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Key indicators

Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(F-B) = 0.002$ Å
 R factor = 0.045
 wR factor = 0.140
Data-to-parameter ratio = 14.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

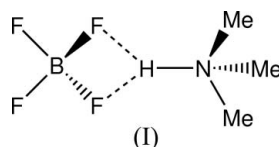
Trimethylammonium tetrafluoroborate at 100 K

The crystal structure of the title compound, $C_3H_{10}N^+ \cdot BF_4^-$, has been redetermined at 100 K and shows the BF_4^- anion to be ordered at this temperature. Both the anion and the cation lie on a mirror plane and they are connected by $N-H \cdots F$ and $C-H \cdots F$ hydrogen bonds.

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Comment

Trimethylammonium tetrafluoroborate, (I), is known to have three solid phases above approximately 100 K (Zabinska *et al.*, 1988). These solid phases have been characterized by 1H and ^{19}F NMR (Ishida *et al.*, 1992), as well as by powder and single-crystal X-ray diffraction (Ishida *et al.*, 2000). The two polymorphic phase transitions are interrelated with changes in the mobility of the ions in the crystal structure. The high-temperature cubic phase is stable above 453 K and is an ionic plastic phase (Ikeda, 2004), where both cation and anion perform isotropic rotation as well as self-diffusion over the 1H and ^{19}F NMR time scales. In the intermediate tetragonal phase, stable between 384 and 453 K, onset of self-diffusion of the anions and isotropic rotation of the cations was observed. In the low-temperature phase, reorientational motions of the methyl-H atoms about the C–N bond axis, and of the entire cation around the N–H bond axis, were detected by NMR. In addition, isotropic rotation of the anion was detected.



Single crystal X-ray diffraction data measured at 300 K showed the displacement parameters of the BF_4^- anion to be extremely large, probably due to large thermal vibration and libration or positional disorder. Therefore, the structure was refined using a disordered model, in which the anion is disordered with respect to its central position as well as to its orientation, with an abundance ratio of about 3:3:1:1. In the present study, we have redetermined the structure of the title compound (Fig. 1) at 100 K to clarify the state of the anion, as well as the nature of the interactions between the ions at this reduced temperature.

The unit-cell parameters at 100 K are essentially the same as those at 300 K [$P2_1/m$, $a = 5.7017$ (8), $b = 8.5724$ (9), $c = 7.444$ (1) Å and $\beta = 102.76$ (1)° (Ishida *et al.*, 2000)], but the BF_4^- anion is ordered at this temperature. The F1, F2 and B1 atoms of the anion and the N1 and C2 atoms of the cation lie on a mirror plane. The disorder of the anion observed at 300 K, therefore, can be classified as continuous positional disorder. This is consistent with the observation that no

obvious thermal anomaly nor discontinuous change in the mobility of the ions was observed in the temperature range 100–270 K (Ishida *et al.*, 1992, 2000). In the crystal structure, the cation and the anion are connected by a bifurcated N—H···F hydrogen bond (Fig. 1 and Table 2). There are also weak C—H···F interactions, resulting in a molecular tape running parallel to the *b* axis (Fig. 2).

Experimental

Compound (I) was prepared by neutralizing an aqueous solution of trimethylamine (28% in water, 10 ml) with tetrafluoroboric acid (42%, *ca* 9 ml). Single crystals were obtained by slow evaporation of a methanol solution of (I).

Crystal data

$C_3H_{10}N^+ \cdot BF_4^-$	$D_x = 1.457 \text{ Mg m}^{-3}$
$M_r = 146.92$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/m$	Cell parameters from 3348 reflections
$a = 5.460$ (6) Å	$\theta = 3.7\text{--}30.0^\circ$
$b = 8.496$ (7) Å	$\mu = 0.16 \text{ mm}^{-1}$
$c = 7.433$ (6) Å	$T = 100 \text{ K}$
$\beta = 103.80$ (4)°	Prism, colourless
$V = 334.9$ (5) Å ³	$0.30 \times 0.20 \times 0.12 \text{ mm}$
$Z = 2$	

Data collection

Rigaku R-Axis RAPID diffractometer	760 reflections with $F^2 > 2\sigma(F^2)$
ω scans	$R_{\text{int}} = 0.045$
Absorption correction: none	$\theta_{\text{max}} = 30.0^\circ$
4017 measured reflections	$h = -7 \rightarrow 7$
1038 independent reflections	$k = -11 \rightarrow 10$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[0.002F_o^2 + \sigma(F_o)^2]/(4F_o^2)$
$wR(F^2) = 0.140$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$
1038 reflections	$\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$
71 parameters	

Table 1

Selected geometric parameters (Å).

F1—B1	1.392 (2)	N1—C1	1.4904 (16)
F2—B1	1.402 (2)	N1—C2	1.493 (2)
F3—B1	1.3836 (13)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1···F1	0.89 (2)	2.30 (2)	2.972 (4)	132 (2)
N1—H1···F2	0.89 (2)	2.04 (2)	2.904 (4)	166 (2)
C1—H4···F3 ⁱ	0.96 (2)	2.55 (2)	3.424 (4)	152 (2)
C2—H5···F3 ⁱⁱ	0.97 (2)	2.47 (2)	3.373 (4)	156 (1)

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x + 1, y + \frac{1}{2}, -z + 1$.

H atoms were located in a Fourier map and refined isotropically, with N—H = 0.89 (2) Å and C—H bond lengths in the range 0.93 (2)–0.98 (2) Å.

Data collection: *RAPID-AUTO* (Rigaku/MSK and Rigaku Corporation, 2004); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK and Rigaku Corporation, 2005);

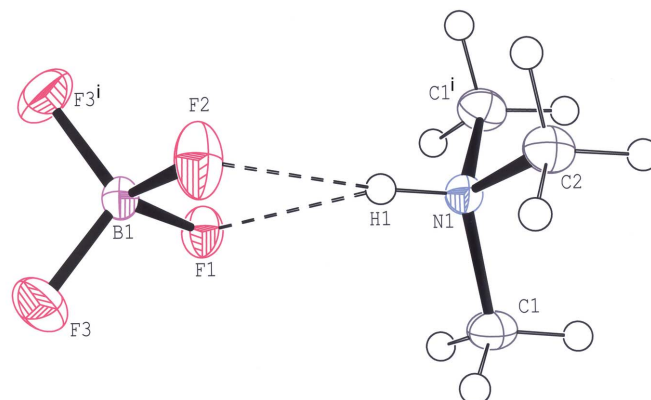


Figure 1

Drawing of (I), showing the atom numbering. Displacement ellipsoids are drawn at the 50% probability level. N—H···F hydrogen bonds are indicated by dashed lines (symmetry code as given in Table 2).

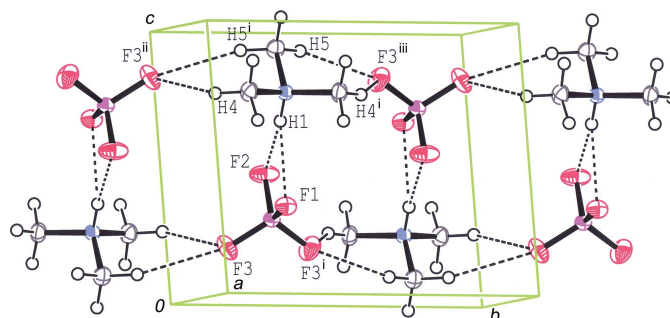


Figure 2

Packing diagram of (I), showing the molecular tape formed by N—H···F and C—H···F hydrogen bonds (symmetry codes as given in Table 2).

program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* and *PLATON* (Spek, 2003).

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