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Key indicatorsSingle-crystal X-ray study
 $T = 295\text{ K}$
Mean $\sigma(\text{P}-\text{O}) = 0.002\text{ \AA}$
 R factor = 0.022
 wR factor = 0.065
Data-to-parameter ratio = 12.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**Langbeinite-type mixed-valence
(NH₄)(H₃O)Ti^{III}Ti^{IV}(PO₄)₃**

The anionic component of the langbeinite-type title compound, ammonium oxonium dititanium(III,IV) tris(phosphate), is an infinite three-dimensional [Ti₂(PO₄)₃]²⁻ network based on PO₄ tetrahedra corner-linked to TiO₆ octahedra; the charge-balancing ammonium and oxonium cations occupy the cavities in the network and interact by way of N–H···O and O–H···O hydrogen bonds. The two independent Ti atoms, the ammonium N atom and the oxonium O atom lie on special positions of site symmetry 3.

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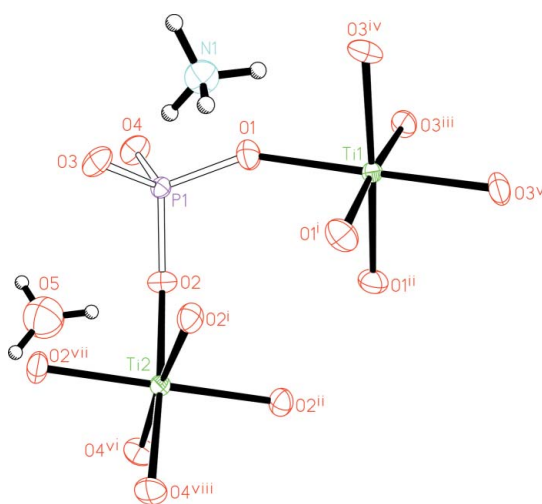
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Comment

The non-stoichiometric potassium titanophosphate $\text{K}_{2-x}\text{Ti}_2(\text{PO}_4)_3$ ($x = 0$ to $\frac{1}{2}$), which belongs to the langbeinite structure type, features mixed valences of titanium (Ti^{III} and Ti^{IV}); other univalent cations can replace the potassium cations (Leclaire *et al.*, 1989). This paper describes our attempts to synthesize the ammonium analog using a hydrothermal method, and it follows the report on the nasicon-related ammonium titanophosphate, $(\text{NH}_4)\text{Ti}_2^{IV}(\text{PO}_4)_3$, which is trigonal (Horiuchi & Ono, 1986). The synthesis yielded instead the title compound, ammonium oxonium dititanium tris(phosphate), (I), which is yet another member of the langbeinite class. The Ti atoms have mixed 3+/4+ valencies, this feature being confirmed by an XPS measurement. There is no suggestion that any preferential ordering occurs over the two distinct titanium sites.

In the crystal structure of $(\text{NH}_4)(\text{H}_3\text{O})\text{Ti}_2(\text{PO}_4)_3$ (Fig. 1), the anionic [Ti₂(PO₄)₃]²⁻ network is made up of phosphate

**Figure 1**

Fragment of (I), showing 70% displacement ellipsoids (H atoms drawn as spheres of arbitrary radius). [Symmetry codes: (i) y, z, x ; (ii) z, x, y ; (iii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $y - \frac{1}{2}, \frac{1}{2} - z, -x$; (v) $\frac{1}{2} - z, -x, y - \frac{1}{2}$; (vi) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (vii) $\frac{1}{2} - y, 1 - z, \frac{1}{2} + x$; (viii) $1 - z, \frac{1}{2} + x, \frac{1}{2} - y$.]

tetrahedra that are corner-linked to TiO_6 octahedra (Table 1). The ammonium and oxonium cations occupy cavities in the framework and interact with it by way of $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 2).

Experimental

Titanium powder (99%, 0.48 g, 0.01 mmol), phosphoric acid (85%, 10.0 ml, 0.15 mmol), excess ammonium hydrogen fluoride (99.0%, 1.7 g) and water (5 ml) were sealed in a Teflon-lined stainless steel Parr bomb. The bomb was heated at 473 K for a week. Upon cooling, crystals of (I) were collected and washed with water. IR: 3450 (broad), 3277 (s), 3026 (s), 2833 (s), 1651 (m), 1424, 990, 933 cm^{-1} ; the broad band is assigned to the $\text{O}-\text{H}$ vibration mode of the oxonium cation.

Crystal data

$(\text{NH}_4)(\text{H}_3\text{O})\text{Ti}_2(\text{PO}_4)_3$	Cell parameters from 8307 reflections
$M_r = 417.78$	$\theta = 3.4\text{--}28.1^\circ$
Cubic, $P2_13$	$\mu = 2.20 \text{ mm}^{-1}$
$a = 9.9384 (4) \text{ \AA}$	$T = 295 (2) \text{ K}$
$V = 981.63 (4) \text{ \AA}^3$	Block, black
$Z = 4$	$0.19 \times 0.19 \times 0.12 \text{ mm}$
$D_x = 2.827 \text{ Mg m}^{-3}$	
Mo $K\alpha$ radiation	

Data collection

Bruker APEX area-detector diffractometer	816 independent reflections
φ and ω scans	815 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.026$
$T_{\text{min}} = 0.666$, $T_{\text{max}} = 0.778$	$\theta_{\text{max}} = 28.4^\circ$
10934 measured reflections	$h = -13 \rightarrow 13$
	$k = -13 \rightarrow 13$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 1.2965P]$
$R[F^2 > 2\sigma(F^2)] = 0.022$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.065$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$
816 reflections	$\Delta\rho_{\text{min}} = -0.45 \text{ e \AA}^{-3}$
68 parameters	Absolute structure: Flack (1983), 339 Friedel pairs
All H-atom parameters refined	Flack parameter: 0.02 (4)

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ti1—O1	2.025 (2)	Ti2—O2	1.961 (2)
Ti1—O3 ⁱ	2.020 (2)	Ti2—O4 ⁱⁱ	1.922 (2)
O4 ⁱⁱ —Ti2—O4 ⁱⁱⁱ	89.5 (1)	P1—O3—Ti1 ^{iv}	151.6 (1)
P1—O1—Ti1	151.3 (1)	P1—O4—Ti2 ^v	174.7 (2)
P1—O2—Ti2	134.5 (1)		

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

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O5—H3 \cdots O2	0.86 (1)	2.30 (5)	2.966 (4)	135 (6)
N1—H1 \cdots O3	0.86 (1)	2.03 (1)	2.864 (3)	165 (4)
N1—H2 \cdots O4 ^{vi}	0.85 (1)	2.35 (1)	3.039 (4)	138 (1)
N1—H2 \cdots O4 ^{iv}	0.85 (1)	2.35 (1)	3.039 (4)	138 (1)
N1—H2 \cdots O4 ^{vii}	0.85 (1)	2.35 (1)	3.039 (4)	138 (1)

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

The two independent H atoms (one on a general position and the other on a threefold rotation axis) attached to atom N1 were located in a difference map, and were refined with a distance restraint of $\text{N}-\text{H} = 0.85 (1) \text{ \AA}$. Their displacement parameters were also refined. The oxonium cation was initially refined as another ammonium cation; however, only the H atom on the general position could be refined whereas that on the threefold symmetry axis had an unacceptably large displacement parameter. It was decided that the resulting four-atom species was not a neutral ammonia molecule but a planar H_3O^+ oxonium cation having somewhat large atomic displacement parameters. The O atom of the cation is probably disordered above and below the plane consisting of the H atoms, but this could not be verified from the present data. The cation was refined with an $\text{O}-\text{H}$ distance restraint of $0.85 (1) \text{ \AA}$.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

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