Crystal Structure of Trimethylammonium Perchlorate in Three Solid Phases Including the Ionic Plastic Phase Obtainable above 480 K

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The crystal structures of $(CH_3)_3NHClO_4$ in three solid phases were studied by X-ray diffraction techniques. X-ray powder patterns taken at ca. 500 and 445 K revealed that the plastic phase (Phase I) attainable above 480 K crystallizes in a CsCl-type cubic structure with $a = 5.845$ (1) Å, $Z = 1$, $V = 199.7$ (2) Å^3, and $D_x = 1.327$ g cm^{-3}, while Phase II, stable between 480 and 396 K, forms a tetragonal structure with $a = 9.912$ (4), $c = 7.01$ (2) Å, $Z = 4$, $V = 689$ (3) Å^3, and $D_x = 1.54$ g cm^{-3}. The room temperature phase (Phase III) was studied by single crystal X-ray diffraction and found to form a monoclinic lattice with space group $P2_1$, $a = 5.749$ (1), $b = 8.670$ (1), $c = 7.5585$ (9) Å, $\beta = 102.66$ (1)°, $Z = 2$, $V = 367.6$ (2) Å^3, and $D_x = 1.441$ g cm^{-3}. Thermal measurements, differential thermal analysis and differential scanning calorimetry, were carried out on these solid phases, and the obtained results were compared with those observed for $(CH_3)_3NHBF_4$.

Key words: Crystal structure; X-ray diffraction; Thermal measurements; Ionic plastic phase.

Introduction

The three solid phases of trimethylammonium perchlorate were revealed by Stammler et al. from studies of high-temperature powder X-ray diffraction and differential thermal analysis (DTA) [1]. They reported that the highest-temperature solid phase, named Phase I, is stable above 480 K and forms a tetragonal lattice with $a = 8.20$, $c = 6.56$ Å, and $Z = 2$. The structures of Phase II and III existing at 480–389 K and below 389 K, respectively, were unknown. The interrelation between the phase transitions and excited motional modes of $(CH_3)_3NH^+$ and ClO_4^- ions were extensively investigated by Jurga et al. using differential scanning calorimetry (DSC), and ^1H, ^2H and ^{35}Cl NMR techniques [2, 3]. They revealed that in Phase I the cations perform isotropic reorientation as well as self-diffusion. This motional behaviour implies that Phase I is an ionic plastic phase [4], and hence probably forms a cubic structure, which is, however, inconsistent with previous results reported by Stammler et al. [1].

In the present investigation, we redetermined the structure of Phase I by using powder X-ray diffraction. In addition, the structures of Phase II and III were studied by powder and single crystal X-ray diffraction techniques, respectively.

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Experimental

$(CH_3)_3NHClO_4$ was prepared by neutralizing trimethylamine with perchloric acid. The obtained crystals were recrystallized twice from methanol. Phase-transition temperatures and the transition enthalpies were redetermined by a home-made DTA apparatus [5] and a Perkin-Elmer DSC 7 calorimeter, respectively; heating rates employed were 1 and 5 K min^{-1} in the same order. Powder X-ray patterns in Phase I and II were taken at ca. 500 and 445 K, respectively,

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Table 1. Experimental conditions for the crystal structure determination and crystal structure data of $(CH_3)_3NHClO_4$ in Phase III at 300 K.

Experimental conditions	
Crystal colour, habit, and size	colorless, prismatic $(0.40 \times 0.35 \times 0.30)$ mm^3
Diffractometer	Rigaku AFC-5R
Radiation and wavelength	Mo Kα, $\lambda = 0.71073$ Å
Absorption coefficient	$\mu = 0.47$ mm^{-1}
Scan	$\omega/2\theta$
$2\theta_{max}$	50.0°
Range of h, k, l	$0 \le h \le 6, 0 \le k \le 10, -8 \le l \le 8$
Cell parameters from 25 reflections ($2\theta = 21$–$23°$)	
Absorption correction	empirical, ψ-scan correction $T_{min} = 0.95$, $T_{max} = 1.00$
Number of measured reflections	770
Number or independent reflections	707 ($R_{int} = 0.013$)
3 standard reflections (−2 0 0), (−2 0 1), and (−1 3 3), monitored every 97 reflections intensity variation:	0.5%
Refinement on F	
$R = \Sigma \lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert / \Sigma \lvert F_o \rvert$	0.054
$wR = \{\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w F_o^2\}^{1/2}$	0.060 [$w = 4F_o^2/\sigma^2(F_o^2)$]
S	2.43
Number of observed reflections	602 [$I > 3\sigma(I)$]
Number of parameters	86
Coefficient of secondary extinction correction	2.66×10^{-6}
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)	
H atoms were located in the difference Fourier map, and only H(10) was refined.	
Crystal data	
Space group	$P2_1$
Unit-cell dimensions	$a = 5.749(1)$ Å $b = 8.670(2)$ Å $c = 7.5585(9)$ Å $\beta = 102.66(1)°$
Volume of the unit cell	$V = 367.6(2)$ Å^3
Formular units per unit cell	$Z = 2$
D_x	1.441 g/cm^3
$(\Delta/\sigma)_{max}$	2.02
$\Delta\varrho_{max}$, $\Delta\varrho_{min}$	0.41, −0.25 e Å^{-3}

using a Rigaku Rint 1000 diffractometer equipped with a copper anticathode (40 kV, 200 mA); the obtained 2θ values were calibrated with those of silicon. 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 (40 kV, 200 mA). The structure was solved by the direct method using MITHRIL [6] and DIRDIF [7].

Table 2. Observed and calculated 2θ values of X-ray powder patterns in Phase I of $(CH_3)_3NHClO_4$ at ca. 500 K (cubic, $a = 5.845(1)$ Å, and $Z = 1$).

$2\theta_{obsd}$/° (±0.02)	Intensity	$2\theta_{calcd}$/°	h k l
15.17	15	15.16	1 0 0
21.50	100	21.50	1 1 0
26.42	5	26.41	1 1 1
30.59	5	30.59	2 0 0
34.32	3	34.31	2 1 0
37.69	2	37.70	2 1 1

Table 3. Observed and calculated 2θ values of X-ray powder patterns in Phase II of $(CH_3)_3NHClO_4$ at ca. 445 K (tetragonal, $a = 9.912(4)$, $c = 7.01(2)$ Å, and $Z = 4$).

$2\theta_{obsd}$/° (±0.03)	Intensity	$2\theta_{calcd}$/°	h k l
15.52	30	15.48	1 0 1
20.04	90	20.03	1 2 0
23.78	100	23.75	1 2 1
25.42	10	25.41	0 0 2
		25.42	2 2 0
31.25	10	31.26	1 3 1
		31.26	2 0 2
32.57	8	32.57	2 3 0
		32.57	1 2 2
35.01	2	35.06	2 3 1
37.38	5	37.40	3 0 2
43.83	3	43.79	1 2 3
47.65	5	47.67	3 0 3

All calculations were performed on a VAX 3100 computer using TEXSAN [8], Experimental conditions and crystal data are summarized in Table 1.

Results and Discussion

Two solid-solid phase transitions were located at $T_{tr}(\text{III} \rightarrow \text{II}) = 396$ K and $T_{tr}(\text{II} \rightarrow \text{I}) = 480$ K by DTA. The melting point could not be determined owing to sample decomposition occurring around 555 K. The enthalpy changes, $\Delta H(\text{III} \rightarrow \text{II})$ and $\Delta H(\text{II} \rightarrow \text{I})$, determined by DSC were 1.0 ± 0.2 and 3.96 ± 0.05 kJ mol^{-1}, respectively; the associated entropy changes, ΔS, were evaluated to be 2.5 and 8.25 J K^{-1} mol^{-1}, respectively. The observed T_{tr}'s are in good agreement with those reported by Jurga et al. [3], whereas their data of $\Delta H(\text{III} \rightarrow \text{II}) = 2.36$ kJ mol^{-1} ($\Delta S = 5.94$ J K^{-1} mol^{-1}) and $\Delta H(\text{II} \rightarrow \text{I}) = 4.64$ kJ mol^{-1} ($\Delta S = 9.59$ J K^{-1} mol^{-1}) are large compared with our results [3]. Our ΔH and ΔS values are comparable with those ob-

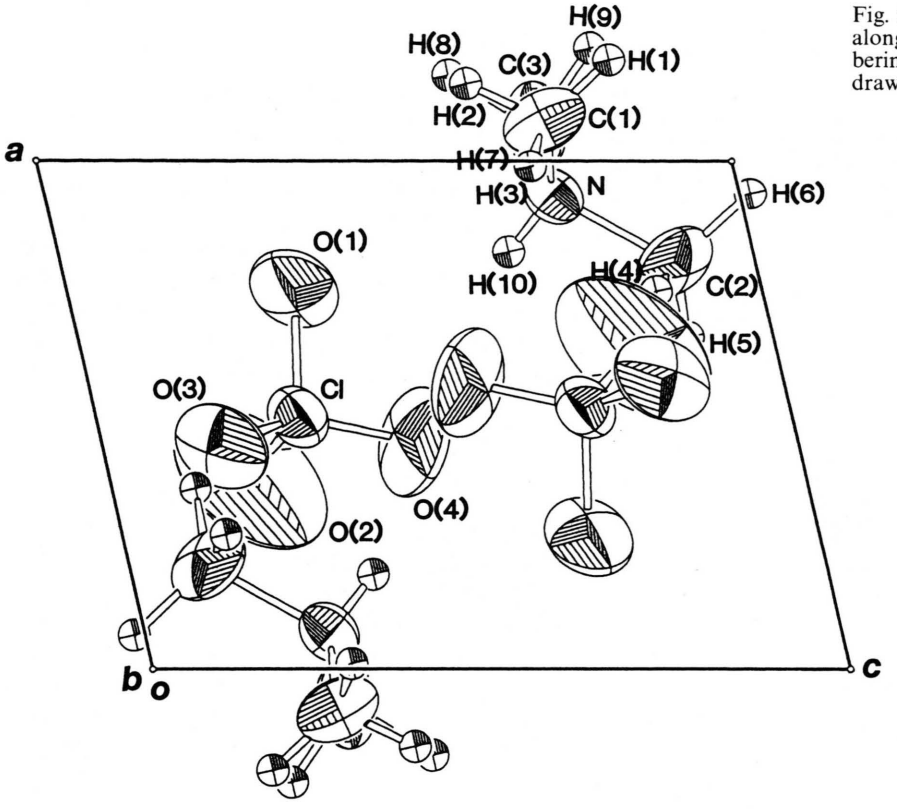

Fig. 1. An ORTEPII [13] view along the b axis and atomic numberings. Thermal ellipsoids are drawn at the 50% probability level.

Table 4. Positional and thermal parameters in Phase III of $(CH_3)_3NHClO_4$. The coefficients U_{ij} of the anisotropic temperature factor expression are defined as follows:

$$\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)].$$

	x	y	z	U_{11}/U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	0.4907(3)	0.2500	0.2922(2)	0.0492(9)	0.059(1)	0.0416(7)	−0.003(2)	0.0010(6)	0.008(2)
O(1)	0.743(1)	0.242(2)	0.3295(7)	0.078(4)	0.167(6)	0.088(3)	0.074(7)	−0.000(3)	−0.024(8)
O(2)	0.372(3)	0.138(2)	0.203(2)	0.26(2)	0.19(1)	0.24(2)	−0.17(1)	−0.06(1)	0.02(1)
O(3)	0.434(2)	0.377(1)	0.173(1)	0.093(5)	0.073(5)	0.100(5)	0.005(5)	−0.003(4)	0.051(4)
O(4)	0.442(1)	0.221(3)	0.4521(8)	0.154(6)	0.43(2)	0.078(4)	−0.13(1)	0.055(4)	0.04(1)
N	0.9286(9)	0.259(2)	0.7328(7)	0.044(3)	0.038(4)	0.041(2)	0.002(6)	0.001(2)	0.004(7)
C(1)	1.079(2)	0.399(1)	0.745(2)	0.055(7)	0.032(5)	0.090(8)	−0.015(5)	0.031(6)	0.006(7)
C(2)	0.797(1)	0.246(2)	0.8843(8)	0.065(4)	0.073(4)	0.081(4)	0.01(1)	0.037(3)	−0.02(1)
C(3)	1.069(3)	0.117(2)	0.731(2)	0.10(1)	0.057(7)	0.047(6)	0.001(8)	0.015(6)	−0.007(6)
H(1)	1.197	0.392	0.857	0.045					
H(2)	1.151	0.380	0.644	0.045					
H(3)	0.989	0.486	0.710	0.045					
H(4)	0.739	0.324	0.848	0.068					
H(5)	0.648	0.164	0.878	0.068					
H(6)	0.933	0.255	1.016	0.068					
H(7)	0.949	0.044	0.720	0.106					
H(8)	1.167	0.103	0.622	0.106					
H(9)	1.220	0.105	0.834	0.106					
H(10)	0.82(1)	0.23(2)	0.650(8)	0.06(2)					

tained for the two solid-solid phase transitions in $(CH_3)_3NHBF_4$ [9] having three solid phases (named as Phase I, II, and III in the order of decreasing temperature) and ΔH (ΔS) (III → II) = 1.1 kJ mol^{-1} (2.9 J K^{-1} mol^{-1}) and ΔH (ΔS) (II → I) = 3.36 kJ mol^{-1} (7.4 J K^{-1} mol^{-1}). Phase I was revealed to be an ionic plastic phase, where both cations and anions perform self-diffusion and isotropic reorientation [9]. The motional states of the cations and anions in Phase I of both crystals are, therefore, considered to be similar to each other.

Table 5. Bond lengths (Å), angles (°), intermolecular O···H distances (Å), and A–H···O angles (°) (A = N, C).

Cl–O(1)	1.420(5)	N–H(10)	0.83(8)	C(3)–H(7)	0.92
Cl–O(2)	1.29(1)	C(1)–H(1)	0.97	C(3)–H(8)	1.11
Cl–O(3)	1.415(8)	C(1)–H(2)	0.96	C(3)–H(9)	1.04
Cl–O(4)	1.323(6)	C(1)–H(3)	0.92		
N–C(1)	1.48(1)	C(2)–H(4)	0.78		
N–C(2)	1.508(8)	C(2)–H(5)	1.11		
N–C(3)	1.47(2)	C(2)–H(6)	1.12		

O(1)–Cl–O(2)	118(1)	O(3)–Cl–O(4)	132(1)
O(1)–Cl–O(3)	104.2(6)	C(1)–N–C(2)	113(1)
O(1)–Cl–O(4)	102.9(5)	C(1)–N–C(3)	112.0(5)
O(2)–Cl–O(3)	103.4(6)	C(2)–N–C(3)	108(1)
O(2)–Cl–O(4)	98(1)		

O(1)···H(10)	2.37(6)	N–H(10)···O(1)	134(8)
O(4)···H(10)	2.34(6)	N–H(10)···O(4)	162(11)
O(4)···H(8)	2.47	C(3)–H(8)···O(4)	147
O(3)···H(1)	2.48	C(1)–H(1)···O(3)	169
O(3)···H(5)	2.55	C(2)–H(5)···O(3)	139

The powder X-ray diffraction angles (2θ) obtained for Phase I could be well interpreted by a simple cubic lattice with $a = 5.845\,(1)$ Å. The adequacy of the present analysis is shown in Table 2. We conclude from these data that Phase I is an ionic plastic phase having a CsCl-type cubic structure. Our preliminary measurement of X-ray powder patterns showed that Phase I of $(CH_3)_3NHBF_4$ also forms a CsCl-type structure [10]. The angles (2θ) observed for Phase II are shown in Table 3. These angles correspond to a tetragonal lattice with $a = 9.912\,(4)$ and $c = 7.01\,(2)$ Å. The crystal structure of Phase III is shown in Fig. 1, and the atomic parameters are summarized in Table 4. The large thermal ellipsoids associated with the O-atoms suggest the existence of a large-amplitude thermal libration and/or disordering of the orientation of the ClO_4^- ion. However, it was difficult to resolve the disordered position of the O-atoms. In Table 5 are given the intramolecular bond lengths and angles as well as the selected intermolecular O···H distances shorter than 2.6 Å given by the sum of the van der Waals radius of O and H atoms [11], and the A–O···H angles (A = N, C). The intermolecular contacts, O(1)···H(10): 2.37 Å and O(4)···H(10): 2.34 Å, are rather long compared with O···H distances (1.91 and 2.29 Å) found in $[(CH_3)_3NH][HC_2O_4]$ [12]. The cation forms a weak bifurcated hydrogen bond with the ClO_4^- anion. This may cause the ClO_4^- ion to reorient anisotropically, as detected by ^{35}Cl NMR [3]. From the C–H···O contacts given in Table 5, the cations are considered to form very weak, if any, hydrogen bonds of C–H···O.

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