INORGANIC COMPOUNDS

α-Ammonium Vanadium Hydrogen Phosphate, α-(NH4)V(HPO4)2

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Abstract

α-Ammonium vanadium(III) bis(hydrogen phosphate) is a new ammonium vanadium(III) phosphate built up from a three-dimensional framework of VO_6 octahedra and HPO_4 tetrahedra [d_{av}(V—O) = 2.008, d_{av}(P— O) = 1.538, d_{av}(N···O) = 3.086 Å and θ_{av}(V—O— P) = 139.5°]. It is isostructural with α-$RbV(HPO_4)_2$ and complements the previously described β-NH_4V-$(HPO_4)_2$: α-$NH_4V(HPO_4)_2$ contains both four-ring (two VO_6 and two HPO_4) and lantern (two VO_6 and three HPO_4) groupings, whereas β-$NH_4V(HPO_4)_2$ contains only four-ring polyhedral groupings.

Comment

Haushalter *et al.* (1995) recently demonstrated that polymorphism is possible for rubidium vanadium(III) hydrogen phosphates: the hydrothermally prepared phases α-$RbV(HPO_4)_2$ and β-$RbV(HPO_4)_2$ were shown to crystallize with different three-dimensional architectures of vertex-sharing VO_6 and HPO_4 building blocks. The same authors reported the phase $NH_4V(HPO_4)_2$ to be isostructural with β-$RbV(HPO_4)_2$.

We report here the characterization of a new polymorph of ammonium vanadium(III) hydrogen phosphate, which we denote α-$NH_4V(HPO_4)_2$ to distinguish it from the previously reported phase, which is now termed β-$NH_4V(HPO_4)_2$ (Haushalter *et al.*, 1995). This new α-$NH_4V(HPO_4)_2$ polymorph is isostructural with α-$RbV(HPO_4)_2$.

α-$NH_4V(HPO_4)_2$ is built up from ammonium cations and a three-dimensional network of vertex-sharing VO_6 octahedra and tetrahedral HPO_4 units, fused together *via* V—O—P bonds (Figs. 1 and 2). N1 occupies an inversion centre, and hence its four protons must be disordered over at least two equivalent sets of sites. The N2-centred ammonium cation makes three fairly long hydrogen bonds [2.1 Å < d(H···O) < 2.2 Å, based on a restrained refinement of the positions of the H atoms] to framework O atoms (two V—O—P

and one P—OH species). Both distinct vanadium(III) centres adopt a typical, essentially regular, octahedral coordination [d_{av}(V1—O) = 2.013 (1) and d_{av}(V2—O) = 2.002 (1) Å] with respect to their O-atom neighbours. The site symmetry of V1 is $\bar{1}$. Bond-valence-sum (BVS) calculations (Brown, 1996) yielded values of 2.89 for V1 and 3.00 for V2 (3.00 is expected for pure V^{III} character). Each V atom makes six V—O—P bonds to adjacent HPO_4 groups, covering a fairly wide range of bond angles and with an average value of 139.5°. The three P atoms show typical tetrahedral coordination [d_{av}(P1—O) = 1.536 (1) Å, BVS(P1) = 4.99; d_{av}(P2— O) = 1.543 (1) Å, BVS(P2) = 4.90; d_{av}(P3—O) = 1.536 (1) Å, BVS(P3) = 5.00]. Each of these units makes three P—O—V links and possesses one P— OH grouping, with this component showing a typical lengthening of the P—O bond (Lightfoot & Masson, 1996). All these protons are involved in P—OH···O hydrogen bonds, with the acceptor O atom forming part of a V—O—P bridge.

The polyhedral connectivity in α-$NH_4V(HPO_4)_2$ results in a complicated packing of distinctive lantern-like groupings of two octahedra, connected by three tetrahedra (Fig. 1). The inversion centre at V1 gives rise to dimer-like units of two lanterns in this phase. A similar lantern motif has been observed in $Ca_2V(PO_4)(HPO_4)_2.H_2O$ (Lii *et al.*, 1992). In the calcium phase, the lanterns are fused into infinite chains.

One way to visualize the building up of the α-$NH_4V(HPO_4)_2$ structure is by way of the V2, P2 and P3-centred polyhedra, which form four-ring (two oc-
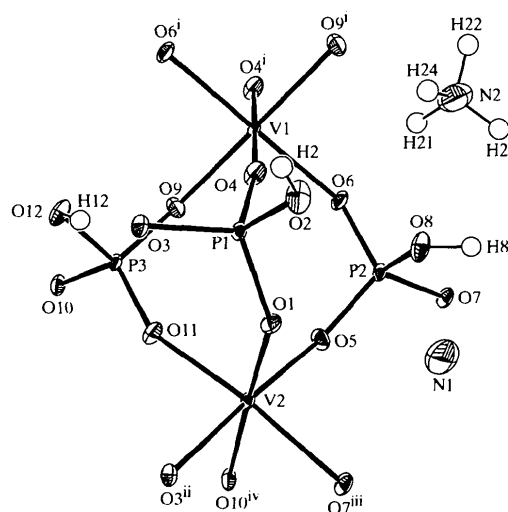

Fig. 1. View of the lantern-like building unit in α-$NH_4V(HPO_4)_2$. Displacement ellipsoids are shown at 50% probability. Symmetry codes are as given in Table 1.

tahedra plus two tetrahedra) chains propagating along [001]. An intrachain O8—H8···O10 hydrogen bond occurs. Pairs of P1-centred tetrahedra fuse V2 octahedra in adjacent chains into contorted sheets lying normal to [001]. Two more hydrogen bonds, O2—H2···O10 and O12—H12···O3, are involved in this interchain connectivity. Finally, the V1-centred octahedra provide intersheet connectivity in the [001] direction, resulting in a three-dimensional network of strictly alternating VO$_6$ and HPO$_4$ building blocks. The N1H$_4^+$ groups appear to occupy small channels propagating along [001]. The N2H$_4^+$ species occupies small interstices which are visible in both the [100] and [010] directions as distorted eight-ring (four VO$_6$ and four HPO$_4$ units, strictly alternating) channels, although there is no suggestion that these extra-framework cations are mobile in this phase.
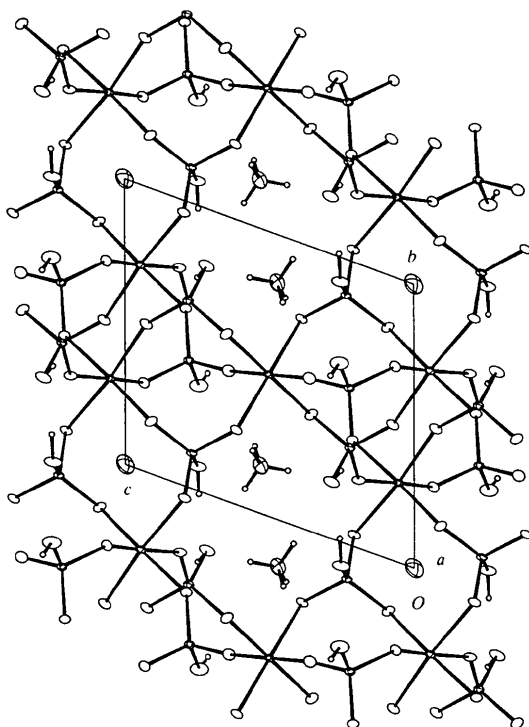
maximum cation–oxygen contact distance considered is 3.4 Å in each case).

Based on unit-cell data, the synthetic phases NH$_4$Al(HPO$_4$)$_2$, KAl(HPO$_4$)$_2$, NH$_4$Fe(HPO$_4$)$_2$ and KFe(HPO$_4$)$_2$ (Smith & Brown, 1959) are probably isostructural with these vanadium-containing materials. α-NH$_4$V(HPO$_4$)$_2$ complements its polymorph, β-NH$_4$V(HPO$_4$)$_2$ (Haushalter et al., 1995), this latter phase having a different three-dimensional VO$_6$/HPO$_4$ polyhedral connectivity based only on four-ring groupings of VO$_6$ and HPO$_4$ units. The newly reported NH$_4$(Al$_{0.64}$Ga$_{0.36}$)(HPO$_4$)$_2$ (Stalder & Wilkinson, 1998) is also isostructural with the title compound.

Experimental

α-NH$_4$V(HPO$_4$)$_2$ was prepared from a mixture of VCl$_3$ (1.09 g), 85% H$_3$PO$_4$ (3.20 g), 25% NH$_4$OH solution (1.70 g), and 10 ml deionized water (starting molar ratio of NH$_4$:V:P = 1:1:4). The components were sealed in a 23 ml capacity Teflon-lined hydrothermal bomb and heated to 453 K for 48 h. After slow cooling, the bomb was opened to reveal a mixture of dark green rods of the title compound and lime-green chunks of β-NH$_4$V(HPO$_4$)$_2$ (Haushalter et al., 1995). After recovery by vacuum filtration and washing with water, both phases appear to be indefinitely stable under ambient conditions. We have not yet been able to prepare pure α-NH$_4$V(HPO$_4$)$_2$. Hydrothermal reactions always result in a mixture of the two polymorphs of NH$_4$V(HPO$_4$)$_2$. Under slightly different conditions, Haushalter et al. (1995) may have prepared α-NH$_4$V(HPO$_4$)$_2$ as a green powder during their preparation of β-NH$_4$V(HPO$_4$)$_2$.

Fig. 2. Unit-cell packing of α-NH$_4$V(HPO$_4$)$_2$.

α-NH$_4$V(HPO$_4$)$_2$ is isostructural with α-RbV(HPO$_4$)$_2$ (Haushalter et al., 1995), with the V, P and O components of the two phases having very similar geometries. The NH$_4^+$ and Rb$^+$ cations occupy similar extra-framework sites in these two phases. For α-NH$_4$V(HPO$_4$)$_2$, d_{av}(N1···O) = 3.096 (2) and d_{av}(N2···O) = 3.076 (2) Å; for α-RbV(HPO$_4$)$_2$, d_{av}(Rb1—O) = 3.080 and d_{av}(Rb2—O) = 3.077 Å (the

Crystal data

(NH$_4$)$_3$V$_3$(HPO$_4$)$_6$	Mo $K\alpha$ radiation
M_r = 782.8	λ = 0.71073 Å
Triclinic	Cell parameters from 35
$P\bar{1}$	reflections
a = 7.173 (2) Å	θ = 7.5–12.5°
b = 8.841 (2) Å	μ = 1.94 mm^{-1}
c = 9.458 (2) Å	T = 298 K
α = 65.08 (2)°	Rod
β = 70.68 (2)°	0.4 × 0.1 × 0.1 mm
γ = 69.59 (2)°	Dark green
V = 497.7 (2) Å^3	
Z = 1	
D_x = 2.61 Mg m^{-3}	
D_m not measured	

Data collection

Siemens $P4$ diffractometer	R_{int} = 0.04
$2\theta/\omega$ scans	θ_{max} = 30°
Absorption correction:	h = −9 → 6
ψ scans (North et al., 1968)	k = −11 → 11
	l = −12 → 13
T_{min} = 0.591, T_{max} = 0.824	3 standard reflections
4975 measured reflections	every 97 reflections
2821 independent reflections	intensity decay: none
2226 reflections with	
$I > 3\sigma(I)$	

Refinement

Refinement on F

$R = 0.033$

$wR = 0.037$

$S = 1.096$

2226 reflections

168 parameters

$(\Delta/\sigma)_{max} = 0.0006$

$\Delta\rho_{max} = 0.68$ e Å^{-3}

$\Delta\rho_{min} = -0.62$ e Å^{-3}

Extinction correction: Larson (1967)

Extinction coefficient: 7 (3)

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

V1—O4	2.007 (2)	P1—O1	1.522 (2)
V1—O4^i	2.007 (2)	P1—O2	1.579 (2)
V1—O6	2.010 (2)	P1—O3	1.538 (2)
V1—O6^i	2.010 (2)	P1—O4	1.505 (2)
V1—O9	2.022 (2)	P2—O5	1.519 (2)
V1—O9^i	2.022 (2)	P2—O6	1.528 (2)
V2—O1	1.963 (2)	P2—O7	1.532 (2)
V2—O3^{ii}	2.022 (2)	P2—O8	1.593 (2)
V2—O5	1.949 (2)	P3—O9	1.534 (2)
V2—O7^{iii}	2.077 (2)	P3—O10	1.526 (2)
V2—O10^{iv}	2.018 (2)	P3—O11	1.494 (2)
V2—O11	1.983 (2)	P3—O12	1.590 (2)
V2—O1—P1	131.8 (1)	V2^{iii}—O7—P2	124.0 (1)
V2^{ii}—O3—P1	135.6 (1)	V1—O9—P3	132.1 (1)
V1—O4—P1	162.5 (1)	V2^{iv}—O10—P3	139.0 (1)
V2—O5—P2	146.0 (1)	V2—O11—P3	153.8 (1)
V1—O6—P2	130.6 (1)		

Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, -z$; (iii) $-x, 2 - y, -z$; (iv) $-x, 1 - y, -z$.

Table 2. *Hydrogen-bonding geometry (Å)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$
O2—H2$\cdots$O9^i	0.84	1.91	2.742 (3)
O8—H8$\cdots$O10^{ii}	0.82	1.81	2.574 (2)
O12—H12$\cdots$O3	0.93	1.80	2.720 (3)
N2—H21$\cdots$O8	0.87	2.37	3.025 (4)
N2—H22$\cdots$O3^{iii}	0.82	2.16	2.858 (3)
N2—H23$\cdots$O12^{ii}	0.82	2.14	2.938 (4)
N2—H24$\cdots$O6^i	0.95	2.17	3.060 (4)

Symmetry codes: (i) $1 + x, y, z$; (ii) $x, 1 + y, z$; (iii) $1 - x, 1 - y, 1 - z$.

H-atom parameters were constrained by riding on their O or N partner atoms. Atoms H2, H8, H12, H21, H22 and H23 were located from difference maps, and H24 was placed geometrically [d(N—H) = 0.95 Å]. H atoms were refined isotropically. A Tukey–Prince weighting scheme fitted by a three-term Chebychev polynomial with coefficients 0.279, 0.218 and 0.115 was used (Carruthers & Watkin, 1979).

Data collection: *P4 Software* (Siemens, 1995). Cell refinement: *P4 Software*. Data reduction: *P4 Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1996). Molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1996) and *ORTEP*3 (Farrugia, 1997). Software used to prepare material for publication: *CRYSTALS*.

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Ammonium Zinc Vanadium Phosphate, $(NH_4)_3Zn_2V(PO_4)_2(HPO_4)_2$

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Abstract

The title compound, triammonium dizinc vanadium bis(phosphate) bis(hydrogen phosphate), $(NH_4)_3Zn_2V(PO_4)_2(HPO_4)_2$, is the first ammonium zinc vanadium phosphate. It is built up from a three-dimensional network of vertex-sharing VO_6 octahedra and ZnO_4, PO_4 and HPO_4 tetrahedra fused together *via* V—O—P and Zn—O—P bonds [d_{av}(V—O) = 2.001 (2), d_{av}(Zn—O) = 1.949 (2) and d_{av}(P—O) = 1.538 (2) Å; θ_{av}(V—O—P) = 142.5 and θ_{av}(Zn—O—P) = 131.6°]. NH_4^+ cations occupy two different types of interstices in the Zn–V–P–O framework.

Comment

Vanadium(III) phosphates have been structurally characterized only recently (Lavrov *et al.*, 1981; Lii *et al.*, 1992; Haushalter *et al.*, 1995). Here, we describe the synthesis and characterization of $(NH_4)_3Zn_2V(PO_4)_2$-$(HPO_4)_2$, the first ammonium zinc vanadium(III) phos-