

The correct space group of $\text{NaPF}_6 \cdot \text{H}_2\text{O}$

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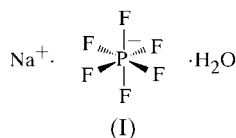
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The structure of sodium hexafluorophosphate monohydrate, $\text{NaPF}_6 \cdot \text{H}_2\text{O}$, has been inadvertently redetermined, revealing that the previously reported space group, *Imma*, was assigned incorrectly, with the *a* and *b* axes interchanged. The correct space group is *Pnna*. The program *PLATON* [Spek (2003). *J. Appl. Cryst.* **36**, 7–13] suggested both *Imma* and *Pmma* as possible space groups, but only *Pnna* is consistent with the systematic absences. The inter-ionic and hydrogen-bonding interactions in the lattice form a three-dimensional network.

Comment

During the process of crystallization of a peptide, crystals of $\text{NaPF}_6 \cdot \text{H}_2\text{O}$, (I), were isolated as thin tubes. A fragment of a tube was mounted on a diffractometer for determination of the crystal structure. The unit-cell volume [$505.1(4) \text{ \AA}^3$] suggested that the compound was not the expected peptide, but since the unit cell obtained was not present in the Cambridge Structural Database (CSD; Allen, 2002), a full data collection was undertaken.



The true composition of (I) was determined upon structure solution and refinement. A subsequent search of the Inorganic Crystal Structure Database (FIZ Karlsruhe/Gmelin Institut, 1999) revealed that the structure of (I) was reported by Bode & Teufer (1956), who described an orthorhombic unit cell [$a = 7.962(5) \text{ \AA}$, $b = 10.594(10) \text{ \AA}$ and $c = 6.116(5) \text{ \AA}$] in space group *Imma*. Our orthorhombic unit cell has a different axis setting [*viz.* $a = 10.559(4) \text{ \AA}$, $b = 7.899(3) \text{ \AA}$ and $c = 6.057(3) \text{ \AA}$] in space group *Pnna*. It is hard to fault the original study, since those results were obtained 47 years ago and were based on only 102 reflections, while our own conclusion is based on the measurement of 4199 reflections. The program *PLATON* (Spek, 2003) suggested space group *Imma* for the unit cell, which would be inconsistent with the

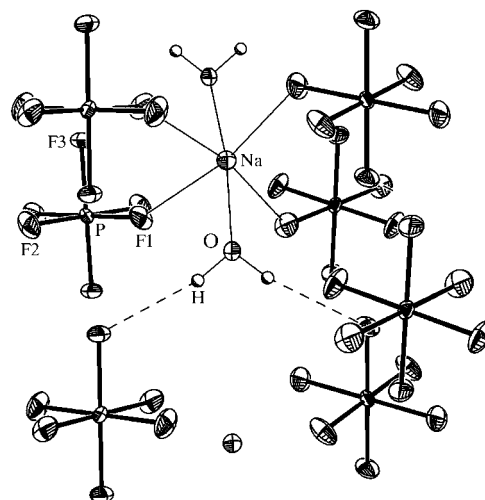


Figure 1

A partial view of the structure of (I). The $\text{H} \cdots \text{F}_3$ hydrogen bonds are shown as dashed lines.

observed systematic absences, as the body centering is certainly absent. *PLATON* also suggested space group *Pmma* as a possibility, but the presence of two diagonal glide planes perpendicular to the *a* and *b* axes is very clear from the data. Previously, we reported that crystallographic checking software can misinterpret systematically weak data and that caution needs to be exercised in the evaluation of the output of programs such as *checkCIF* and *PLATON* (Guzei *et al.*, 2002).

In the structure of (I) (Fig. 1), the P atom occupies an inversion center while the O and Na atoms reside on twofold axes. The geometry of the PF_6^- anion is octahedral, with an average P–F distance of $1.597(2) \text{ \AA}$. Bode & Teufer (1956) reported two types of P–F bonds, including four equatorial bonds of 1.58 \AA and two axial bonds of 1.73 \AA . A CSD search for PF_6^- anions returned 1591 P–F bond lengths, ranging between 1.303 and 1.707 \AA [mean $1.55(3) \text{ \AA}$]. A density functional theory (DFT) optimization of the geometry of an

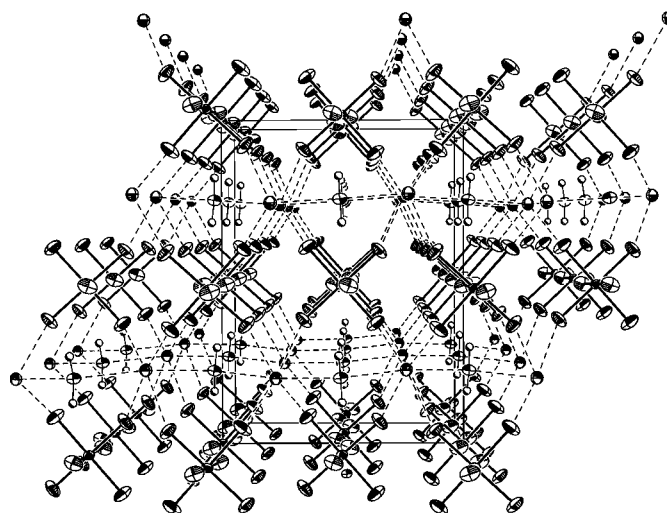


Figure 2

The crystal lattice of (I), viewed along the *c* axis. Hydrogen bonds have been omitted for clarity.

O_h -symmetric PF_6^- anion at the B3LYP/6-311+G* level (GAUSSIAN98; Frisch *et al.*, 1998) produced a P–F distance of 1.646 Å. DFT calculations tend to overestimate distances in some octahedral anions by 2–4% (Guzei, 2003), and therefore the calculated length can be adjusted to 1.60 (1) Å (0.97×1.646 Å), which is in reasonable agreement with the experimental data. The P–F distance of 1.73 Å reported in the literature is much longer than the calculated value of 1.646 Å and hence is highly likely to be erroneously long.

The environment about the Na atom is octahedral, with four shorter Na–F equatorial distances [2.293 (2) Å] and two longer axial Na–O distances [2.4012 (17) Å]. Each water molecule participates in four intermolecular interactions, two of which are symmetry independent. One is the Na···O contact just mentioned and the other is a charge-assisted interionic O–H···F hydrogen-bonding interaction, with an O···F separation of 3.064 (2) Å and an O–H···F angle of 168 (4)° (Table 1). A CSD search for relevant hydrogen-bonding interactions returned over 50 entries; however, those with O–H···F angles below 150° were eliminated from the list. In the remaining 29 entries, the average O···F separation is 3.04 (14) Å, with the O–H···F angle averaging 160 (7)°. Thus, the interactions observed in the structure of (I) fall in the expected range.

The inter-ionic and hydrogen-bonding interactions in the lattice of (I) form a three-dimensional network, as shown in Fig. 2.

Experimental

The title compound was obtained serendipitously during the isolation of a peptide and is inconsistent with the reactants used.

Crystal data

NaPF ₆ ·H ₂ O	Mo <i>K</i> α radiation
$M_r = 185.98$	Cell parameters from 741 reflections
Orthorhombic, <i>Pnna</i>	$\theta = 2\text{--}25^\circ$
$a = 10.559$ (4) Å	$\mu = 0.69$ mm ^{−1}
$b = 7.898$ (3) Å	$T = 100$ (2) K
$c = 6.057$ (3) Å	Needle, colorless
$V = 505.1$ (4) Å ³	$0.43 \times 0.32 \times 0.26$ mm
$Z = 4$	
$D_x = 2.446$ Mg m ^{−3}	

Data collection

Bruker CCD 1000 area-detector diffractometer	520 independent reflections
ω scans	449 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2000–2003)	$R_{\text{int}} = 0.046$
$T_{\text{min}} = 0.756$, $T_{\text{max}} = 0.841$	$\theta_{\text{max}} = 26.4^\circ$
3685 measured reflections	$h = -13 \rightarrow 13$
	$k = -9 \rightarrow 9$
	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0347P)^2 + 0.8605P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.098$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.18$	$\Delta\rho_{\text{max}} = 0.38$ e Å ^{−3}
520 reflections	$\Delta\rho_{\text{min}} = -0.52$ e Å ^{−3}
48 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Hydrogen-bonding 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>
O–H···F3 ¹	0.88 (3)	2.198 (9)	3.064 (2)	168 (4)

Symmetry code: (i) $1 - x, y - \frac{1}{2}, z - \frac{1}{2}$.

The O–H distances were constrained to 0.880 (1) Å, while the positional and displacement parameters of the H atoms were allowed to refine.

Data collection: SMART (Bruker, 2000–2003); cell refinement: SMART; data reduction: SAINT (Bruker, 2000–2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2000–2003); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1021). Services for accessing these data are described at the back of the journal.

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