[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Crystal Structures of Rubidium and Ammonium Fluoborates

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Introduction

Potassium and rubidium fluoborates have been reported[1] to be isomorphous with the corresponding perchlorates, which are known[2] to possess the barite structure. No crystallographic data have been reported for ammonium fluoborate, a compound of most interesting chemical properties.[3] Although an ammonium salt is expected usually to be isomorphous with the analogous potassium or rubidium salt, the formation in a number of fluorides of hydrogen bonds between nitrogen and fluorine has been observed[4] to result in fundamental changes in structural type. Inasmuch as no fluoborate had been previously studied by x-ray methods, and since, moreover, we considered it quite possible that hydrogen bonds might exist in the ammonium salt and cause it to assume a different structural type, we have carried through structure determinations for rubidium fluoborate and ammonium fluoborate. We have found that both compounds belong to the barium sulfate structural type; the structure of the ammonium salt seems, however, to be somewhat modified as a result of hydrogen bond formation.

Ammonium fluoborate was prepared by adding ammonia to a solution of boric acid in 45% hydrofluoric acid, and evaporating to dryness. The ammonium fluoborate was purified by sublimation and recrystallized from aqueous solution.

Rubidium fluoborate was crystallized from a solution prepared by dissolving equivalent quantities of rubidium chloride and boric acid in 45% hydrofluoric acid. Even after recrystallization under conditions of constant temperature at 0°, no specimen was obtained measuring as much as 1 mm. in its longest dimension.

Data for the x-ray study were obtained from Laue and oscillation photographs.

Determination of the Structure

Using the notation of Wyckoff,[2] which is also the assignment of axes customarily used by crystallographers for crystals with the barite structure, the smallest unit of structure of ammonium fluoborate is an orthorhombic one with $a_0 = 9.06$ Å., $b_0 = 5.64$ Å., $c_0 = 7.23$ Å., containing $4NH_4BF_4$. The similar unit of rubidium fluoborate has $a_0 = 9.07$ Å., $b_0 = 5.60$ Å., $c_0 = 7.23$ Å., also containing four molecules. Although lattice constants are known only to within about half a per cent., it seems sure that b_0 is definitely smaller in the rubidium salt. The units in both cases are confirmed by extensive Laue and oscillation data.

All lattices except the simple orthorhombic are eliminated by the appearance of "forbidden" reflections. The regular vanishings[5] are those required by the space groups C_{2v}^9 and V_h^{16}. The morphology of the crystals is apparently holohedral, and we are able to base a satisfactory structure on V_h^{16}-*Pnma*.

Upon investigation we find it possible to assign both ammonium and rubidium fluoborates to the barite structural type. The positions of the various kinds of atoms together with the parameter values which lead to reasonably good agreement between calculated and observed intensities are given below (the notation is that of Wyckoff, Reference 2, page 283). The positions used are

$4(c)$: $u\frac{1}{4}v$; $u + \frac{1}{2}, \frac{1}{4}, \frac{1}{2} - v$, $\bar{u}\frac{3}{4}\bar{v}$; $\frac{1}{2} - u, \frac{3}{4}, v + \frac{1}{2}$, and $8(d)$: xyz; $x, \frac{1}{2} - y, z$; $x + \frac{1}{2}, y, \frac{1}{2} - z$; $x + \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$; $\bar{x}\bar{y}\bar{z}$; $\bar{x}, y + \frac{1}{2}, \bar{z}$; $\frac{1}{2} - x, y, z + \frac{1}{2}$; $\frac{1}{2} - x, y + \frac{1}{2}, z + \frac{1}{2}$.

We find

$RbBF_4$

4 Rb in $4(c)$ with $u = 0.315$, $v = 0.335$; 4 B in $4(c)$ with $s = 0.932$, $t = 0.696$; 4 F_I in $4(c)$ with $o = 0.069$, $p = 0.597$; 4 F_{II} in $4(c)$ with $m = 0.813$, $n = 0.567$; 4F_{III} in $8(d)$ with $x = 0.923$, $y = 0.043$, $z = 0.810$.

NH_4BF_4

4 NH_4 in $4(c)$ with $u = 0.308$, $v = 0.328$; 4 B in $4(c)$ with $s = 0.947$, $t = 0.697$; 4 F_1 in $4(c)$ with $o = 0.086$, $p = 0.603$; 4 F_{II} in $4(c)$ with $m = 0.830$, $n = 0.563$; 4 F_{III} in $8(d)$ with $x = 0.936$, $y = 0.043$, $z = 0.811$.

We next outline the procedure followed in determining the listed parameter values.

The relatively large atomic number of rubidium

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[1] F. Zambonini, *Z. Krist.*, **41**, 57 (1905); T. V. Barker, *J. Chem. Soc.*, **101**, 2484 (1912).

[2] R. W. G. Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York City, 2d ed., p. 289.

[3] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longman, Green and Co., New York City, 1924, Vol. V, p. 127.

[4] Linus Pauling, *Z. Krist.*, **85**, 380 (1933).

[5] Astbury and Yardley, "Tabulated Data for the Examination of the 230 Space Groups by Homogeneous X-Rays," *Phil. Trans.*, **224**, 221 (1924).

causes it to assume a dominating role in the x-ray scattering by rubidium fluoborate. As a first approximation we neglect the scattering of the lighter atoms, and use the intensity data to fix rough values of the rubidium parameters; because of the near identity in size of NH_4^+ and Rb^+ we may assume that we also obtain by this process approximate values of the ammonium parameters. We then introduce other atoms in the general regions to be anticipated, and calculate intensities for various combinations of the parameter values until we obtain a fairly detailed agreement with the observed intensities. This procedure is greatly simplified by the reasonable assumption of a regular BF_4^- tetrahedron. The size of the tetrahedron thus assumed can be determined, although only roughly, from a consideration of the (0*k*0) reflections, which involve but one degree of freedom. Thermal vibrations of the atoms within the lattice are responsible for a large and unknown decrease in atomic scattering powers. We can say only that observed intensity data fix the parameter of fluorine along *b* so as to limit the B–F separation (assuming a regular tetrahedron) to the range between about 1.40 and 1.47 Å. A value[6] of 1.43 Å. for this interatomic distance, obtained from the theoretical work of Pauling on ionic and covalent radii, is employed in the parameter determinations reported in this paper.

In Table I we give comparisons between calculated and observed intensities of x-ray reflections for a variety of planes. The *f*-values of Pauling and Sherman[7] are employed throughout this paper. No temperature factor is included, so that with increasing sin Θ continually mounting discrepancies between calculated and observed intensities are to be anticipated. By comparison with a scale prepared for the purpose, we have visually estimated the listed intensities; large differences in intensities, irregular crystal shapes, and the collection of data from various photographs combine to make these estimates rather uncertain. We have, nevertheless, attached numerical values to them, for we regard this scheme as more illuminating and somewhat more precise than the appellations "strong," "weak," etc. To compare relative intensities of corresponding reflections between the two salts, the values given for rubidium fluoborate must be multiplied by five.

TABLE I

COMPARISON OF CALCULATED WITH OBSERVED INTENSITIES OF X-RAY REFLECTIONS

	$RbBF_4$			NH_4BF_4	
	Intensities			Intensities	
(*hkl*)	Calcd.	Obsd.	(*hkl*)	Calcd.	Obsd.
200	14	16	200	42	36
400	4.5	3	400	14	9
600	1.4	1	600	9.6	2
800	33	8	800	28	4
020	86	96	020	54	48
040	65	32	040	62	12
060	16	3	060	11	1.5
080	4.0	0	080	1.4	0
002	43	36	002	53	48
004	14	9	004	8.6	3
006	13	6	006	1.2	<1
008	7.0	2	008	8.4	1.5
011	18	12	011	22.5	32
022	0.3	0	022	49.0	32
031	26	16	031	3.6	2
042	6.0	0	042	0.2	0.5
051	1.6	0	051	10.9	3
101	0.6	0	101	8.9	12
201	3.5	3	201	26.0	32
301	5.1	3	301	15.0	4
401	53	24	401	53.0	32
501	13	2	501	0.3	0
102	34	24	102	1.9	2
103	17	8	103	23.0	12
104	4.5	2	104	2.2	2
105	4.5	1	105	19.0	6
210	79	96	210	43	32
220	41	36	220	52	16
230	7.0	3	230	1.7	1
240	5.1	2	240	2.9	0
410	68	48	410	38	16

In consideration of the many parameters which are involved and the uncertainties already mentioned the intensity data of Table I seem quite consistent. The true parameter values may well differ appreciably from those given; we believe, however, that the structures of these two compounds are actually somewhat different. This point is made clear in the next section.

Discussion of the Structure

A diagram of the structure of ammonium fluoborate is shown in Fig. 1. A list of the interatomic separations which have a direct bearing upon the question of the stability of these structures is given in Table II.

The coördination of fluoride about rubidium ions is such as to place 12 F^- about each Rb^+ at distances ranging from 2.90 to 3.46 Å., with an average value of 3.05 Å. Each NH_4^+ is surrounded by 12 F^- at distances ranging from 2.83 to 3.39 Å., also with an average value of 3.05 Å.

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(6) Private communication from Professor Pauling.

(7) Pauling and Sherman, *Z. Krist.*, **81**, 1 (1932).

TABLE II

INTERATOMIC DISTANCES IN RUBIDIUM AND AMMONIUM FLUOBORATES

RbBF$_4$			NH$_4$BF$_4$		
Atom	Neighbor	Separations, Å.	Atom	Neighbor	Separations, Å.
B	F_I, F_{II}, 2F_{III}	1.43	B	F_I, F_{II}, 2F_{III}	1.43
Rb	F_I	2.91	N	F_I	2.83
Rb	F_{II}	2.92	N	F_{II}	2.83
Rb	2F_{III}	2.89	N	2F_{III}	2.86
Rb	2F_{III}	2.91	N	2F_{III}	2.94
Rb	2F_{III}	2.97	N	2F_{III}	3.08
Rb	2F_I	3.11	N	2F_I	3.18
Rb	2F_{II}	3.44	N	2F_{II}	3.39
F_{II}	2F_{III}	3.17	F_{III}	2F_{III}	3.01
F_{III}	2F_{III}	3.18	F_I	2F_{II}	3.16
F_I	2F_I	3.28	F_I	F_{II}	3.27

In $(NH_4)_2SiF_6$ each NH_4^+ is equidistant from 12 F^- with NH_4-F = 2.99 Å.

Leaving out of consideration the (seemingly unavoidably) large values of 3.13 and 3.46 Å., we see that the eight smaller Rb-F separations vary within the narrow ran with an average of 2.9 structure is certainly to ing with the rubidium i is spherically symmetric lar assignment of para monium salt leads to in are in some cases rather to be entirely rid of the necessary to introduce t to be described.

Examination of an ammonium fluoborate structure with the parameters of the rubidium salt shows that there is just one reasonably satisfactory way in which each ammonium ion might form its maximum number of four hydrogen bonds with fluoride ions. Our assignment of parameter values in ammonium fluoborate surrounds each nitrogen by four fluoride ions at tetrahedron corners, F_I and F_{II} at a distance of 2.83 Å., and 2 F_{III} at 2.86 Å. We find two tetrahedral (bond) angles of 119.5°, a third of 134°, and the fourth of only 84.5°. The interatomic separations indicate that the hydrogen bonds are rather weak, since in NH_4HF_2 the average N-F separation is 2.76 ± 0.06 Å. We believe that the N-F separations in ammonium fluoborate may well be somewhat smaller than those given, for we have introduced what we regard as the minimum amount of distortion from the RbBF$_4$ parameters necessary to account for the intensity data. It seems possible, moreover, that the two hydrogen bonds involving F_I and F_{II} may be somewhat stronger than those involving F_{III}, since the unavoidably large M-F separations of Table II involve F_I and F_{II}. Such an assignment of parameter values, which leads to entirely satisfactory predictions, and to N-F_I = 2.80 Å., N-F_{II} = 2.80 Å., N-F_{III} = 2.87 Å., is as follows: u = 0.308, v = 0.332; s = 0.947, t = 0.693; m = 0.833, n = 0.555; o = 0.089, p = 0.605; x = 0.933, y = 0.043, z = 0.807. We regard it as quite possible that still smaller N-F separations exist within the structure, but we see no possibility of ascertaining the precise state of affairs.

In NH_4F and NH_4HF_2 the formation of hydrogen bonds between nitrogen and fluorine causes these compounds to assume structures belonging to crystal classes entirely different from the corresponding potassium or rubidium salts. That hydrogen bonds in ammonium fluoborate seems quite probable but their presence results in but arameter values or in

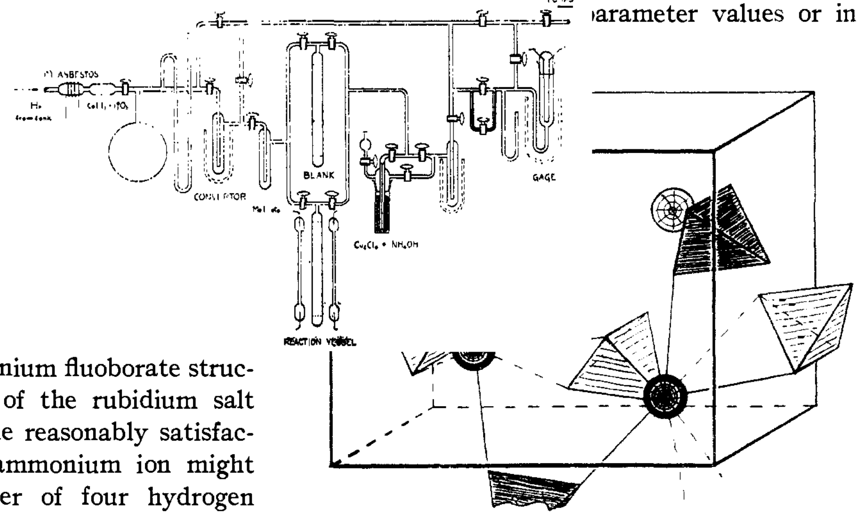

Fig. 1.—The structure of ammonium fluoborate. The positions of nitrogen atoms and of fluoborate ions are indicated respectively by the circles and the regular tetrahedra. Figures heavily shaded are centered in the plane $y = {}^1/_4$, those lightly shaded in $y = {}^3/_4$. The coördination of fluoride about ammonium ions is shown by the lines connecting vertices of the tetrahedra with the circles; the solid lines indicate hydrogen bonds.

Summary

x-Ray data show rubidium fluoborate and ammonium fluoborate to possess similar orthorhombic units of structure with a_0 = 9.07 Å., b_0 = 5.60 Å., c_0 = 7.23 Å. and a_0 = 9.06 Å., b_0 = 5.64 Å., c_0 = 7.23 Å., respectively. Both compounds crystallize with the barium sulfate type of structure, space group V_h^{16}-*Pnma*, being aggregates of

BF_4^- tetrahedra and Rb^+ or NH_4^+ ions. A regular BF_4^- tetrahedron with B-F = 1.43 Å., is assumed in order to determine the eleven parameters of the structure. The rubidium ions are first placed approximately by neglecting the scattering of the other much lighter atoms; these are then assigned parameter values which lead to a generally acceptable agreement between calculated and observed intensities of x-ray reflections. An identical assignment of parameter values in ammonium fluoborate leads to only fair agreement between calculated and observed intensities; these are much improved by the introduction of small distortions which may be interpreted as a tendency toward the formation of hydrogen bonds between nitrogen and fluorine.

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Derivatives of Piperazine. VII. Procaine Analogs, Part I

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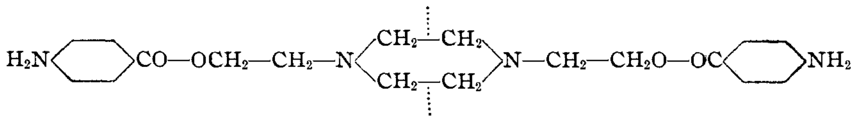
Considerable work has been done in the field of alkyl *p*-aminobenzoates to ascertain the relationship between chemical constitution and physiological action. Such investigations have included the preparation of procaine analogs containing dissimilar alkylamino groups,[1] aliphatic and aryl aliphatic acids in the place of *p*-aminobenzoic acid[2] and unsaturated groups in the side chain of the acids.[2] Other studies have shown the effect of increase in the length of the carbon chain of the alkyl group and the effect of branched-chain alkyl derivatives in the procaine series.[3] Soderman and Johnson[4] and Roberts and Johnson[5] have studied procaine analogs containing different aromatic acids. Numerous other investigations, far too extensive to list here, have been carried out to determine the effect of increasing molecular weight on the anesthetic properties of compounds of the procaine type.

The purposes of the present investigation were (1) to study the effect of cyclic diamines, such as piperazine, and various types of aliphatic secondary amines on the therapeutic properties of the procaine molecule, (2) to determine the effects thus produced by the increased nitrogen content of the molecule and (3) to devise a simple method for obtaining piperazino-1,4-bis-(β-ethanol) in good yield.

Pyman[6] has prepared the latter compound in 41% yield from piperazine and 2-chloroethanol. The present workers have prepared piperazino-1, 4-bis(β-ethanol) in quantitative yield by a method analogous to that used by Horne and Shriner[7] in the preparation of β-diethylaminoethanol.

It is apparent that the di-*p*-aminobenzoate of piperazino-1,4-bis-(β-ethanol) is in reality a "double" procaine molecule. If the molecule is split into symmetrical halves as indicated by the dotted lines, it is logical to consider the molecule as being composed of two similar parts, each of which has a smaller molecular weight than procaine. The percentage of nitrogen in procaine is 11.86, whereas the di-*p*-aminobenzoate of piperazino-1,4-bis-(β-ethanol) contains 13.59% N. Hence the new molecule contains more nitrogen per unit molecular weight than procaine and in addition possesses a cyclic diamino linkage. It will be interesting to learn the modifications which these two effects will produce in the therapeutic properties of procaine.



Experimental

Piperazino-1,4-bis-(β-ethanol).—Twenty-one grams of anhydrous piperazine[8] was dissolved in an equal weight of boiling methanol contained in a flask fitted with a condenser. A stream of ethylene oxide was passed into the solution until the theoretical quantity had been absorbed.

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(1) Brill, THIS JOURNAL, **54**, 2484 (1932).

(2) Brill and Bulow, *ibid.*, **55**, 2059 (1933); Brill and Cook, *ibid.*, **55**, 2062 (1933).

(3) Adams, Rideal, Burnett, Jenkins and Dreger, *ibid.*, **48**, 1758 (1926).

(4) Soderman and Johnson, *ibid.*, **47**, 1390 (1925).

(5) Roberts and Johnson, *ibid.*, **47**, 1396 (1925).

(6) Pyman, *J. Chem. Soc.*, **93**, 1793 (1908).

(7) Horne and Shriner, THIS JOURNAL, **54**, 2925 (1932).

(8) Pollard, Bain and Adelson, *ibid.*, **57**, 199 (1935).