Crystal Structure of Trimethylammonium Tetrafluoroborate in Three Solid Phases

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The crystal structure of $(CH_3)_3NHBF_4$ was studied in three solid phases by X-ray diffraction techniques. The structures of the ionic plastic phase (Phase I) stable above 453 K and Phase II between 384 and 453 K are CsCl-type cubic (a = 5.772(4) Å) and tetragonal (a = 9.815(5) and c = 6.895(5) Å), respectively. The room temperature phase (Phase III) forms a monoclinic lattice (space group $P2_1/m$, a = 5.7017(8), b = 8.5724(9), c = 7.444(1) Å, and β = 102.76(1)°). BF_4^- ions in this phase were shown to be disordered in four orientations.

Key words: Crystal Structure; X-ray Diffraction; Ionic Plastic Phase; Disorder.

Introduction

The three solid phases (Phase I, II, and III in the order of decreasing temperature) of trimethylammonium tetrafluoroborate, $(CH_3)_3NHBF_4$, were revealed by Zabinska et al. by differential scanning calorimetry (DSC) [1], but the crystal structures of these phases are unknown. Our previous study of ^1H and ^{19}F NMR [2] showed that Phase I, existing above 453 K, is an ionic plastic phase where the cation and the anion perform isotropic rotation as well as self-diffusion. In Phase II, stable between 384 and 453 K, the onset of anionic self-diffusion and cationic isotropic rotation was observed. These facts imply highly symmetric crystal structures in Phase I and II where the cation and anion are highly disordered.

Trimethylammonium perchlorate, $(CH_3)_3NHClO_4$, containing anions of a similar shape and size as BF_4^-, is also known to form three solid phases [3]. The crystal structures of $(CH_3)_3NHClO_4$ in Phase I, II, and III in the order of decreasing temperature are CsCl-type cubic (a = 5.845(1) Å), tetragonal (a = 9.912(4) and c = 7.01(2) Å), and monoclinic (space group $P2_1$, a = 5.749(1), b = 8.670(1), c = 7.5585(9) Å, β = 102.66(1)°) [4]. Phase I is assigned to an ionic plastic phase [5 - 7] because the dynamical behaviour of the ions is similar to that in Phase I of tetrafluoroborate. In Phase II the cation undergoes random tumbling about axes inclined by *ca.* 20° to the N-H bond axis, while the anion performs an axial motion [6].

In the present study we determined the structures of Phase I and II of tetrafluoroborate by powder X-ray diffraction, and that of Phase III by single crystal X-ray diffraction to compare the structures with those of the perchlorate. The BF_4^- ions in ionic crystals with pyridinium [8], methylammonium [9], tetramethylammonium [10], and tert-butylammonium [11] are disordered at room temperature. The disordered state of BF_4^- in our crystal is of additional interest.

Experimental

$(CH_3)_3NHBF_4$ was prepared by neutralizing trimethylamine with tetrafluoroboric acid. The obtained crystals were recrystallized from methanol. Powder X-ray patterns in Phase I and II were taken at ca. 470 and ca. 320 K, respectively, using a Rigaku Rint1000 diffractometer equipped with a copper anticathode (λ = 1.5418 Å, 40 kV, 200 mA). Single crystal X-ray measurements were carried out on Phase III at 300 K using a Rigaku AFC-5R diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å, 40 kV, 200 mA) of the X-ray Laboratory of Okayama University. The data were collected using the ω-2θ scan technique to a maximum 2θ value of 55.0°; scans of $(1.63 + 0.03 \tan \theta)°$ were made at a speed

Table 1. Crystal data of $(CH_3)_3NHBF_4$ in Phase III at 300 K and experimental conditions for the structure determination.

Crystal data:	
Crystal colour, habit	colorless, prismatic
Crystal dimensions / mm	$0.30 \times 0.35 \times 0.35$
Crystal system	monoclinic
Space group	$P2_1/m$ (#11)
a / Å	5.7017(8)
b / Å	8.5724(9)
c / Å	7.444(1)
β /°	102.76(1)
V / Å^3	354.83(7)
Z value	2
D_wx / Mg m^{-3}	1.375
$F(000)$	152
μ(Mo Kα) / mm^{-1}	0.154
Experimental conditions:	
Cell parameters from 25 reflections (2θ = 20 - 23)	
Refls. measured	957 [Unique: 875 ($R_{\mathrm{int}} = 0.011$)]
h, k, l	$h = 0 \rightarrow 7$, $k = 0 \rightarrow 11$, $l = -9 \rightarrow 9$
Corrections	Absorption: ψ scans [14] $T_{\mathrm{min}} = 0.913$, $T_{\mathrm{max}} = 0.955$ Extinction: Zachariasen [15] (coefficient: $2.5(2) \times 10^{-5}$)
Refinement	Full-matrix least-squares on F^2
Anomalous dispersion	All non-hydrogen atoms
Refls. used	875
Variables	67
R[a], R_w[b]	0.076; 0.140 ($I > 2\sigma(I)$)
Goodness of fit	2.81
$(\Delta/\sigma)_{\mathrm{max}}$	0.01
$\Delta\rho_{\mathrm{max}}, \Delta\rho_{\mathrm{min}}$ / e$^-$ Å^{-3}	0.34, –0.36
Scattering factors from International Tables for Crystallography (1992, Vol. C)	

[a] $R = \Sigma \big| |F_o| - |F_c| \big| / \Sigma |F_o|$. [b] $R_w = [\Sigma(w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Observed and calculated 2θ values of powder X-ray patterns of $(CH_3)_3NHBF_4$ in Phase I and II, taken at ca. 470 and ca. 320 K, respectively. (Phase I: cubic, $a = 5.772(4)$ Å, $Z = 1$, $V = 192.3(4)$ Å^3 and $D_x = 1.269$ Mg m^{-3}; Phase II: tetragonal, $a = 9.815(5)$, $c = 6.895(5)$ Å, $Z = 4$, $V = 664(2)$ Å^3 and $D_x = 1.47$ Mg m^{-3}).

– Observed –		– Calculated –	
2θ/°	Intensity	2θ/°	$h\,k\,l$
Phase I: (± 0.05)			
15.33	10	15.35	1 0 0
21.79	100	21.77	1 1 0
26.72	5	26.75	1 1 1
31.02	7	30.99	2 0 0
34.73	3	34.75	2 1 0
Phase II: (± 0.03)			
15.69	10	15.71	1 0 1
20.20	100	20.23	2 1 0
24.03	50	24.03	2 1 1
25.67	5	25.67	2 2 0
31.64	5	31.61	3 1 1
32.91	5	32.90	3 2 0
37.90	5	37.91	3 0 2
39.17	3	39.20	0 0 3
44.40	2	44.50	2 1 3
48.33	2	48.40	3 0 3

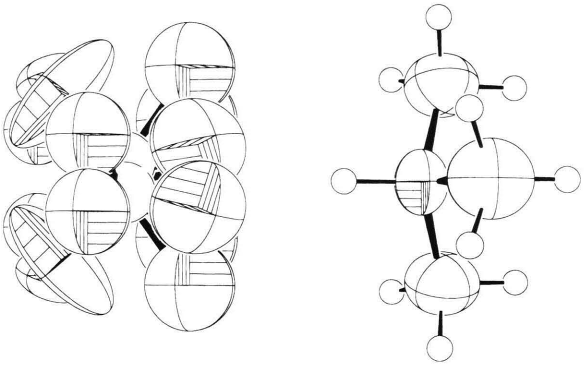

Fig. 1. ORTEP-3 [16] drawing of the disordered structure of $(CH_3)_3NHBF_4$. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of arbitrary size.

of 6.0°/min (in ω). Three standard reflections were measured after every 97 reflections; the intensity variation was 0.62% over the course of data collection. The structure was solved by the direct method SIR97 [12] and refined by a full-matrix least-squares method. The quantity minimized was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o)$. All calculations were performed using the TEXSAN crystallographic software package [13]. Crystal data and experimental conditions for the structure determination are summarized in Table 1.

Results and Discussion

The powder X-ray diffraction angles (2θ) in Phases I and II, taken at ca. 470 and ca. 320 K, respectively, are shown in Table 2. The structure of Phase I could be interpreted by a simple cubic lattice with a = 5.772(4) Å, isomorphous with that of the perchlorate. Thus we conclude that Phase I is an ionic plastic phase of CsCl-type just as in case of Phase I of perchlorate.

Phase II can be indexed by a tetragonal lattice with a = 9.815(5) and c = 6.895(5) Å. Since the powder patterns resemble those of perchlorate obtained in Phase II [4], the structures in Phase II of both salts are

Table 3. Positional and displacement parameters of $(CH_3)_3NHBF_4$ in Phase III.

	x	y	z	occup.	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F1	0.7288(5)	0.230(2)	0.3302(4)	0.76	0.065(1)	0.111(9)	0.098(2)	0.038(6)	0.005(1)	0.009(4)
F2	0.4276(6)	0.2922(7)	0.4487(3)	0.76	0.176(3)	0.120(9)	0.090(2)	0.016(3)	0.079(2)	−0.013(2)
F3	0.449(1)	0.3863(5)	0.1733(8)	0.76	0.134(4)	0.041(2)	0.087(2)	0.001(2)	0.032(2)	0.018(2)
F4	0.369(1)	0.1366(7)	0.210(1)	0.76	0.122(5)	0.174(5)	0.172(5)	−0.093(4)	0.035(3)	−0.102(3)
F5	0.63(2)	0.33(1)	0.37(2)	0.24	0.159(8)					
F6	0.47(2)	0.10(1)	0.42(2)	0.24	0.118(5)					
F7	0.23(1)	0.30(1)	0.30(2)	0.24	0.100(3)					
F8	0.45(2)	0.18(1)	0.13(1)	0.24	0.070(4)					
N	0.9278(3)	0.25	0.7309(2)	1.0	0.055(1)	0.067(1)	0.047(1)	0	0.0007(9)	0
C1	1.0767(3)	0.3923(2)	0.7371(2)	1.0	0.090(1)	0.064(1)	0.084(1)	−0.008(1)	0.024(1)	0.004(1)
C2	0.7916(4)	0.25	0.8783(4)	1.0	0.075(2)	0.094(2)	0.097(2)	0	0.044(2)	0
B1	0.4878(7)	0.264(2)	0.2834(6)	0.76	0.055(1)					
B2	0.45(1)	0.23(1)	0.31(1)	0.24	0.055(1)					
H1	0.8202	0.25	0.6144	1.0	0.070					
H2	1.1332	0.4054	0.6325	1.0	0.095					
H3	1.2048	0.3908	0.8454	1.0	0.095					
H4	0.9763	0.4835	0.7529	1.0	0.095					
H5	0.6922	0.1586	0.8611	1.0	0.102					
H6	0.8945	0.25	0.9905	1.0	0.102					

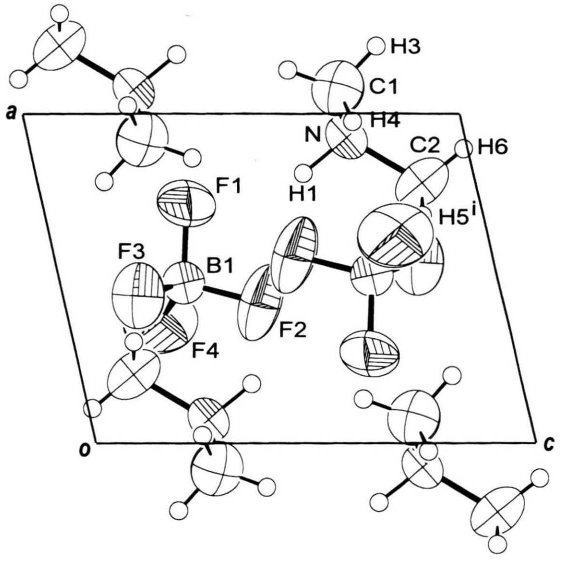

Fig. 2. ORTEP-3 packing diagram of $(CH_3)_3NHBF_4$ viewed down the *b* axis and atomic numberings. B2 and F5 - F8 atoms are omitted for clarity. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of arbitrary size.

Table 4. Bond lengths (Å) and angles (°) of $(CH_3)_3NHBF_4$ in Phase III.

B1-F1	1.37(1)	B1-F2	1.370(8)
B1-F3	1.32(2)	B1-F4	1.34(2)
B2-(F5∼F8)	1.36		
N-C1	1.482(3)	N-C2	1.477(4)
N-H1	0.95	C1-H2	0.91
C1-H3	0.96	C1-H4	0.99
C2-H5	0.96	C2-H6	0.91
F1-B1-F2	104.2(6)	F1-B1-F3	110(2)
F1-B1-F4	109(2)	F2-B1-F3	112(2)
F2-B1-F4	108(2)	F3-B1-F4	113.2(7)
C1-N-C1^i	110.9(3)	C1-N-C2	111.6(2)

Symmetry code: (i) *x*, 1/2 − *y*, *z*.

considered to be isomorphous. The fact that the ions in tetrafluoroborate are more excited [2] than those in Phase II of perchlorate [6] may be explained by the difference in weight of the two anions.

Phase III was found to be monoclinic and its space group was determined to be $P2_1/m$ (#11) from systematic absences of $0k0$, $k = 2n + 1$ and a statistical analysis of the intensity distribution. The molecular structure of $(CH_3)_3NHBF_4$ is shown in Fig. 1, and the atomic parameters are listed in Table 3. Two kinds of crystallographically nonequivalent BF_4^- ions (group 1 and 2) were observed, and both ions are disordered with respect to the mirror plane perpendicular to the *b* axis. Group 1 has an occupancy factor about three times larger than that of group 2. Consequently, the anion is disordered as to its central position as well as to its orientation with an abundance ratio of about 3:3:1:1. The C2 and N atoms lie on the mirror plane. The non-H atoms of the cation and the F atoms of group 1 were refined anisotropically, while the B atom of this group was refined isotropically. The BF_4^- ion of group 2 was treated as a rigid group with a tetrahedral symmetry and a B-F bond length of 1.36 Å. The central position and the orientation of this anion, and the isotropic displacement parameter (U_{iso}) of each atom were refined. The H atoms were located on difference syntheses. The coordinates were fixed and the U_{iso} values were assumed to be 1.2 times those of the equivalent isotropic displacement parameters of their parent atoms.

A packing diagram viewed down the *b* axis is shown in Fig. 2, and intramolecular bond lengths and angles are listed in Table 4. The crystal packing in Fig. 2 is remarkably similar to that in perchlorate [4], except for the hydrogen bonding patterns. The cation forms an N-H... F type hydrogen bond with the anion (N... F1 2.963(5) Å, H1... F1 2.07 Å, and N-H1... F1 154.6°; N... F5 2.932(2) Å, H1... F5 2.03 Å, and N-H1... F5 159.2°), while the cation in perchlorate forms a bifurcated hydrogen bond with the ClO_4^- ion. The H... F distances are rather short compared to 2.55 Å, the sum of the van der Waals radius of H and F atoms [17], but the H-bond is not strong enough to prevent the disordering of the anion at room temperature.

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