

SHORT COMMUNICATION

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The structure of tetramethylammonium hexafluorophosphate.* By Y. WANG,† L. D. CALVERT‡ and S. K. BROWNSTEIN, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9

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Abstract

Crystals of $[\text{N}(\text{CH}_3)_4]\text{PF}_6$ are tetragonal with space group $P4/nmm$, $a = 8.436$ (2), $c = 6.089$ (2) Å, $Z = 2$, $D_x = 1.68$ Mg m⁻³. A full-matrix least-squares refinement of 584 observed diffractometer data collected at 170 K with Mo $K\alpha$ radiation gave $R = 0.070$. The structure is similar to that of $[\text{N}(\text{CH}_3)_4]\text{ClO}_4$ but with the anion ordered. The $[\text{N}(\text{CH}_3)_4]^+$ cation has distorted-tetrahedral ($42m$) symmetry, with the N atom on $2(a)$ [$\text{N}-\text{C} = 1.486$ (5) Å; the C–N–C angles are equal within experimental error at 109.5 (3)°]; the PF_6^- anion, with symmetry $4mm$, has a distorted-octahedral symmetry with the P atom on $2(c)$ and P–F distances of 1.585 (5), 1.591 (6) (axial) and 1.568 (3) Å (equatorial) and F–P–F angles equal to 90 or 180°, within experimental error.

Crystals of the title compound were prepared by the slow reaction of $[\text{N}(\text{CH}_3)_4](\text{CH}_3\text{CO}_2)$ and PF_3 with SO_2 as the solvent. The material was identified by comparison of its fluorine magnetic resonance spectrum with that of an authentic hexafluorophosphate (Chevrier & Brownstein, 1980). 682 reflections, comprising a full unique set, were measured on a computer-controlled diffractometer (Grant & Gabe, 1974) with the profile-analysis technique (Grant &

Gabe, 1978) at 170 K using a cold-nitrogen-gas cooling device; 584 reflections were considered as observed [$I > 2\sigma(I)$]. The structure was solved by a difference Fourier synthesis using the heavy-atom coordinates given by McCullough (1964) for $[\text{N}(\text{CH}_3)_4]\text{ClO}_4$. A full-matrix least-squares refinement (Larson & Gabe, 1978), with allowance for anomalous dispersion and isotropic extinction, isotropic thermal parameters for H atoms and anisotropic thermal parameters for the other atoms, gave $R_1 = \sum | \Delta F | / \sum F_o = 0.070$ and $R_2 = (\sum w | \Delta F |^2 / \sum w F_o^2)^{1/2} = 0.083$, where $w = 1 / [\sigma^2(F_o)]$. The final results are given in Table 1. §

The N atom of the cation has distorted-tetrahedral symmetry ($42m$), being bonded to four C atoms at 1.486 (5) Å, with four C–N–C angles of 109.5 (1) and two of 109.4 (3)°; thus, the cation can be considered to be tetrahedral ($43m$) within experimental accuracy. Each C atom is tetrahedrally bonded to three H atoms at 2×1.06 (3), 1×1.08 (8) Å and one N atom, with H–C–H angles 112 (3) $\times 2$ and 111 (3)° $\times 1$, and H–C–N angles of 107 (2) $\times 2$ and 108 (5)° $\times 1$, respectively. The P atom has square-pyramidal symmetry ($4mm$) with axial P–F bonds [1.585 (5), 1.591 (6) Å] slightly longer than the four square-planar ones of 1.568 (3) Å; F–P–F angles are equal to 90 or 180° within experimental error, the values being 180.0 (0), 179.7 (2) $\times 2$, 89.8 (1) $\times 4$, 90.2 (1) $\times 4$ and 90.00 (1)° $\times 4$. The structure is similar to that of $[\text{N}(\text{CH}_3)_4]\text{ClO}_4$ (McCullough, 1964); however, the anion in that structure is disordered.

§ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35151 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Atomic fractional coordinates ($\times 10^4$; for H $\times 10^3$) and isotropic thermal parameters

The origin is taken at a centre (2/m).

Site set	x	y	z	B_{iso} (Å ²)*	
N	2(a)	7500	2500	0	1.8 (2)
C	8(i)	7500	1063 (6)	1411 (8)	3.4 (2)
P	2(c)	2500	2500	4119 (3)	1.6 (1)
F(1)	2(c)	2500	2500	1505 (9)	4.6 (3)
F(2)	8(j)	3815 (3)	3815 (3)	4111 (6)	7.3 (2)
F(3)	2(c)	2500	2500	6721 (8)	3.8 (2)
H(1)	8(i)	496 (10)	750	36 (14)	9.5 (22)
H(2)	16(k)	387 (4)	647 (4)	239 (5)	4.0 (8)

* B_{iso} = isotropic equivalent.

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