Structures of Complex Fluorides.[1] Ammonium Hexafluosilicate–Ammonium Fluoride, (NH₄)₂SiF₆·NH₄F

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Introduction

Recent X-ray studies have demonstrated the existence of discrete seven-coördination complexes in a number of crystalline complex fluorides. Cubic crystals of potassium and ammonium heptafluozirconates[2] contain the $ZrF_7^=$ ion with the point-group symmetry of C_{3v}–$3m$. The $CbOF_6^=$ ion has a similar configuration in cubic crystals of potassium oxyhexafluocolumbate,[3] K_3CbOF_6. Monoclinic crystals of the isomorphous compounds potassium heptafluocolumbate and potassium heptafluotantalate[1b] contain on the other hand the discrete complexes $CbF_7^=$ and $TaF_7^=$ with the point-group symmetry of C_{2v}–mm. With these unusual stereochemical data in mind it has seemed of particular interest to determine the structure of the crystalline compound, first prepared by Marignac,[4] of empirical formula $(NH_4)_3SiF_7$ to see whether the $SiF_7^=$ ion exists within the crystal.

A priori, it seems unlikely that the $SiF_7^=$ ion can be stable. The ratio of the univalent radii[5] for Si^{4+} and F^- is only 0.48, much less than the minimum value, about 0.59, required for stability of a seven-coördination group. The resulting electron distribution in an $SiF_7^=$ group, whatever its precise character, would seem to involve such strong steric interactions between adjacent coördinated fluorine atoms as to make this complex unstable.

Our X-ray analysis shows indeed that crystals of composition $(NH_4)_3SiF_7$ do not contain $SiF_7^=$ ions, but are ordered aggregates of NH_4^+, F^-, and octahedral $SiF_6^=$ ions; in line with this result we shall use the double salt formula, $(NH_4)_2SiF_6$·NH_4F.

Determination of Structure.—The ammonium hexafluosilicate–ammonium fluoride used in the X-ray study was prepared and analyzed in this Laboratory by Mr. C. G. Polzer working under the direction of Professor A. W. Laubengayer. The material used crystallized in tetragonal prisms conforming to the description given in the literature.[4,6] Since the crystals are somewhat unstable when in contact with moist air each specimen used in gathering the X-ray data was given a thin protective coating of shellac.

Using Cu Kα radiation, complete sets of oscillation photographs were taken with c and with a as rotation axes. Each specimen was ground to a cylindrical form of sufficiently small diameter as to make the variation of absorption with scattering angle inappreciable. With such specimens the absorption correction can be neglected in considerations involving only relative intensities.

The tetragonal unit of structure has $c = 5.845$, $a = 8.04$ Å., each accurate to within about 0.01 Å., and contains two stoichiometric molecules. The photographs conform exactly to the symmetry of the point-group D_{4h}–$4/mm$, and reflections of the type $(h0l)$, h odd are absent. These data indicate that the space-group is one of the set[7] D_{4h}^5–$P4/mbm$, C_{4v}^2–$P4bm$, D_{2d}^7–$C\bar{4}2b$. We must place 2 Si, 6 NH_4, and 14 F within the primitive tetragonal unit in agreement with the symmetry operations of one (or more) of these space-groups.

A number of general conclusions regarding possible structures for this crystal can be drawn from an analysis of the symmetry requirements. Since each of these space-groups furnishes a minimum of two equivalent positions, the two silicon atoms must be structurally equivalent. It follows that either $SiF_6^=$ or $SiF_7^=$ complexes, but not both, might be present in the structure.

Inspection of the possibilities[7] for placing two equivalent silicon atoms shows that the complex anion must possess at least the symmetry of one of the following point-groups: D_2, C_{2v}, D_{2h}, S_4, C_4, or C_{4h}. This requirement eliminates as a structural possibility an $SiF_7^=$ complex having a

(1) For earlier papers in this series see (a) THIS JOURNAL, **57**, 1985 (1935); (b) *ibid.*, **61**, 1252 (1939); (c) **61**, 2849 (1939); (d) **62**, 3126 (1940); (e) **63**, 11 (1941).

(2) G. C. Hampson and L. Pauling, *ibid.*, **60**, 2702 (1938).

(3) M. B. Williams and J. L. Hoard, unpublished material.

(4) Ch. de Marignac, *Annales de mines*, **15**, 223 (1859).

(5) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1940.

(6) P. Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1906, Vol. I, p. 462.

(7) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntraeger, Berlin, Zweiter Band.

configuration exactly or approximately like that of $ZrF_7^=$ (which cannot have a two-fold axis). Furthermore, only the positions[7] 2(b): $\frac{1}{2}$ 0 z; 0 $\frac{1}{2}$ z, of the space group C_{4v}^2 are allowable for silicon atoms of $SiF_7^=$ ions having a configuration like that found for $CbF_7^=$ or $TaF_7^=$. The symmetry of these positions, C_{2v}, is indeed just the highest type that the $CbF_7^=$ configuration could possess. We proceed to examine possible structures based upon C_{4v}^2 which would contain $SiF_7^=$ ions of the permissible symmetry.

The symmetry character of the seven-coördination group makes the choice of positions unique for fluorine as well as for silicon. We must have 2F in 2(b), 4F in 4(c): x, $\frac{1}{2}$ + x, z; etc. (the mirror planes), and 8F in the general position 8(d); xyz; etc., of C_{4v}^2. From the known M–F separations in $SiF_6^=$ (1.71 Å.), $CbOF_5^=$ (1.88 Å.), and $CbF_7^=$ (1.97 Å.), the Si–F distance in $SiF_7^=$ may be taken as 1.80 Å. The relative dimensions in $SiF_7^=$ may be taken as identical with those in $CbF_7^=$, for which the effects of steric repulsion of adjacent coördinated atoms seem to be minimized. $SiF_7^=$ ions of this type fit satisfactorily into the unit of structure, there being no F–F separations between adjacent complexes less than about 3.0 Å.

The short c axis, 5.845 Å., makes it dimensionally impossible to put ammonium ions in 2(b), for we would have NH_4–F separations of only 1.7 Å. It is necessary then to put 4N in 4(c) and 2N in 2(a): 00z; $\frac{1}{2}$ $\frac{1}{2}$ z. It is possible to assign x and z parameters to the ammonium ions in 4(c) so that the dimensional relations are entirely reasonable. It is only possible, however, for an ammonium ion in 4(a) to have as near neighbors four fluorine atoms whereas a minimum of six and preferably more (twelve in $(NH_4)_2SiF_6$) is to be expected. But in view of the properties of the crystal the packing relations of the proposed structure might still be adequate.

This proposed structure, however, is definitely eliminated through a comparison of calculated with observed amplitudes of X-ray reflections. This comparison is best made for $(hk0)$ reflections, for which the contributions of 2Si, 2F, and 2N do not depend on any variable parameter, while the probable variations in the x and y parameters of the other atoms can be fixed within fairly narrow limits. A few examples of the pronounced disagreement between calculated and observed reflection amplitudes are as follows. Among $(h00)$ reflections, (400) is calculated to be by far the strongest but is observed to be much the weakest of the group; the adjacent (600) reflection is calculated to be the weakest but is observed to be next to the strongest in the group. It is clear, moreover, that permissible variations in the x and y parameters of fluorine and nitrogen cannot materially alter the pronounced character of this disagreement.

With the definite rejection of the only possible structure which could have $SiF_7^=$ ions of the $CbF_7^=$ type present, it becomes quite certain that seven-coördination complexes do not exist in this compound. For we have now eliminated both of the sterically favored configurations for MF_7 groups, and only these have been observed previously. The only other configuration for an MF_7 group which suggests itself is that in which seven fluorine atoms are arranged at the vertices of a pentagonal bipyramid about the central atom. Sterically, this coördination group seems quite improbable. Although, from the standpoint of symmetry, such groups could be centered in 2(b) of C_{4v}^2, calculation shows that fluorine atoms belonging to adjacent $SiF_7^=$ ions would be only 2.2 Å. apart; this distance is not only much smaller than that expected from past experience but is actually less than the separation required of adjacent fluorine atoms within an $SiF_7^=$ group of either the $CbF_7^=$ or $ZrF_7^=$ type. Thus the pentagonal bipyramidal configuration must be rejected also.

As stated previously, our analysis shows that crystals of $(NH_4)_2SiF_6 \cdot NH_4F$ are ordered aggregates of NH_4^+, F^-, and $SiF_6^=$ ions. If the octahedral $SiF_6^=$ ion were oriented with a four-fold axis parallel to c, the separation of fluorine atoms of adjacent complexes would be only about 2.4 Å. This means that a two-fold axis of the octahedron must be parallel to c (Fig. 2), and that silicon must be placed in one of the following sets of positions: 2(c) or 2(d) of D_{2d}^7, 2(b) of C_{4v}^2, 2(c) or 2(d) of D_{4h}^5. In all cases the orientation of the $SiF_6^=$ ion is essentially the same, and the elucidation of the structure described below follows in a virtually unique manner. It is convenient to base our description upon D_{4h}^5–$P4/mbm$, the space-group of highest symmetry.

If we place 2Si in 2(d): 0 $\frac{1}{2}$ 0; $\frac{1}{2}$ 0 0 of D_{4h}^5, then nearly regular SiF_6 octahedra with Si–F = 1.71 Å. can be present if we place 4F in 4(g): u, $\frac{1}{2}$ + u, 0; etc., with u = 0.349, and 8F in 8(k): v,

$1/2 + v$, w; etc., with $v = 0.106$, $w = 0.207$. Structurally equivalent combinations involving a transformation of axes, but no others, are possible. The placement of 4N in 4(h): x, $1/2 + x$, $1/2$; etc., with x about 0.315, of 2N in 2(a): 000; $1/2$ $1/2$ 0, and 2F$^-$ in 2(b): 001/2; $1/2$ $1/2$ $1/2$, is then dictated by the packing relations. For with this distribution each ammonium ion has only fluorine atoms or ions as near neighbors, and, moreover, the "extra" fluoride ions of 2(b) have only ammonium ions at reasonable distances as close neighbors. This is the only structure made up of NH_4^+, F^-, and octahedral $SiF_6^=$ ions and based on D_{4h}^5 which can fulfill this obvious requirement for stability.

The possible distortions from this atomic arrangement which could be introduced by basing it upon one of the sub-groups C_{4v}^2 or D_{2d}^7 seem wholly improbable. If, as is highly probable, the SiF_6 ion can be assumed to have regular octahedral symmetry within experimental error its position including orientation within the structure is necessarily the same in all three space-groups. For the remaining atoms the possibilities afforded by D_{2d}^7 and D_{4h}^5 are identical. C_{4v}^2 would permit ammonium and the "extra" fluoride ions to have variable parameters along the tetragonal axis. A close examination of the possibilities indicates strongly that any deviations in these parameters from the values given above can result only in making the structure less stable.

In order to substantiate the structure just described for $(NH_4)_2SiF_6 \cdot NH_4F$, we have (1), compared calculated and experimentally evaluated reflection amplitudes for large classes of X-ray reflections, and (2), constructed Fourier projections of relative electron density on the (100) and (001) faces of the unit cell.

The experimental intensities of the diffraction spots were gotten by visual comparison with a calibrated intensity scale. Each diffraction maximum was recorded simultaneously on two coaxial non-screen Agfa films, the intensity ratio for the two being taken as 2.8. The experimental amplitudes were taken proportional to the square root of the quantities obtained after correction of the intensities by the Lorentz and polarization factors.

Comparisons between calculated and observed reflection amplitudes were made first upon the basis of the parameter values already given. Allowing for the omission of a temperature factor from the calculated amplitudes, the results were

in qualitative agreement, generally speaking. For several reflections, however, the comparisons were quite unsatisfactory. It was for this reason that Fourier projections of relative electron density on (100) and (001) were made. The more important of these, that for (001), is reproduced in Fig. 1. The plot agrees in general with the
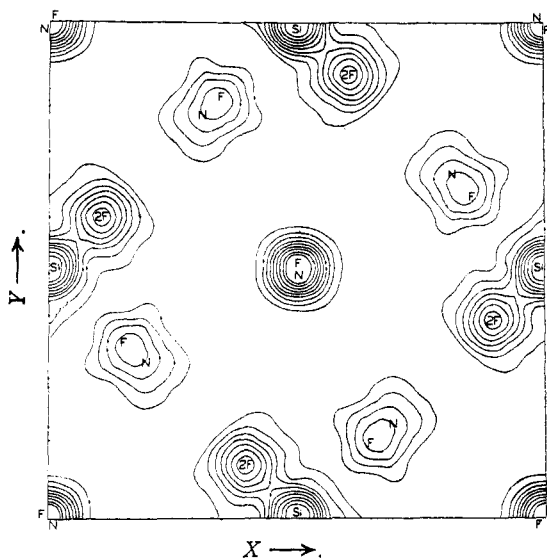

Fig. 1.—Projection of relative electron density upon (001).

postulated structure (Fig. 2), and, with the exception of ammonium in 4(h), for which a value for x of about 0.30 is indicated, is consistent with the x and y parameters already given. Recalculation of the $(hk0)$ reflection amplitudes with this
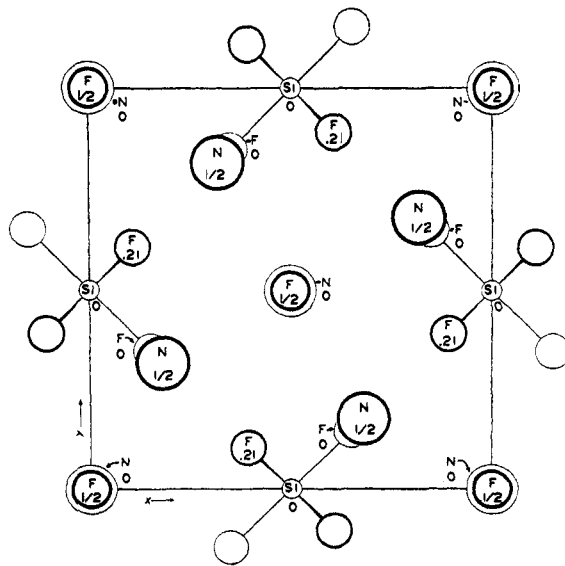

Fig. 2.—Diagrammatic projection of the unit of structure upon (001). The distance of each atom above the plane $z = 0$ is indicated.

single change in parameter results in a definite improvement in the comparisons with the experimentally derived values, although some notable discrepancies are not completely removed.

In Table I calculated and observed amplitudes for (hk0) and (0kl) reflections are compared. Values of the variable parameters used are: N in 4(h), $x = 0.300$; F in 4(g), $u = 0.349$; F in 8 (k), $v = 0.106$, $w = 0.207$. Although the general agreement seems adequate to confirm the correctness of the derived structure certain discrepancies, e. g., in the case of (400), call for further discussion. The lack of quantitative agreement in these cases is probably due in small part to inaccuracies in the atomic positions, in larger

TABLE I

Reflection (hkl)	Amplitude Calcd.[a]	Obsd.	Reflection (hkl)	Amplitude Calcd.[a]	Obsd.
110	17	17	940	1.4	0
200	12	12	770	6.4	2.1
210	1.0	1.7	860	4.3	2.4
220	27	22	10·0·0	11	2.6
310	20	11	10·1·0	1.0	0
320	19	13	10·2·0	6.7	2.0
400	8.0	1.7	950	4.0	1.4
410	17	10	001	22	11
330	15	4.0	021	13	8.6
420	11	7.6	002	19	13
430	4.8	3.6	022	2.0	1.5
510	11	2.6	003	6.0	3.0
520	4.4	3.2	041	7.3	2.2
440	22	11	023	5.7	3.4
530	1.8	2.9	042	20	8.3
600	9.6	5.1	004	31	12
610	6.9	1.9	043	6.6	3.2
620	6.3	5.5	024	6.5	4.6
540	4.6	1.4	061	6.2	3.7
630	4.7	0	062	21	7.1
710	2.6	0	044	2.7	2.4
550	14	3.4	005	16	4.8
640	12	5.1	025	7.8	3.5
720	12	2.8	063	12	3.5
730	0.8	2.4	045	8.0	0
650	1.2	1.4	081	8.8	2.3
800	12	2.7	064	9.8	1.9
810	6.8	1.4	006	15	5.5
740	1.2	1.4	082	2.2	2.6
820	11	3.8	026	3.7	1.3
660	14	3.7	083	3.5	1.7
830	7.7	1.8	065	1.0	0
750	0.8	0	046	5.5	1.6
840	2.2	3.0	007	1.7	0
910	5.5	1.2	084	7.6	1.6
760	4.5	0	027	2.9	1.4
920	2.8	0	0·10·1	0.6	0.7
850	4.2	0	066	9.2	2.2
930	0.2	0	0·10·2	0.8	1.2

[a] Temperature factor not included.

degree to uncertainties in the atomic form factors, but predominantly to the omission of the temperature factor in the calculated amplitudes.

Crystals of $(NH_4)_2SiF_6 \cdot NH_4F$ are extremely soft. The unusually rapid decrease of intensity with increasing scattering angle is immediately obvious upon a first qualitative examination of the X-ray photographs, particularly on those taken with c as the rotation axis. It is clear that an isotropic temperature factor cannot be adequate in this case, both on account of the symmetry of the structure and because of the presence of the compact stable octahedral SiF_6^- groups. Inspection of the structure (Fig. 2) and of the interatomic distances which are discussed in the last section indicates that one of these complexes might be rotated from the equilibrium orientation through a considerable angle, particularly around the tetragonal axis, before the restoring torque would become very large. It is reasonable to suppose that among the normal modes of vibration of the crystal there appear some which involve coupled torsional oscillations of the octahedral anions as units about axes passing through the equilibrium positions occupied by silicon atoms. At room temperature the amplitudes of such oscillations, particularly around c, might well be large. Evidently this would result in a marked decrease in the scattering power of the fluorine atoms involved; the associated temperature factor would be definitely non-isotropic, of course.

Upon examination we find that in general the large discrepancies between calculated and observed reflection amplitudes occur for reflections for which the contribution of fluorine of the anion to the calculated amplitudes is particularly large. Qualitatively, it appears that if we should apply an especially large temperature correction to the fluorine scattering, not only would these notable discrepancies be largely removed, but the agreement between calculated and observed values would be improved in general.

Some support for the hypothesis outlined above is given by the Fourier plot (Fig. 1), in which it is clear that the peak values for fluorine of the complex anion are relatively small, thus indicating an abnormally diffuse electron distribution. This evidence should not be taken too seriously, however, for the amplitude data are only semi-quantitative and the assignment of phase to a few of the weaker reflections is perhaps doubtful.

It would be of interest to obtain diffraction data from $(NH_4)_2SiF_6 \cdot NH_4F$ at liquid air temperatures, in which case the abnormally large effects of thermal vibrations on the X-ray scattering should be largely eliminated.

Discussion of the Structure.—The structure established for $(NH_4)_2SiF_6 \cdot NH_4F$ (Fig. 2) is an ordered aggregate of ammonium, fluoride, and regular octahedral hexafluosilicate ions, the latter with Si–F = 1.71, F–F = 2.42 Å. Each ammonium ion in 4(h) has as near neighbors eight fluorine atoms of neighboring fluosilicate groups and two fluoride ions in 2(b). The N–F separations vary between 2.79 and 3.09 Å., the average of all ten values being 2.97 Å.; in cubic ammonium fluosilicate, $(NH_4)_2SiF_6$, each ammonium ion is equidistant from twelve fluorine atoms at 2.98 Å.

An ammonium ion in 2(a) has an effective coordination number of only six, having as nearest neighbors two fluoride ions in 2(b) at a distance of 2.92 Å., four fluorine atoms of $SiF_6^=$ ions at 3.05 Å., and eight others at about 3.5 Å. Since an N–F separation of about 2.8 Å. would be anticipated for coördination number six (or a still smaller value if hydrogen bonds were formed) this aspect of the packing relations is not ideal for greatest stability.

Each of the fluoride ions of 2(b) (which are not bound to silicon) has as near neighbors two ammonium ions at 2.92 Å. and four others at 2.89 Å. These distances also are somewhat larger than the ideal values.

The closest distance of approach between two ammonium ions is about 4.0 Å., and of two fluorine atoms or ions not belonging to the same complex about 3.01 Å.

In its general aspects the distribution of positive and negative charge indicates that this structure should be quite stable. The ionic framework is, however, more open and not so tightly bound together as compared with either the cubic[8] or the hexagonal[1c,9] forms of ammonium hexafluosilicate. This result can be correlated with the very soft character and relatively low stability of the double salt, which indeed can be crystallized from aqueous solution only when the ratio of

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

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

ammonium fluoride to ammonium hexafluosilicate is extremely large.

Summary

X-Ray data obtained from crystals of a compound of empirical formula $(NH_4)_3SiF_7$ lead to a tetragonal unit of structure with $a = 8.04$, $c = 5.845$ Å., containing two stoichiometric molecules. The complete absence of $(h0l)$ reflections for h odd together with the observed holohedral symmetry limits the probable space-group to D_{2d}^7, C_{4v}^2, or D_{4h}^5. Upon the basis of these data it is possible to eliminate definitely all structures containing discrete seven-coördination complexes, $SiF_7^=$, having either of the configurations previously observed to be stable for certain MF_7 groups, namely, that[1b] found for $CbF_7^=$ and $TaF_7^=$ (point-group symmetry C_{2v}) and that[2,3] of $ZrF_7^=$ and $CbOF_6^=$ (C_{3v}). Instead the X-ray data lead to a structure (Fig. 2), most conveniently described in terms of D_{4h}^5–$P4/mbm$, which is an ordered aggregate of ammonium, octahedral hexafluosilicate, and "extra" fluoride ions. The correctness of this structure is supported by the general agreement between calculated and observed amplitudes of X-ray reflections (Table I) and by Fourier projections of relative electron density upon the (001) (Fig. 1) and (100) faces of the unit cell.

The distribution of charge in the derived structure indicates a fair degree of stability, for each ion has as near neighbors only ions of opposite charge. The fact that some of the interatomic distances are as much as 10% larger than anticipated for the coördination numbers involved is correlated with the very soft character and limited stability of the crystals, and with the unusually large effects of thermal vibrations on the observed intensities of the diffraction maxima. The agreement between experimentally derived amplitudes and those calculated without temperature factor is not entirely satisfactory. It seems probable, however, that the inclusion of a non-isotropic temperature factor of the sort indicated qualitatively by the nature of the structure would remove the important discrepancies.

In line with the character of the derived structure it is preferable to use the double salt formula $(NH_4)_2SiF_6 \cdot NH_4F$, for this crystalline compound.