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A new modification of diammonium hexafluorosilicate, $(NH_4)_2SiF_6$

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A hexagonal modification ($P6_3mc$) of $(NH_4)_2SiF_6$ was grown accidentally. This new modification has the unit-cell *c* parameter doubled with respect to a previously reported trigonal form ($P\overline{3}m1$) of the title compound. The H atoms in the present structure are ordered. Three or even four F atoms are hydrogen-bond acceptors for each H atom. The structure is isostructural with modifications of $(NH_4)_2MnF_6$, K_2GeF_6 and Rb_2GeF_6.

Key indicators

Single-crystal X-ray study
$T = 290$ K
Mean σ(Si–F) = 0.001 Å
R factor = 0.018
wR factor = 0.022
Data-to-parameter ratio = 11.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Until now, two modifications of $(NH_4)_2SiF_6$ have been known (ICSD; Bergerhoff *et al.*, 2001; PDF-2: ICDD, 2001): trigonal $P\overline{3}m1$ (Schlemper & Hamilton, 1966; PDF-2 44–1424 and 72–1548) and cubic $Fm\overline{3}m$ (Hanic, 1966; PDF-2 07–0013, 72–1552 and 72–1759). The trigonal and cubic modifications are also known by their respective mineralogical names bararite and cryptohalite. The cubic modification is stable at room temperature (Schlemper & Hamilton, 1966). In the cubic modification, the positions of the H atoms were determined; they were not determined in the trigonal modification. According to both the neutron-diffraction study (Schlemper & Hamilton, 1966) and the electron-diffraction study (Vainshtein & Stasova, 1956) the H atoms in the cubic modification are disordered.

In this study, two modifications were grown in the same beaker, *viz*. hexagonal and cubic. The crystals of each modification were quite easily distinguishable in cross-polarized light as well as by their habit. While the habit of the cubic modification was cubic, the hexagonal modification grew as trigonal or hexagonal pyramids. The typical size of both crystal modifications was several tenths of a millimetre.

Attempts at chemical analysis were hindered by the small amount of available crystals. An electron microprobe analysis [JEOL JXA733 (JEOL Ltd, Tokyo, Japan) with X-ray analyzer KEVEX (Delta Class Analyzer; Kevex Instruments, San Carlos, California, USA)] was not successful in the determination of the proportion of constituent elements P, Si, O and F because of the fluffy grains on the surface of the sample. These fluffy grains contained predominantly Si, F and K. It should be noted that the microprobe analysis was not performed on the sample that was used for the structure determination. Nevertheless, the satisfactory result of the structure analysis shows that $(NH_4)_2SiF_6$ can also form a superstructure, either as a transitory state or stabilized by traces of K.

The previously determined trigonal modification shows similarities with the present structure in the orientation of the Si—F bonds with regard to the unit-cell axes. It should be noted that the structure determined in this study is isostruc-

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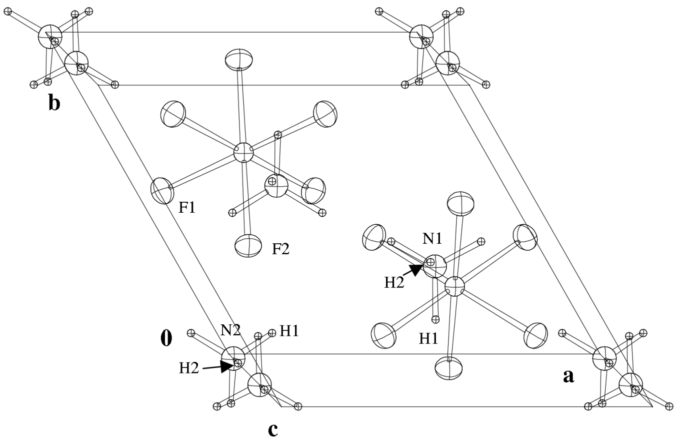

Figure 1
The unit-cell contents of $(NH_4)_2SiF_6$ viewed along the *c* axis. Ellipsoids are at the 30% probability level (*ORTEP*III; Burnett & Johnson, 1996).

tural with one of the known modifications of K_2GeF_6 (Bode & Brockmann, 1952) and Rb_2GeF_6 (*ibid*.). The structure is also isostructural with $(NH_4)_2MnF_6$ (Kaskel & Straehle, 1997) for which the positions of the H atoms were determined.

The H atoms were readily seen in the difference Fourier maps and could be easily refined with no applied constraints or restraints. All the H atoms are ordered. Each N atom in the structure is surrounded by six F atoms with fairly similar N···F distances. The distribution of four H atoms among six surrounding F atoms results in the distances between the H and F atoms being unequal despite the regularity of the N···F distances. Table 2 lists the closest N···F distances and angles.

Experimental

The present compound grew from a solution which was prepared by neutralization of stoichiometric amounts of $(NH_4)_2CO_3$ and H_2PO_3F in the molar proportion 1:1. Most probably some of the fluorophosphate anions have decomposed with production of HF which reacted with the glass of the beaker. In addition to the structure which is reported here, the cubic modification was also grown, in fact, in larger amount. Its lattice parameters corresponded to those determined by *e.g.* Hanic (1966).

Crystal data

$2(NH_4)\cdot(SiF_6)$
$M_r = 178.15$
Hexagonal, $P6_3mc$
$a = 5.8955$ (10) Å
$c = 9.599$ (1) Å
$V = 288.93$ (8) Å^3
$Z = 2$
$D_x = 2.047$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 68 reflections
$\theta = 8.5$–19.1°
$\mu = 0.46$ mm^{-1}
$T = 290$ K
Pyramid, colourless
0.40 × 0.35 × 0.30 mm

Data collection

Kuma KM-4 diffractometer
$w/2\theta$ scans
1682 measured reflections
361 independent reflections
348 reflections with $I > 3\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 30.0°$

$h = -7 \rightarrow 7$
$k = 0 \rightarrow 7$
$l = -13 \rightarrow 13$
3 standard reflections every 200 reflections intensity decay: 1.5%

Refinement

Refinement on F
$R = 0.018$
$wR = 0.022$
$S = 1.70$
361 reflections
31 parameters

All H-atom parameters refined
$w = 1/(\sigma^2(F) + 0.0001F^2)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Table 1
Selected distances (Å).

Si—F1 (× 3)	1.700 (1)	Si—F2 (× 3)	1.695 (1)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*n*1···F1^{i}	0.85 (3)	2.49 (4)	2.975 (2)	117 (3)
N1—H1*n*1···F1^{ii}	0.85 (3)	2.65 (4)	2.962 (2)	103 (3)
N1—H1*n*1···F2^{iii}	0.85 (3)	2.28 (2)	2.972 (1)	139 (3)
N1—H1*n*1···F2^{ii}	0.85 (3)	2.28 (2)	2.972 (1)	139 (3)
N2—H1*n*2···F1^{iv}	0.82 (3)	2.58 (3)	3.023 (1)	115 (2)
N2—H1*n*2···F1^{v}	0.82 (3)	2.58 (3)	3.023 (1)	115 (2)
N2—H1*n*2···F2^{vi}	0.82 (3)	2.29 (3)	3.022 (2)	149 (3)
N1—H2*n*1···F1^{vii}	0.8 (1)	2.45 (7)	2.962 (2)	124 (3)
N1—H2*n*1···F1^{viii}	0.8 (1)	2.45 (7)	2.962 (2)	124 (3)
N1—H2*n*1···F1^{ii}	0.8 (1)	2.45 (7)	2.962 (2)	124 (3)
N2—H2*n*2···F2^{iv}	0.86 (8)	2.62 (5)	3.241 (2)	130 (1)
N2—H2*n*2···F2^{ix}	0.86 (8)	2.62 (5)	3.241 (2)	130 (1)
N2—H2*n*2···F2^{x}	0.86 (8)	2.62 (5)	3.241 (2)	130 (1)

Symmetry codes: (i) $1+x-y, x, \frac{1}{2}+z$; (ii) $-x+y, -x, z$; (iii) $1-y, x-y, z$; (iv) $x-y, x, \frac{1}{2}+z$; (v) $y-1, -1-x+y, \frac{1}{2}+z$; (vi) $-y, x-y, z$; (vii) $1+x, y, z$; (viii) $1-y, 1+x-y, z$; (ix) $y, x, \frac{1}{2}+z$; (x) $-x, -y, \frac{1}{2}+z$.

The inversion-twinning proportion determined by refinement turned out to be insignificant.

Cell refinement: *KM*4*B*8 (Gałdecki *et al.*, 1997); data reduction: *JANA*2000 (Petříček & Dušek, 2000); structure solution: *JANA*2000; program(s) used to refine structure: *JANA*2000; molecular graphics: *ORTEP*III (Burnett & Johnson, 1996).

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