[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Structures of Complex Fluorides. Potassium Hexafluogermanate and Ammonium Hexafluogermanate

BY J. L. HOARD AND W. B. VINCENT

Among compounds of type formula R_2MX_6, in which R = K, NH_4; M = Si, Ge, Sn, Ti, Zr, Mn, only the fluosilicates have been prepared in crystalline modifications possessing the familiar fluorite-like arrangement of R^+ and $MX_6^=$ ions known as the ammonium chloroplatinate structural type.[1] Most of these complex fluorides crystallize in the hexagonal system with crystal habits and axial ratios which suggest a general isomorphism within the group. In the present paper we report the determination by means of X-rays of the atomic arrangement which exists within crystals of ammonium and potassium fluogermanates. The structure of these compounds proves to be of the same general type as that of the hexagonal modification of ammonium fluosilicate, which has been studied by Gossner and Kraus.[2]

Using filtered CuK α radiation complete sets of oscillation photographs were prepared from small, well-formed crystals of both compounds. In each case the symmetry of the patterns obtained from carefully oriented specimens is that of $D_3^d - \overline{3}\,m$. The fundamental lattice is hexagonal with the following values of the lattice constants, accurate to within 0.01 Å.: ammonium fluogermanate, $a = 5.85$, $c = 4.775$ Å., $c/a = 0.816$; potassium fluogermanate, $a = 5.62$, $c = 4.65$ Å., $c/a = 0.827$. Groth[3] gives $c/a = 1.6078$ for the potassium salt as derived from goniometric measurements.

For one stoichiometric molecule within the unit cell the calculated densities are 2.60 g./cc. for the ammonium salt and 3.43 g./cc. for the potassium compound; approximate experimental values determined by the pycnometer method are, respectively, 2.64 g./cc. and 3.32 g./cc.

Symmetry planes belong to the form {11·0} rather than to {10·0}. Since, moreover, all classes of reflections are observed, the possible space groups are limited to $C_{3v}^1 - C3\,m$, $D_3^2 - C32$, and $D_{3d}^3 - C\overline{3}\,m$. The actual atomic arrangement is found to possess the complete symmetry of D_{3d}^3, and we shall base our description of the structure upon this space group.

Using the standard notation,[4] we place Ge in (a): 000; 2K or $2NH_4$ in 2(d): $^1/_3$, $^2/_3$, u; $^2/_3$, $^1/_3$, $\bar{u}$; 6F in 6(i): $x\bar{x}z$; x, $2x$, z; $2\bar{x}$, $\bar{x}$, z; $\bar{x}x\bar{z}$; $\bar{x}$, $2x$, $\bar{z}$; $2x$, x, $\bar{z}$ of D_{3d}^3. The values of these atomic coördinates as derived from the diffraction data are as follows: ammonium fluogermanate, $u = 0.695$, $x = 0.143$, $z = 0.214$; potassium fluogermanate, $u = 0.700$, $x = 0.148$, $z = 0.220$. Table I contains a comparison of observed with calculated reflection amplitudes for several types of reflections. The agreement is seen to be very good; details of the calculations follow.

TABLE I

Ammonium Fluogermanate $\sqrt{I}$ Calcd.[a]	Obsd.	(hkl)	Potassium Fluogermanate $\sqrt{I}$ Calcd.[a]	Obsd.
106	105	10·0	76	62
93	90	00·1	76	67
80	90	10·1	106	95
73	90	10·$\bar{1}$	47	57
1	0	20·0	− 17	16
− 43	32	00·2	− 67	63
− 34	26	20·1	− 51	51
111	90	20·$\bar{1}$	134	114
12	12	10·2	5	6
43	45	10·$\bar{2}$	64	63
47	37	20·2	68	57
73	64	20·$\bar{2}$	65	51
14	23	30·0	44	51
12	18	00·3	29	36
1	0	30·1	1	0
47	26	30·$\bar{1}$	36	36
18	15	10·3	10	4
17	15	10·$\bar{3}$	25	14
22	22	30·2	13	12
38	22	30·$\bar{2}$	22	10
57	37	20·3	57	36
7	10	20·$\bar{3}$	− 10	0
9	6	40·0	1	0
41	26	40·1	57	51
1	0	40·$\bar{1}$	− 12	9
40	26	00·4	45	36
34	26	10·4	43	44
17	13	10·$\bar{4}$	4	0
38	23	30·3	49	18

(1) R. W. G. Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York, N. Y., 2d ed., 1931, p. 304.

(2) B. Gossner and O. Kraus, *Z. Krist.*, **88**, 223 (1934).

(3) P. Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1906, Erster Teil, p. 486.

(4) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntraeger, Berlin, 1935, Erster Band, Gruppentheoretische Tafeln, p. 258.

TABLE I (*Concluded*)

$\sqrt{I}$ Calcd.[a]	$\sqrt{I}$ Obsd.	(*hkl*)	$\sqrt{I}$ Calcd.[a]	$\sqrt{I}$ Obsd.
20	13	$30\cdot\bar{3}$	32	16
33	20	$40\cdot2$	31	17
27	13	$40\cdot\bar{2}$	39	18
22	19	$20\cdot4$	5	5
2	3	$20\cdot\bar{4}$	12	11
6	1	$50\cdot0$	2	0
9	10	$40\cdot3$	− 7	0
29	18	$40\cdot\bar{3}$	31	17
30	13	$50\cdot1$	17	15
6	0	$50\cdot\bar{1}$	19	9
22	15	$30\cdot4$	21	14
7	10	$30\cdot\bar{4}$	12	14
26	15	$00\cdot5$	12	20
22	20	$10\cdot5$	24	28
27	20	$10\cdot\bar{5}$	28	32
29	20	$50\cdot2$	37	32
16	10	$50\cdot\bar{2}$	12	11
6	10	$20\cdot5$	9	16
14	10	$20\cdot\bar{5}$	22	22
6	6	$40\cdot4$	13	14
12	14	$40\cdot\bar{4}$	1	8
10	6	$50\cdot3$	9	12
18	15	$50\cdot\bar{3}$	8	12
20	20	$60\cdot0$	32	24
3	1	$30\cdot5$	− 4	0
7	10	$30\cdot\bar{5}$	2	0
8	12	$60\cdot1$	9	8
10	12	$60\cdot\bar{1}$	7	8
10	10	$00\cdot6$	10	24
54	62	$11\cdot0$	79	108
36	44	$11\cdot1$	24	26
20	20	$21\cdot0$	16	18
34	42	$11\cdot2$	23	18
47	32	$21\cdot1$	32	30
21	22	$21\cdot\bar{1}$	50	58
51	42	$21\cdot2$	61	60
28	22	$21\cdot\bar{2}$	23	20
30	26	$31\cdot0$	21	20
40	30	$11\cdot3$	51	45
34	20	$31\cdot1$	45	54
22	22	$31\cdot\bar{1}$	14	18
18	11	$21\cdot3$	16	12
29	24	$21\cdot\bar{3}$	13	8
18	11	$31\cdot2$	13	12
23	20	$31\cdot\bar{2}$	36	24
19	14	$11\cdot4$	20	22
21	14	$41\cdot0$	32	24
9	0	$41\cdot1$	5	0
26	16	$41\cdot\bar{1}$	19	6
12	7	$31\cdot3$	2	0
18	10	$31\cdot\bar{3}$	18	16
5	0	$21\cdot4$	− 6	0
24	22	$21\cdot\bar{4}$	34	28
13	6	$41\cdot2$	4	0
20	14	$41\cdot\bar{2}$	8	7
9	6	$51\cdot0$	5	0
18	12	$31\cdot4$	27	30
13	10	$31\cdot\bar{4}$	1	0
23	14	$41\cdot3$	32	30
13	14	$41\cdot\bar{3}$	23	25
8	9	$11\cdot5$	− 5	0
11	12	$51\cdot1$	5	7
16	12	$51\cdot\bar{1}$	25	25
14	16	$21\cdot5$	21	32
11	14	$21\cdot\bar{5}$	16	20
19	12	$51\cdot2$	28	30
16	12	$51\cdot\bar{2}$	13	10
7	14	$41\cdot4$	22	28
10	24	$41\cdot\bar{4}$	16	25
14	16	$51\cdot3$		
10	14	$51\cdot\bar{3}$		
15	16	$31\cdot5$		
13	24	$31\cdot\bar{3}$		

[a] Temperature factor and absorption correction not included.

The intensities of reflections appearing on photographs taken from hexagonal tablets, of diameter about 0.25 and 0.50 mm., respectively, for potassium and ammonium fluogermanate, were visually estimated by comparison with an intensity scale prepared for this purpose; the observed amplitudes of Table I are proportional to the square roots of these data. Theoretical amplitudes were calculated by means of the formula

$$I = \text{Constant}\left(\frac{1 + \cos^2 2\theta}{2 \sin 2\theta}\right)^{1/2} S$$

in which the structure factor is

$$S = f_{Ge} + 2f_N \cos 2\pi\left(\frac{h + 2k}{3} + lu\right) + 2f_F\,[\cos 2\pi\,(hx - kx + lz) + \cos 2\pi\,(hx + 2kx + lz) + \cos 2\pi\,(2hx - kx + lz)]$$

The atomic f-values of Pauling and Sherman[5] are used throughout this paper.

As a matter of fact, the calculated amplitudes are but little altered by introducing small variations from the coördinates of fluorine and ammonium listed above. The parameter values given are essentially those derived from approximate Fourier projections of relative electron density on $(1\bar{2}\cdot0)$ using experimental $(h0l)$ data. The reflection amplitudes used in calculating these projections were taken proportional to the square roots of the quantities obtained after correction of the estimated intensities by the Lorentz and polarization factor. The formula required in making the projection is

$$\rho(x,z) = \Sigma_h\, \Sigma_l\, F_{(h0l)} \cos 2\pi(hx + lz)$$

The method of Lipson and Beevers[6] was used in making the summations.

The resulting simple projections of relative electron density need not be reproduced here since their important features can be described in

(5) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).
(6) Lipson and Beevers, *Phys. Soc. London*, **48**, 772 (1936).

few words. Excepting that potassium shows up more prominently than does ammonium, the contour maps are very similar for the two compounds. The values of the fluorine parameters as read from the peak arising from the superposition of two fluorine atoms on the projection are for ammonium fluogermanate $x = 0.147$, $z = 0.205$; for potassium fluogermanate $x = 0.148$, $z = 0.215$. The corresponding Ge–F separations in the almost regular octahedral GeF_6 groups are, respectively, 1.77 and 1.755 Å. Neither the ammonium nor the potassium peak is completely resolved from that of a single fluorine atom in each plot but it is possible, nevertheless, to determine the atomic positions with a fair degree of accuracy. It is probable that $u_K = 0.700$ is reliable to within a few thousandths, and that $u_N = 0.695$ is not in error by more than 0.015.

We see that the parameter values derived from the Fourier analyses of the (*h*0*l*) data are very nearly those used in calculating the reflection amplitudes of Table I. In the latter case we have assumed the complex anions to be regular octahedra with Ge–F = 1.77 Å.

An additional Fourier projection of relative electron density on (00·1) using experimental (*hk*·0) reflection amplitudes was made for ammonium fluogermanate. Peaks for germanium at 00; for ammonium at $^1/_3$, $^2/_3$ and $^2/_3$, $^1/_3$; and for fluorine at x, $2x$, etc., with $x = 0.150$ are observed. The value of the fluorine parameter is slightly larger than that obtained from the analysis of the (*h*0*l*) data. The Fourier data do not indicate completely regular complex anions for either compound: in ammonium fluogermanate the octahedron appears to be slightly flattened perpendicular to the unique axis; in potassium fluogermanate the octahedron appears to be slightly elongated along this axis. Within the accuracy of the data, however, we may conclude that both compounds contain practically regular octahedral GeF_6 groups with Ge–F = 1.77 Å.

The experimental Ge–F separation, 1.77 Å., may be compared with the sum of the "univalent" ionic radii[7] corrected for the actual ionic charges, 1.74 Å., with the sum of the "normal valence" radii,[8] 1.86 Å., and with the quite approximate value, 1.8 Å., derived from the X-ray study of the cubic cesium fluogermanate.[9] The more appropriate "octahedral" radius of germanium is probably somewhat larger than the "normal valence" or "tetrahedral" value. In the light of numerous electron diffraction data dealing with gaseous fluorides, however, we might well expect the Ge–F separation to be appreciably smaller than the sum of the covalent radii.

The parameter data used in calculating the reflection amplitudes of Table I lead to a regular GeF_6 group with Ge–F = 1.77 Å., F–F = 2.51 Å. Between adjacent anions, F–F = 3.11 Å. $(K–F)_1$ = 2.84 Å. (six of these), $(K–F)_2$ = 2.86 Å. (3), $(K–F)_3$ = 3.01 Å. (3), $(NH_4–F)_1$ = 2.97 Å. (6), $(NH_4–F)_2$ = 3.00 Å. (3), $(NH_4–F)_3$ = 3.14 Å. (3). We may accept the conclusion that three of the twelve potassium–fluorine separations are appreciably larger than the others; this is very probably true for the ammonium–fluorine separations as well. The coördination number of the univalent cation is then nine, although the approximation to coördination number twelve is not bad.

Drawings of the structure of potassium fluogermanate are shown in Fig. 1. The atomic arrangement can be described qualitatively as based on hexagonal closest-packing of fluorine and potassium atoms, from which, however, there are very considerable distortions. With the cubic ammonium chloroplatinate arrangement, fluorine and potassium atom would be in approximate cubic closest-packing, potassium being required by symmetry to possess twelve equidistant neighbors. These relations have been pointed out previously in the case of the dimorphous ammonium fluosilicate by Gossner and Kraus.[2] These authors have suggested approximate values for the parameters of ammonium and fluorine in the hexagonal modification of ammonium fluosilicate which lead to nine ammonium–fluorine separations of about 2.92 Å. as compared with about 2.98 Å. in the present work on the fluogermanate.

The hexagonal or low temperature modification of ammonium fluosilicate has a density about 7% larger than that of the cubic or high temperature form. As mentioned previously, the fluogermanates have been prepared only with the hexagonal structure.

Qualitatively, it appears that a considerable degree of ionic character in the M–F bonds of the complex would favor the assumption of the hexagonal rather than the cubic structure. This conclusion could be checked by calculating

(7) L. Pauling, THIS JOURNAL, **49**, 769 (1927).

(8) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

(9) R. W. G. Wyckoff and J. H. Muller, *Am. J. Sci.*, **13**, 347 (1927).

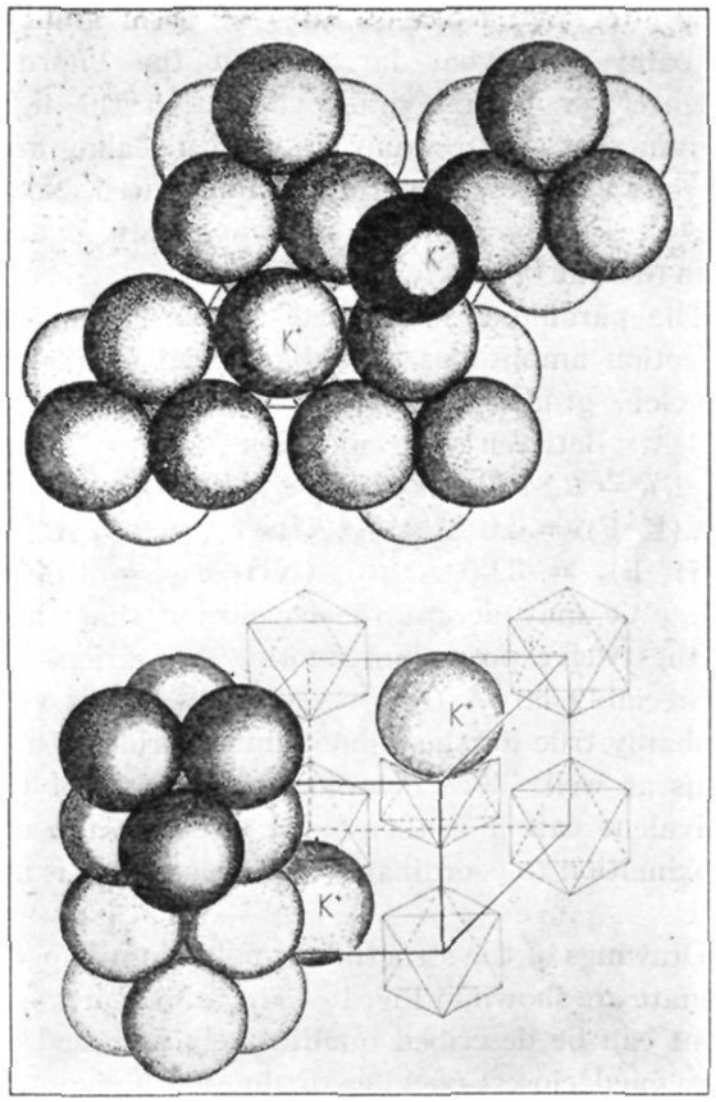

Fig. 1a.—Packing drawing along the hexagonal axis of the structure of potassium fluogermanate (upper). Fig. 1b.—View of the structure along the normal to (011) (lower).

the difference of potential energy between the two structural types for various distributions of charge over the anion, assuming an equal contribution of covalent binding to the M–F bond in both structures. With absorption of thermal energy the more symmetrical cubic structure becomes relatively more stable, although it is not possible at present to set up the partition functions required for quantitative calculations. Only complex fluorides have been prepared with the hexagonal structural type.

We have found that crystals of rubidium fluogermanate prepared at ordinary temperatures possess neither of the structures discussed above. Although hexagonal, the unit cell of this compound contains two stoichiometric molecules with the approximate axial lengths $a = 5.96$ Å., $c = 9.72$ Å. Our diffraction data are incomplete as yet, but the values of the lattice constants suggest that the structure is one in which rubidium ion has accurately a coördination number of twelve.

Although it appears certain that a system of fixed hydrogen bridges does not exist in ammonium fluogermanate, it is probable, nevertheless, that the interactions of hydrogen with fluorine are larger than would be the case for any structural type in which ammonium would have twelve equidistant neighbors. In ammonium fluogermanate it is reasonable to suppose that the ammonium ion is oriented so that three protons lie nearly in the plane of the six fluorine atoms which are about 2.97 Å. from each nitrogen atom. In the absence of any effect of this kind we would expect ammonium and rubidium fluogermanates to be isomorphous.

Summary

It is deduced from X-ray data that crystals of the isomorphous ammonium and potassium fluogermanates possess one-molecule hexagonal units of structure with $a = 5.85$ Å., $c = 4.775$ Å. and $a = 5.62$ Å., $c = 4.65$ Å., respectively, space-group D^3_{3d}–$C3\ m$. The structure is an aggregate of univalent cations (K^+, NH_4^+) and nearly regular octahedral anions (GeF_6^{-4}) with Ge–F = 1.77 Å. Each cation is surrounded by nine nearly equidistant fluorine atoms and three others at somewhat greater distances. This structure has been found only in the case of complex fluorides, for which at ordinary temperatures it is usually preferred to the cubic ammonium chloroplatinate structural type.

ITHACA, NEW YORK RECEIVED JULY 20, 1939