

SHORT STRUCTURAL PAPERS

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Hydrogen Bonding in Diammonium Hexafluorotitanate

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Abstract. $(\text{NH}_4)_2\text{TiF}_6$, $M_r = 197.98$, trigonal, space group $P\bar{3}m1$, $Z = 1$. At 293 K $a = 5.968$ (2), $c = 4.821$ (1) Å, $D_m = 2.24$ (3) (floatation), $D_x = 2.21$ Mg m⁻³. The structure was refined from 150 independent diffractometer-measured reflections to $R_w = 0.019$. At 153 K $a = 5.920$ (2), $c = 4.702$ (1) Å and $D_x = 2.30$ Mg m⁻³. The structure was refined from 147 independent diffractometer-measured reflections to $R_w = 0.018$. At 153 K the H atoms are ordered but show large anisotropic thermal motion. At room temperature this motion is much greater and can be represented equally well by a disordered model in which the NH_4^+ ion is twisted 19° away from the threefold axis.

Introduction. Commercial $(\text{NH}_4)_2\text{TiF}_6$ of Alfa Inorganic Inc. (Beverly, Massachusetts) stock TI-100 was used without recrystallization. The intensities of the X-ray reflections were measured at both 293 and 153 K from a single cylindrically shaped crystal, 0.26 (3) mm in diameter and 0.19 (3) mm long elongated along [001], using a Syntex $P2_1$ diffractometer at the same voltage and current setting. The cell parameters were calculated from 15 well-centered reflections having $13^\circ < 2\theta < 28^\circ$ using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å).

At room temperature the intensities of 687 reflections with $2\theta \leq 55^\circ$ were measured using a θ - 2θ scan. These reflections had $0 \leq k \leq 10$ and $-10 \leq l \leq 10$ for the $h = 0$ layer, and $-10 \leq k \leq 10$ and $-10 \leq l \leq 10$ for the layers with $1 \leq h \leq 10$. An absorption correction was not considered necessary ($\mu R = 0.20$). The intensities of two standard reflections, $2\bar{3}2$ and $3\bar{2}2$, measured at regular intervals, showed no systematic variation and agreed within three times the standard errors based on counting statistics. At 153 K low temperature was maintained by an LT-1 Syntex cold nitrogen gas flow attachment. 724 reflections with $2\theta \leq 55^\circ$ and $0 \leq h \leq 10$, $-10 \leq k \leq 10$, $-10 \leq l \leq 10$

were measured. The intensities of standard reflections $2\bar{3}2$ and $3\bar{2}2$ again agreed within three standard errors and did not show any systematic variation.

The intensities of equivalent reflections were weighted by σ^{-2} (counting) and averaged to give 150 unique reflections at room temperature and 147 unique reflections at low temperature. With up to six equivalent reflections in each set it was possible to estimate the standard errors σ_A of the average and these values were used to determine a weighting scheme for the least-squares refinement as discussed below.

Cox & Sharpe (1953) showed that the space group of $(\text{NH}_4)_2\text{TiF}_6$ is $P\bar{3}m1$ and that the structure is isomorphous with K_2GeF_6 with Ti in position 1(a), F in 6(i) and N in 2(d). After refining the heavy-atom coordinates we calculated a difference synthesis which clearly showed the H atoms ordered on sites 2(d) and 6(i). All variable positional and anisotropic temperature parameters were then refined by least squares on $\sum w(F_o - F_c)^2$. In the low-temperature structure the temperature factor U_{33} of H(1) refined to a negative value. It was therefore set to zero and held constant while the remaining parameters were refined. Atomic scattering curves for Ti^{4+} , $\text{F}^{2/3-}$, N and H (both neutral) were adapted from *International Tables for X-ray Crystallography* (1974).

An extinction correction of the form $F_c^* = F_c[1 + g\beta(2\theta)F_c^2]^{-1/2}$ (Larson, 1967) was also included in the refinement. The parameter g was found to be 2.6 (4) $\times 10^{-5}$ at room temperature and 2.1 (4) $\times 10^{-5}$ at low temperature. During the refinement the structure factors were weighted by the function $w = \sigma_{\text{total}}^{-2} = [\sigma^2(\text{counting}) + k^2|F_o|^2]^{-1}$ where k was chosen in such a way that σ_{total} was equal on average to the standard error (σ_A) determined experimentally during the averaging of equivalent reflections.

The final value of $R_w = [\sum w(|F_c| - |F_o|)^2 / \sum w|F_o|^2]^{1/2}$ was 0.019 at 293 K and 0.018 at 153 K.

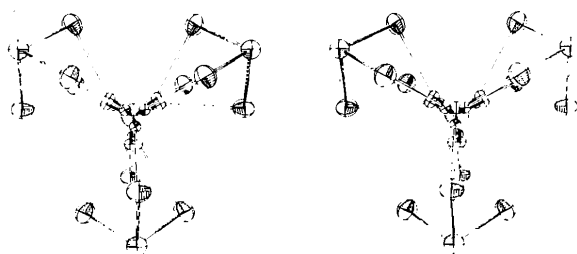


Fig. 1. A stereoscopic view of the rotationally disordered NH_4^+ ion of model (II) viewed down the threefold axis through N. The N-H bonds are shown solid, the H-F bonds by double lines, the F-Ti bonds by triple lines.

In the final cycles of refinement the maximum and average shifts over error were 0.47 and 0.05 at 293 K, and 0.22 and 0.05 at 153 K respectively. The standard deviation of an observation of unit weight was 2.2 at 293 K and 2.8 at 153 K. Since w is based on a realistic estimate of the standard errors, this quantity is expected to have the value 1.0 in a fully refined structure. The large values observed suggest that our model is in some way deficient. We therefore calculated a difference synthesis whose largest peaks were $0.24 \text{ e } \text{\AA}^{-3}$ at 293 K and $0.27 \text{ e } \text{\AA}^{-3}$ at 153 K. These lie at the center of the Ti-F bonds and correspond to bonding electron density not included in our model. Another large feature on the difference map is a peak of $-0.13 \text{ e } \text{\AA}^{-3}$ at 293 K ($-0.11 \text{ e } \text{\AA}^{-3}$ at 153 K) in the neighborhood of the F atoms and indicates that our choice for the residual charge on F was too large.

Because of the very large anisotropy in the H-atom motions at room temperature we tested model (II) in which the NH_4^+ ion was disordered by rotating it 20°

Table 1. Atomic coordinates ($\times 10^4$; $\times 10^3$ for hydrogen) and U_{eq} values ($\times 10^4$; $\times 10^3$ for H)

(I) 293 K (model I); (II) 293 K (model II); (III) 153 K. $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i, a_j)$. For (I) and (III) H(21) is related to H(2) by the threefold axis.

		x	y	z	U_{eq} (\AA^2)
Ti	(I), (II), (III)	0	0	0	187 (3) 186 (3) 86 (3)
F	(I)	2983 (2)	1492 (1)	2171 (2)	331 (4)
	(II)	2984 (2)	1492 (1)	2171 (2)	330 (4)
	(III)	2993 (1)	1496 (1)	2227 (1)	155 (2)
N	(I)	6667	3333	-3178 (6)	315 (9)
	(II)			-3179 (6)	314 (9)
	(III)			-3094 (4)	139 (7)
H(1)	(I)	667	333	-124 (14)	312 (42)
	(II)	609 (33)	304 (16)	-137 (15)	59 (40)*
	(III)	667	333	-120 (9)	97 (25)
H(2)	(I)	733 (3)	466 (6)	-356 (8)	100 (23)
	(II)	727 (44)	489 (17)	-325 (13)	81 (33)*
	(III)	742 (2)	484 (4)	-372 (5)	20 (8)
H(21)	(II)	552 (22)	276 (11)	-441 (20)	61 (45)*

* Isotropic U values.

Table 2. Bond distances (\AA) and angles ($^\circ$)

	293 K (I)	293 K (II)	153 K (III)
Ti-F	1.864 (1) $\times 6$	1.864 (1) $\times 6$	1.857 (1) $\times 6$
N-H(1)	0.93 (7)	0.92 (8)	0.89 (4)
N-H(2)	0.71 (3) $\times 3$	$\left\{ \begin{array}{l} 0.81 (12) \times 2 \\ 0.84 (11) \times 1 \end{array} \right\}$	0.83 (2) $\times 3$
N-H(21)			
H(1)-F	2.52 (4) $\times 3$	$\left\{ \begin{array}{l} 2.34 (13) \\ d \ 2.68 (9) \times 2 \end{array} \right\}$	2.48 (3) $\times 3$
H(2)-F	$\left\{ \begin{array}{l} a \ 2.39 (4) \\ b \ 2.49 (4) \times 2 \end{array} \right\}$	$\left\{ \begin{array}{l} b \ 2.30 (16) \\ c \ 2.42 (21) \\ a \ 2.47 (9) \\ e \ 2.10 (11) \\ f \ 2.70 (7) \times 2 \end{array} \right\}$	$\left\{ \begin{array}{l} a \ 2.20 (2) \\ b \ 2.41 (2) \times 2 \end{array} \right\}$
H(21)-F			
F-Ti-F	91.53 (3)	91.55 (8)	91.36 (2)
F-Ti-F	88.47 (4)	88.45 (4)	88.64 (3)
H(1)-N-H(2)	105 (3)	$\left\{ \begin{array}{l} 99 (19) \\ 116 (23) \end{array} \right\}$	111 (1)
H(1)-N-H(21)			
H(2)-N-H(2)	113 (3)	$\left\{ \begin{array}{l} 134 (23) \\ 104 (13) \end{array} \right\}$	108 (2)
H(2)-N-H(21)			
N-H(1)-F	131 (1)	$\left\{ \begin{array}{l} 156 (18) \\ d \ 117 (8) \end{array} \right\}$	131 (1)
N-H(2)-F	$\left\{ \begin{array}{l} a \ 136 (4) \\ b \ 135 (3) \end{array} \right\}$	$\left\{ \begin{array}{l} b \ 150 (22) \\ c \ 133 (19) \\ a \ 118 (8) \end{array} \right\}$	141 (2)
N-H(21)-F		$\left\{ \begin{array}{l} e \ 174 (7) \\ f \ 105 (6) \end{array} \right\}$	129 (2)

(a) 3 (11 $\bar{1}$), (b) 4 (110), (c) 5 (110), (d) 3 (110), (e) 1 (001), (f) 5 (000).

from the threefold axis so that H(1) was moved closer to one of the F atoms. The crystal symmetry then generated two other orientations of the ion (see Fig. 1). After this model was refined with isotropic temperature factors on the H atoms the NH_4^+ ion was found to be twisted $19 (9)^\circ$ away from the threefold axis. It yielded the same R factor and standard deviation for an observation of unit weight as the ordered model (I). It is not therefore possible to distinguish between them.

The final positional parameters and interatomic distances and angles are given in Tables 1 and 2.*

Discussion. The TiF_6^{2-} ion consists of a very slightly flattened octahedron with bonds whose length, 1.864 (1) \AA , at room temperature is close to that found in a number of other hydrogen-bonded TiF_6^{2-} compounds. We assumed an electrically neutral ion with four electrons transferred from Ti to the six F atoms. The final difference synthesis indicates that some of the excess charge we assigned to F as well as the two additional ionic charges are to be found in the Ti-F bonds.

The bond lengths and angles of the NH_4^+ ion are not sufficiently well determined to bear close scrutiny. The N-H bonds are all shorter than would be expected in a neutron diffraction study because electron density is

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36688 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

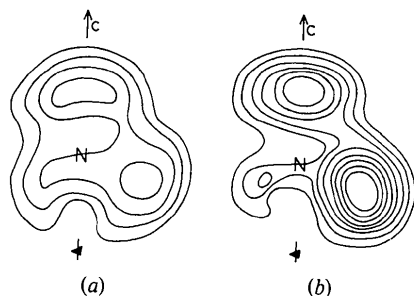


Fig. 2. Hydrogen electron density in the mirror plane containing the threefold axis (a) at 293 K, (b) at 153 K. Contours are drawn at intervals of $0.07 \text{ e } \text{Å}^{-3}$ (lowest contour $0.14 \text{ e } \text{Å}^{-3}$).

shifted from H into the bonding region. The H atoms are, however, well enough located to provide good information on hydrogen bonding. At 153 K each H atom forms a nearly symmetrical trifurcated bond with H–F distances in the range 2.2 to 2.5 Å. The temperature factors for H, as well as the H electron density maps, indicate that the NH_4^+ ion is undergoing a considerable librational motion.

At 293 K the electron density of H(1) becomes cap-shaped (see Fig. 2) suggesting that the vibrations of the NH_4^+ ion have become extremely large (model I) or that the NH_4^+ ion is twisted away from the threefold axis and is rotationally disordered around it (model II).

Our refinement was unable to distinguish between the ordered (I) and disordered (II) models at 293 K. Indeed there may be no clear physical distinction between them. The disorder of the NH_4^+ ion that we propose for trigonal $(\text{NH}_4)_2\text{TiF}_6$ (Fig. 1) is similar to that proposed by Schlemper, Hamilton & Rush (1966) for the *cubic* form of $(\text{NH}_4)_2\text{SiF}_6$ (compare their Fig. 4) and quite different from that found in the *trigonal* form of the same compound (Schlemper & Hamilton, 1966).

The hydrogen bonding in $(\text{NH}_4)_2\text{TiF}_6$ has recently been studied by Knop, Westerhaus & Falk (1980) using infrared spectra measured at different temperatures. They observe that the stretching mode of the isotopically dilute ND bond is split, corresponding to two different types of D atom, and that its frequency increases with decreasing temperature. They propose that this behavior is characteristic of polyfurcated hydrogen bonds. At low temperatures the H atom forms three equally weak bonds. As the temperature increases, the NH_4^+ ion is able to reorient itself so as to make one H–F bond stronger and the other two weaker. This is just the situation that occurs in our model (II).

As a further check on the relative plausibilities of models (I) and (II) we give in Fig. 3 a polar diagram showing the relation between H...F bond length and N–H...F angle. All three models (I, II at room temperature and III at low temperature) show correla-

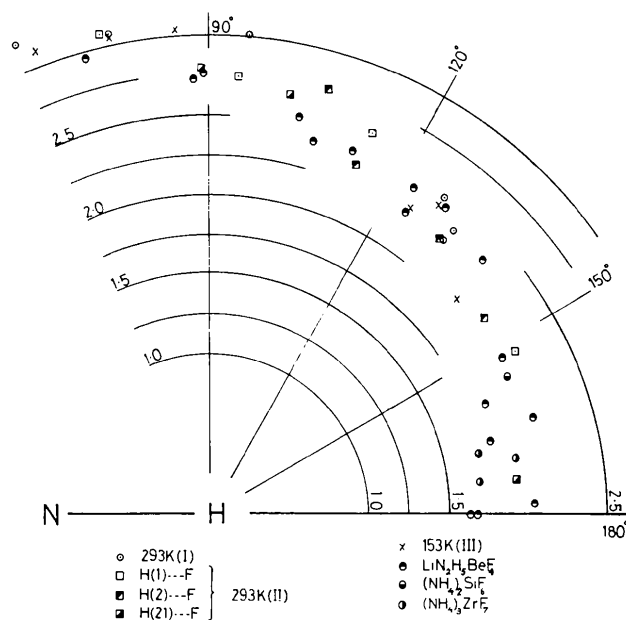


Fig. 3. Polar diagram showing the positions of acceptor F atoms in N–H...F hydrogen bonds. The positions found in the three models are compared with those found in three neutron diffraction determinations. For the purposes of plotting this diagram the H atoms are shifted to give N–H bonds of 1 Å. Data for $\text{LiN}_2\text{H}_3\text{BeF}_4$ are taken from Anderson, Brown & Vilminot (1973), for $(\text{NH}_4)_2\text{SiF}_6$ from Schlemper, Hamilton & Rush (1966) and for $(\text{NH}_4)_3\text{ZrF}_5$ from Hurst & Taylor (1970).

tions typical of those found in other systems indicating that they all give chemically reasonable hydrogen-bond geometries.

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