (1932).

[14] C. A. Lucchesi and D. D. DeFord, *Anal. Chem.*, **29**, 1169 (1957).

of the salt into a glass bulb into which a Teflon-coated magnetic stirring bar had been sealed prior to the bulb being fitted with a stopcock. When the salts from diisopropylethyl amine and triethylamine were studied the chloroform was removed at reduced pressure, then the bulb was stirred in a boron trifluoride atmosphere until absorption was completed at that temperature. Tetra-*n*-butylammonium tetrafluoroborate, which does not become liquid at room temperature when treated with boron trifluoride, was "freeze-dried" to give a solid of large surface area. The chloroform solution was diluted 3 to 1 with benzene, the contents frozen, and then the solvent removed at reduced pressure. In either instance the amount of boron trifluoride absorbed was calculated from the weight gain of the bulb (after correction for the boron trifluoride atmosphere in the bulb).

The infrared spectra were obtained in a NaCl cell. The cell plates were not affected by the salt.

Nmr measurements were made by Varian Associates, Palo Alto, Calif.

CONTRIBUTION FROM THE GORGAS LABORATORY,
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Dimethylfluoramine

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The fluorination of sulfamide in aqueous solution produced N,N-difluorosulfamide in moderate yield.[1] An attempt was made to extend this reaction to include the methyl-substituted sulfamides. It was found that the fluorination of unsymmetrical dimethylsulfamide in an unbuffered solution did not yield the desired dimethyldifluorosulfamide. Instead, dimethylfluoramine was isolated along with small amounts of methyldifluoramine. The yield of dimethylfluoramine could be increased by performing the fluorination under conditions which reduced the local fluorine concentration and promoted the rapid removal of the products from the reactor. For this reason, higher yields were obtained when the fluorination was carried out at 30° rather than at 0°. Potassium dimethylsulfamate could be used instead of the dimethylsulfamide. However, little or no dimethylfluoramine was obtained when tetramethylsulfamide was employed. This is, in part, believed to be due to the low solubility of the tetramethyl derivative in the aqueous media.

Dimethylfluoramine is a colorless volatile liquid which is not stable at ambient temperature (extrapolated bp 29.5°, mp $-113 \pm 0.5°$). The F^{19} nmr spectrum of the compound consists of a septuplet ($J_{HF} = 35$ cps) centered at ϕ 24.5 while the H^1 nmr spectrum is a doublet ($J_{HF} = 35$ cps) centered at -2.95 ppm (*vs.* TMS). The coupling is consistent with that expected for one fluorine and six equivalent protons. The mass cracking pattern of dimethylfluoramine, in addition to containing a peak for the parent molecular ion, $(CH_3)_2NF^+$, contains peaks for both molecular ions, HF^+ and CF^+. This suggests that some rearrangements occurred in the ionization process. The high boiling point relative to dimethylamine is probably due to an increase in the molecular weight of the molecule since the Trouton constant appears normal. The molecular weight of the vapor, determined by the mass spectral effusion method,[2] showed no association (found, 65; calcd, 63.0).

Dimethylfluoramine formed a nonvolatile, slightly yellow oil, on standing at room temperature for several hours. The oil was water soluble and did not oxidize hydrogen iodide. The decomposition could be followed in aqueous solution by F^{19} nmr, and after 30 min the septuplet began to decrease in intensity and a new signal appeared in the fluoride ion region. The half-life of the decomposition at 25° was approximately 3 hr. No decomposition was observed in samples stored at -5 to 0° over a 6-day period. Upon warming these stored samples to ambient temperature, decomposition occurred. The exact nature of the decomposition product is not known although its lack of volatility suggests that it may be polymeric. Dimethylfluoramine reacted with all conventional drying agents such as Drierite, magnesium sulfate, and molecular sieves.

Since difluoramine and methyldifluoramine still retain some basicity,[3] it was of interest to test the basicity of dimethylfluoramine. When dimethylfluoramine was exposed to an atmosphere of dry hydrogen chloride, a white, crystalline solid formed and 1 mole of acid/mole of substrate was absorbed.

$$(CH_3)_2NF + HCl \longrightarrow (CH_3)_2NF \cdot HCl$$

The solid was purified by sublimation under high vacuum at ambient temperature. It was soluble in water and alcohol producing a solution which readily oxidized hydrogen iodide. It was not soluble in acetonitrile, benzene, or methylene chloride. A concentrated aqueous solution decomposed violently when allowed to warm to room temperature. The pure compound melted at 64–65° (sealed tube) and was stable in a dry atmosphere if stored at temperatures below 10°. At higher temperatures slow decomposition occurred producing HCl, HF, and a colorless, nonvolatile oil similar to that formed from the decomposition of the free dimethylfluoramine. The F^{19} nmr spectrum of $(CH_3)_2NF \cdot HCl$ contained a broad, unresolved band at ϕ 8.5 which shows that the product does not contain fluoride ion. Further evidence for the retention of the N–F bond in $(CH_3)_2NF \cdot HCl$ is the fact that dimethylfluoramine could be regenerated from the adduct by treatment with bases such as trimethylamine N-oxide or pyridine.

$$(CH_3)_2NF \cdot HCl + (CH_3)_3N{\rightarrow}O \longrightarrow (CH_3)_2NF + (CH_3)_3NO \cdot HCl$$

This reaction provides an efficient method for the purification of dimethylfluoramine although the recovery of $(CH_3)_2NF$ is not quantitative. The nature of the

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(2) M. Eden, B. E. Burr, and A. W. Pratt, *Anal. Chem.*, **23**, 1735 (1951).

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