

is obvious, and a consistent solution can be obtained only with the indicated assignment of the pair at highest frequency. There is however no clear choice between the ν_1 transition for ^{121}Sb and ν_2 for ^{123}Sb in the assignment of the overlapping resonances near 21 MHz. Solution of the secular equations by the method of Reddoch⁸ according to both possibilities gives the results shown in Table II. Clearly the asymmetry parameters obtained for each isotope are in excellent agreement, and the ratio of the coupling constants obtained for the two antimony isotopes is very close to that reported in the literature. However, no distinction can be made between the two possible assignments of the antimony transitions near 21 MHz based on a significantly better agreement of the derived parameters for one or the other.

Table II. Parameters Calculated from Antimony Assignments for $\text{I}_2\text{Cl}^+\text{SbCl}_6^-$

Assignment	^{121}Sb		^{123}Sb	
	Table I	Alternate ^b	Table I	Alternate ^b
Asym parameter ^a	0.3794	0.3805	0.3811	0.3799
e^2Qq/h , ^a MHz	122.244	122.261	155.843	155.766

Q_{123}/Q_{121} : Table I, 1.27486; alternate,^b 1.27404; ref 9, 1.27474

^a Data measurement errors alone are estimated to give an uncertainty of ± 4 in the last digits shown. ^b t_7 and t_8 reversed in Table I.

The observation of four independent chlorine atoms for the SbCl_6^- anion indicates the group possesses C_s or C_{2v} point symmetry in the crystal, provided of course that all resonances have been observed. If intensities are meaningful, each of the higher frequency transitions (t_9 and t_{10}) corresponds to two equivalent atoms, but this conclusion is necessarily speculative.

Although an antimony asymmetry parameter of 0.38 may seem rather large for the central atom in a nominally octahedral complex, Schneider and DiLorenzo¹⁰ have pointed out that such a value can result from only $\sim 3\%$ imbalance in the p-orbital population relative to axial symmetry. Angular distortions are particularly effective in this respect. The spread of almost 5 MHz in the ^{35}Cl transitions is consistent with (but of course not proof of) the observed asymmetry. Transition averages of 23.7 ± 0.7 MHz with ranges of less than 1 MHz have been cited as characteristic of ^{35}Cl in relatively unperturbed SbCl_6^- ions (at 77°K);⁷ the present ^{35}Cl transitions still average 23.08 MHz without regard to possible multiplicity. Raman data for this compound also support the presence of an SbCl_6^- ion with appreciable distortion, the e_g mode being split by 36 cm^{-1} or 13%.⁴

A distortion of the SbCl_6^- ion of the amount indicated is certainly not without precedent. Variations of over 0.20 Å in antimony-chlorine distances and 3° in angles in other hexachloroantimonate(V) salts have been observed and attributed to packing effects.¹¹ In addition specific interactions with the I_2Cl^+ cation may not be negligible. In the presumably similar $\text{ICl}_2\text{SbCl}_6^-$ the V-shaped cation has two more distant chlorine atom neighbors in anions which complete a roughly rectangular arrangement about the iodine.¹² This (and perhaps packing) then gives a 0.15-Å range (6.5% or 4σ) in Sb-Cl distances and a 13.6° range in angles at antimony in $\text{ICl}_2\text{SbCl}_6^-$.

(8) A. H. Reddoch, *J. Chem. Phys.*, **35**, 1089 (1961).

(9) T.-C. Wang, *Phys. Rev.*, **99**, 566 (1955).

(10) R. F. Schneider and J. V. DiLorenzo, *J. Chem. Phys.*, **47**, 2349 (1967).

(11) S. K. Porter and R. A. Jacobson, *Cryst. Struct. Commun.*, **1**, 431 (1972).

Insufficient nqr data for the present I_2Cl^+ cation, especially ν_2 for the central iodine, make it difficult to judge whether bonding to the anion is reflected in cation transitions. Previous correlations of structural parameters and nqr transitions in ICl_2^+ and I_3^+ were aided by the higher symmetry of the cation. The structures of $\text{ICl}_2^+\text{AlCl}_4^-$ and $\text{ICl}_2^+\text{SbCl}_6^-$ ¹² have not been determined well enough to allow any predictions to be made regarding the relative basicity of the two anions.

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Registry No. $\text{I}_2\text{Cl}^+\text{SbCl}_6^-$, 38656-79-0; ^{35}Cl , 13981-72-1; ^{37}Cl , 13981-73-2; ^{121}Sb , 14265-72-6; ^{123}Sb , 14119-16-5; ^{127}I , 7553-56-2.

(12) C. Vonk and E. Wiebenga, *Acta Crystallogr.*, **12**, 859 (1959).

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Hydrogen Bonding. II. Complex Fluoride Salts of Arylammonium Ions¹

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In the course of investigations² into the possible existence of ions of the type $[(\text{OH}^-)_n\text{F}_{4-n}\text{H}^+_m]^{m-4}$ we became interested in salts of the H_3F_4^- anion, a simple species where $n = 0$ and $m = 3$. Reported examples of solid-phase, crystalline higher hydrogen fluoride complexes fall into two stability classes. With simple metal cations such as the alkali metals the order of anion stability is $\text{HF}_2^- > \text{H}_2\text{F}_3^- > \text{H}_3\text{F}_4^-$,³ which is what would be expected if the H_3F_4^- ion is either a linear extension of the H_2F_3^- ion, which is known⁴ to have two hydrogen fluoride moieties hydrogen bonded to a central fluoride ion, or is a less likely species with three hydrogen fluorides hydrogen bonded to a single fluoride. On the other hand, with hydrogen-bonding cations such as hydronium⁵ or ammonium⁶ the order of anion stability is $\text{HF}_2^- > \text{H}_3\text{F}_4^-$, and the H_2F_3^-

(1) Work supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, and the Oakland University Research Committee. Part I: K. M. Harmon and R. R. Lake, *Inorg. Chem.*, **7**, 1921 (1968).

(2) K. M. Harmon, S. L. Madeira, R. W. Carling, and D. L. Duffy, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Tex., April 13, 1973, No. INOR 163.

(3) (a) H. Moissan, *C. R. Acad. Sci.*, **106**, 548 (1888); (b) H. Wartenberg and G. Klinkott, *Z. Anorg. Allg. Chem.*, **193**, 409 (1930); (c) G. H. Cady, *J. Amer. Chem. Soc.*, **56**, 1431 (1934); (d) E. B. R. Prideaux and K. R. Webb, *J. Chem. Soc.*, **1** (1937); (e) J. S. Morrison and A. W. Jache, *J. Amer. Chem. Soc.*, **81**, 1821 (1959); (f) R. L. Adamczak, J. A. Mattern, and H. Tieckelmann, *J. Phys. Chem.*, **63**, 2063 (1959); (g) A. A. Opalovskii and T. D. Fedotova, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, **50** (1967).

(4) J. D. Forrester, M. E. Senko, A. Zalkin, and D. H. Templeton, *Acta Crystallogr.*, **16**, 58 (1963).

(5) G. H. Cady and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **52**, 3843 (1930).

(6) (a) T. L. Higgins and E. F. Westrum, Jr., *J. Phys. Chem.*, **65**, 831 (1961); (b) R. D. Euler and E. F. Westrum, Jr., *ibid.*, **65**, 1291 (1961).

salt is not observed in the solid phases. This suggests an unexpected stabilization of the H_3F_4^- ion relative to H_2F_3^- in crystalline salts with hydrogen-bonding cations.

One apparent example of this stability was reported by Berliner and Hann,⁷ who, in attempts to prepare a series of anilinium fluorides, obtained remarkably stable crystalline materials with low nitrogen and high fluorine analysis; careful analysis of these compounds led to their formulation as H_3F_4^- salts.

This was of considerable interest to us, as we had found that solution of either aniline or *p*-toluidine in liquid hydrogen fluoride followed by evaporation of solvent gave the hydrogen difluoride salts without any significant halt in vapor pressure until the HF_2^- salt was reached. Thus, if the Berliner compounds were indeed H_3F_4^- salts, they represented a thermodynamically stable species that we had failed to prepare for kinetic reasons.

We have prepared some of the Berliner compounds (not without initial difficulty; see Discussion) and through elemental analyses, infrared spectra, and comparison with materials prepared *via* known routes identified them as hexafluorosilicates. The mistaken identification by Berliner and Hann was the result of a truly remarkable web of fortuitous analytical overlaps.

The preparation of simple anilinium fluorides may well be thermodynamically impossible, except possibly in the case of bases with strong electron-withdrawing groups on the ring; we find that *p*-toluidinium fluoride is unstable with respect to an equimolar mixture of *p*-toluidinium hydrogen difluoride and the free base *p*-toluidine.

Experimental Section

Reactions with anhydrous hydrogen fluoride were carried out in a Monel vacuum system with copper cells, and reactions with 48% hydrofluoric acid were run in polyethylene labware. Eastman Kodak White Label amines were purified by distillation or crystallization as appropriate. Infrared spectra were determined on a Beckman IR-12 spectrophotometer, using Nujol mulls. Silica was prepared by grinding a Beckman ultraviolet cell in a mortar.

Anilinium Hydrogen Difluoride. Excess liquid hydrogen fluoride was condensed on aniline (2.66 g, 28.6 mmol) and then allowed to evaporate; subsequently, the cell was evacuated (1 Torr) for 10 min at room temperature. When opened it contained a 99.5% yield of anilinium hydrogen difluoride (3.78 g, 28.4 mmol) as white crystals. *Anal.* Calcd for $\text{C}_6\text{H}_9\text{NF}_2$: HF, 29.93. Found: HF, 30.01.

***p*-Toluidinium Hydrogen Difluoride.** A similar reaction to the one above using *p*-toluidine (1.30 g, 12.2 mmol) gave a 99.2% yield of *p*-toluidinium hydrogen difluoride (1.78 g, 12.1 mmol) as white prisms. *Anal.* Calcd for $\text{C}_7\text{H}_{11}\text{NF}_2$: HF, 27.19. Found: HF, 27.29.

***p*-Toluidinium Hexafluorosilicate.** Silica (0.902 g, 15.0 mmol) was dissolved in 48% hydrofluoric acid (20 ml) and *p*-toluidine (6.88 g, 64 mmol) added. A crop of crystals formed on standing; these were separated on a plastic frit, washed with water, and dried *in vacuo* to yield 48.7% *p*-toluidinium hexafluorosilicate (2.63 g, 7.34 mmol) as white prisms. *Anal.* Calcd for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{SiF}_6$: C, 46.91; H, 5.62; N, 7.82; F, 31.81; Si, 7.84; neutralization equivalent, 59.73.⁹ Found: C, 46.84; H, 5.46; N, 7.75; F, 32.02; Si, 7.78; neutralization equivalent, 59.15.¹⁰ The salt is nonhygroscopic and stable to air. The infrared spectrum is that of a *p*-toluidinium cation with weak N-H...X hydrogen bonding ($\nu_s(\text{N-H})$ 3180 cm^{-1} (vs)) and in addition shows the two strong bands (715 and 782 cm^{-1}) of the SiF_6^{2-} anion. No O-H or H-F bands are observed.

(7) J. F. T. Berliner and R. M. Hann, *J. Phys. Chem.*, **32**, 1142 (1928).

(8) Contrary to some reports,⁹ the hexafluorosilicate anion is smoothly titrated by base; for our reaction the equation is $2\text{RNH}_3^+ + \text{SiF}_6^{2-} + 6\text{OH}^- = 2\text{RNH}_2 + \text{SiO}_2 + 6\text{F}^- + 4\text{H}_2\text{O}$.

(9) For example: F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1972, p 326.

(10) Elemental analyses by Galbraith Laboratories, Inc.

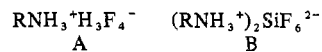
***N*-Ethylanilinium Hexafluorosilicate.** A reaction similar to that above between *N*-ethylaniline (0.958 g, 7.80 mmol) and silica (0.275 g, 4.38 mmol) gave an 86.2% yield of *N*-ethylanilinium hexafluorosilicate (1.317 g, 3.40 mmol) as white microcrystals, mp 170–170.5°. *Anal.* Calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{SiF}_6$: neutralization equivalent, 64.41. Found:⁹ neutralization equivalent, 64.38.

Attempted Preparation of *p*-Toluidinium Fluoride. A slurry of *p*-toluidine (7.02 g, 64.0 mmol) in water was neutralized with 1.19 *N* hydrofluoric acid (55.4 ml, 64 mmol) to the phenolphthalein end point. A clear solution was obtained; however, the odor of *p*-toluidine was still apparent. The water was evaporated at room temperature to yield a solid that appeared to be a mixture of two crystalline types; sublimation of *p*-toluidine occurred during the evaporation. The mixture was triturated with methylene chloride and the residual crystals dried *in vacuo* to yield 100% *p*-toluidinium hydrogen difluoride (4.70 g, 32.0 mmol), identified by its infrared comparison with authentic material; the methylene chloride was evaporated to yield 94.2% (3.30 g, 30.2 mmol) of the missing *p*-toluidine. Reaction mixtures prepared by this route could also be separated quantitatively by sublimation.

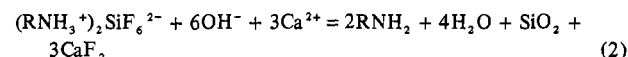
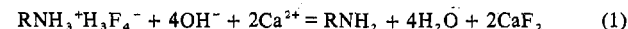
Results and Discussion

Preparation of Compounds. In numerous early attempts to prepare the presumed H_3F_4^- salts reported by Berliner and Hann by addition of 48% hydrofluoric acid to arylamines in ether or acetone we were only able to obtain the hydrogen difluoride salt. In seeking a parameter to explain the difference in our results, we were informed by Dr. Berliner that they had used ceresin wax bottles and labware. We obtained an ancient ceresin wax bottle in which hydrofluoric acid had been sold; use of hydrofluoric acid which had been allowed to stand in the bottle in the above reactions gave, in addition to the hydrogen difluorides, small quantities of materials whose properties resembled the reported " H_3F_4^- " salts; these compounds are hexafluorosilicates, as shown by infrared spectral analysis and the direct synthesis of the *p*-toluidinium salt. The similarity of the melting points of *N*-ethylanilinium hexafluorosilicate (170–170.5°) to that reported⁷ for the " H_3F_4^- " salt of *N*-ethylanilinium ion (170–171°) confirms our belief that the " H_3F_4^- " salts were hexafluorosilicates derived from silica in the ceresin wax or in the hydrofluoric acid.

Analyses of the " H_3F_4^- " Salts. Berliner and Hann⁷ were extremely careful in their approach to the identification of the " H_3F_4^- " salts; their mistaken identification arises from a remarkable web of coincidence. If we consider a salt of a given cation of type A or type B, we find that the



percentage of nitrogen is nearly identical for the whole series of salts that Berliner and Hann examined whether formulated as A or B. The carbon analyses of the B salts are several per cent higher than for the A; however, Berliner and Hann found conventional combustion to give carbon values several per cent too high and used a different method;¹¹ we have not evaluated whether the use of this technique will indeed give low results with this series of salts. The most puzzling ambiguity arises in the fluorine per cent values, which differ considerably for the type A and type B salts. If we consider the precipitation equations for the two types, the ambiguity is explained. (See eq 1 and 2.)



Berliner and Hann first dissolved the salts in base, neutralized

(11) H. D. Wilde and H. L. Lochte, *J. Amer. Chem. Soc.*, **47**, 440 (1925).

the solution, and added calcium ion. Since the salts were hexafluorosilicates the reaction was as shown in eq 2, and the calcium fluoride contained silica; however, if the combined weight of calcium fluoride and silica is *presumed to be calcium fluoride*, the percentage of fluorine calculated for this series of salts fits well with the " H_3F_4^- " type A formulation.

Titration of *p*-toluidinium hexafluorosilicate gives a titration curve that matches the curve obtained by Berliner and Hann, with a sharp break at the theoretical amount of base (pH 7.5) and a gradual rise between pH 9 and 11. This latter consumption of base, which they attributed to the fourth mole of acid in the salts, arises from adsorption of base on hydrous silica.

Infrared Spectrum of *p*-Toluidinium Hydrogen Difluoride. Williams and Schneemeyer¹² have recently published the neutron diffraction structural study of *p*-toluidinium hydrogen difluoride; the anion in this salt has an unsymmetrical linear hydrogen bond and is hydrogen bonded to the ammonium group by two types of N-H...F hydrogen bonds.

(12) J. M. Williams and L. F. Schneemeyer, *J. Amer. Chem. Soc.*, **95**, 5790 (1973).

We find that the infrared spectrum of this salt reflects these properties. There are two N-H stretching bands which reflect respectively strong and very strong hydrogen bonding at 3000 and 2650 cm^{-1} , and the ν_2 bending mode of the anion, which is a degenerate singlet in potassium hydrogen difluoride,¹³ is a deeply cleaved doublet at 1080 and 1230 cm^{-1} as a result of the lifting of this degeneracy in the asymmetric crystal environment¹² in the toluidinium salt. The asymmetric stretching band, ν_3 , of the anion, which is found at 1450 cm^{-1} in the potassium salt, is found as a broad band centered at 1740 cm^{-1} in the *p*-toluidinium salt, which indicates a weaker hydrogen bond in the latter material.

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Registry No. Anilinium hydrogen difluoride, 51004-15-0; *p*-toluidinium hydrogen difluoride, 40999-66-4; *p*-toluidinium hexafluorosilicate, 51065-34-0; *N*-ethylanilinium hexafluorosilicate, 51004-23-0.

(13) J. A. A. Ketelaar and W. Vedder, *J. Chem. Phys.*, **19**, 654 (1951).