

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: SK1004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## (NH<sub>4</sub>)<sub>2</sub>(VO)(VP)O<sub>7</sub>, a Layered Structure Comprising Tetrahedral VPO<sub>7</sub> Groups

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### Abstract

The new mixed-valence ammonium vanadophosphate (NH<sub>4</sub>)<sub>2</sub>(VO)(VP)O<sub>7</sub> (diammonium phosphorus divanadium octaoxide) is isostructural with K<sub>2</sub>VO(X<sub>2</sub>O<sub>7</sub>) (X = P, V). Its structure consists of [V<sub>2</sub>PO<sub>8</sub>]<sub>∞</sub> layers of corner-sharing VO<sub>5</sub> pyramids and VPO<sub>7</sub> groups, interleaved with NH<sub>4</sub><sup>+</sup> ions. The unusual features of this structure are the existence of the VPO<sub>7</sub> groups involv-

ing VO<sub>4</sub> and PO<sub>4</sub> tetrahedra, and the simultaneous presence of V<sup>IV</sup>O<sub>5</sub> and V<sup>V</sup>O<sub>4</sub> polyhedra, observed here for the first time in this class of compounds. The VPO<sub>7</sub> groups are statistically distributed in the framework. Magnetic measurements and bond-valence calculations confirm the mixed-valence character of this phase and show that the VO<sub>5</sub> pyramids and VO<sub>4</sub> tetrahedra are occupied by V<sup>IV</sup> and V<sup>V</sup>, respectively.

### Comment

Ammonium vanadium phosphates are of great interest in the field of catalysis as their decomposition products can exhibit high activity, as shown for β-(NH<sub>4</sub>)VO<sub>2</sub>(HPO<sub>4</sub>) (Pulvin, Bordes, Ronis & Courtine, 1981). Apart from the aforementioned phase, very few crystal structures of ammonium vanadium phosphates have been reported to date (Haushalter, Chen, Soghomonian, Zubieta & O'Connor, 1994; Amoros & Lebail, 1992; Krasnikov *et al.*, 1983). We report here the hydrothermal synthesis and crystal structure of a mixed-valence vanadium phosphate, (NH<sub>4</sub>)<sub>2</sub>(V<sup>IV</sup>O)(V<sup>V</sup>P)O<sub>7</sub>, isotypic with the diphosphate K<sub>2</sub>VOP<sub>2</sub>O<sub>7</sub> (Gorbunova, Linde, Lavrov & Tananaev, 1980) and with the divanadate K<sub>2</sub>VOV<sub>2</sub>O<sub>7</sub> (Galy & Carpy, 1975).

The atomic coordinates (Table 1) clearly show that (NH<sub>4</sub>)<sub>2</sub>(VO)(VP)O<sub>7</sub> is isotypic with K<sub>2</sub>VOX<sub>2</sub>O<sub>7</sub> (X = P, V). Thus, in the first instance, the structure can be described as [V<sub>2</sub>PO<sub>8</sub>]<sub>∞</sub> layers interleaved with NH<sub>4</sub><sup>+</sup> ions. In each [V<sub>2</sub>PO<sub>8</sub>]<sub>∞</sub> layer, there are corner-sharing VO<sub>5</sub> pyramids and (V,P)O<sub>7</sub> groups forming five-sided voids (Fig. 1). Such results reflect only an average structure, since they would imply that one vanadium atom, V2,

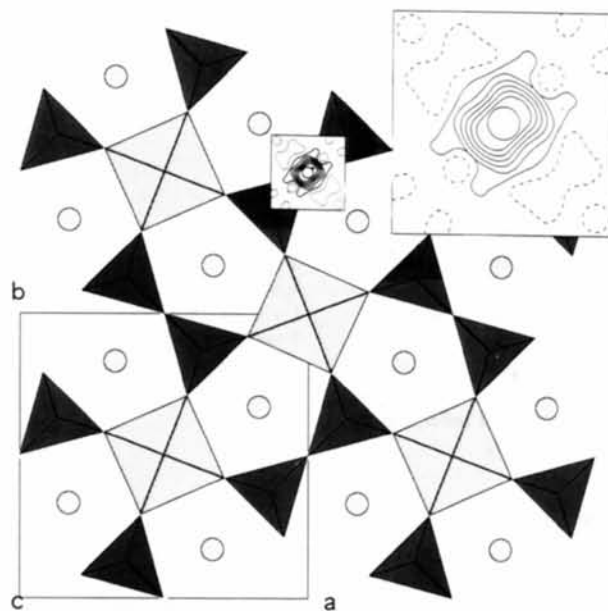


Fig. 1. Projection of (NH<sub>4</sub>)<sub>2</sub>(VO)(VP)O<sub>7</sub> along the *c* axis; inset: difference Fourier map at the bridging O4 site.

and P are distributed statistically over the same crystallographic site, leading to V2/P—O interatomic distances ranging from 1.582 (3) to 1.683 (2) Å (Table 2), distances which are too short for vanadium and too long for phosphorus. In fact, the equivalent isotropic displacement parameters of the O atoms that surround these cations are abnormally high, especially for the bridging O4 atom (Table 1), suggesting that these anionic positions are split. The values of the equivalent isotropic displacement parameters and the elongated shape of the electronic density at the O4 site observed in a difference Fourier map (Fig. 1, inset) on removal of atom O4 strongly support this viewpoint. However, the short distance between the split sites does not allow this splitting to be evidenced.

These results show that P and V2 do not exhibit the same tetrahedral coordination though they are located at the same crystallographic site. Thus, when the P atom is located in one 'O<sub>4</sub>' tetrahedron, the adjacent tetrahedron is occupied by one V2 atom. Consequently, the structure of (NH<sub>4</sub>)<sub>2</sub>(VO)(VP)O<sub>7</sub> differs from that of K<sub>2</sub>VOX<sub>2</sub>O<sub>7</sub> (X = P, V) by the existence of VPO<sub>7</sub> groups distributed at random, instead of diphosphate or divanadate X<sub>2</sub>O<sub>7</sub> (X = P, V) groups. In this way, the mean interatomic distances (Table 2) obtained for V2 and P are compatible with those usually obtained for phosphorus and pentavalent vanadium in tetrahedral coordination.

This structure also differs from that of K<sub>2</sub>VOX<sub>2</sub>O<sub>7</sub> (X = P, V) by the coordination of the ammonium cation, which has ten neighbours at NH<sub>4</sub>—O distances ranging from 2.789 (4) to 3.477 (4) Å (Table 2), instead of the eight neighbours found for K<sup>+</sup> at distances ranging from 2.677 (3) to 3.001 (4) Å (Gorbunova, Linde, Lavrov & Tananaev, 1980) and from 2.77 (4) to 3.191 (6) Å (Galy & Carpy, 1975).

The third important original feature of this phase is the ordered distribution of the V<sup>IV</sup> and V<sup>V</sup> species in the framework. The magnetic susceptibility measurements *versus* temperature show that this phase is indeed paramagnetic and follows the Curie–Weiss law with a Curie constant  $C_M = 0.29$  e.m.u. K mol<sup>-1</sup>, a Weiss constant  $\theta \approx -5.6$  K and an effective magnetic moment of 1.54  $\mu_B$  for one V atom out of two, in agreement with the theoretical value (1.73  $\mu_B$ ). The electronic valence calculations according to the Brown & Altermatt (1985) model demonstrate without ambiguity that the V1 pyramids and V2 tetrahedra are occupied by tetravalent (calculated valence for V1 = 4.08) and pentavalent vanadium (calculated valence for V2/P = 5.09), respectively, according to the formulation (NH<sub>4</sub>)<sub>2</sub>(V<sup>IV</sup>O)(V<sup>V</sup>P)O<sub>7</sub>.

At the end of this work, we compared our results with those of Ninclaus, Retoux, Riou & Férey (1996) concerning the structure of (NH<sub>4</sub>)<sub>2</sub>VO(V<sub>2-x</sub>P<sub>x</sub>O<sub>7</sub>). Both structures are very similar, but an electron diffraction study shows that they correspond to two different forms: the (NH<sub>4</sub>)<sub>2</sub>VO(V<sub>2-x</sub>P<sub>x</sub>O<sub>7</sub>) phase crystallizes in

the space group *P4*, whereas the present phase crystallizes, like K<sub>2</sub>VOX<sub>2</sub>O<sub>7</sub> (X = P, V), in the space group *P4bm*.

## Experimental

A mixture of H(NH<sub>4</sub>)<sub>2</sub>PO<sub>4</sub>, NH<sub>4</sub>VO<sub>3</sub> (in the ratio 1:2), a trace of Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O and 2 ml of water was placed in a 25 ml Teflon vessel and enclosed in a stainless-steel bomb. After heating at 493 K for 24 h, the vessel was cooled to 293 K for 90 h. After filtration, the resulting mixture consisted of white crystals of NH<sub>4</sub>VO<sub>3</sub> and black–brown cubic crystals of (NH<sub>4</sub>)<sub>2</sub>(VO)(VP)O<sub>7</sub>. (Note that the trace amount of cadmium acetate seems to play an indispensable role in either transport or catalysis, since without it synthesis of the (NH<sub>4</sub>)<sub>2</sub>(VO)(VP)O<sub>7</sub> phase is not possible.) The structure was determined from a selected single crystal and all analyses were performed on selected crystals of (NH<sub>4</sub>)<sub>2</sub>(VO)(VP)O<sub>7</sub>. The composition in P and V was confirmed by electron microscopy analysis. The nitrogen content, determined by microanalysis, indicates a weight ratio of 9%, in good agreement with the theoretical values of 10.1%. The IR spectrum clearly shows the stretching and bending vibrations of the NH<sub>4</sub><sup>+</sup> group, centred from 3500 to 2500 cm<sup>-1</sup> and at 1400 cm<sup>-1</sup>, respectively. Thermal gravimetric analysis is in agreement with the theoretical loss of two moles of NH<sub>3</sub> and H<sub>2</sub>O per (NH<sub>4</sub>)<sub>2</sub>(VO)(VP)O<sub>7</sub> formula unit. The decomposition, which occurs above 723 K, gives V<sub>2</sub>O<sub>5</sub> and Cd<sub>2</sub>P<sub>2</sub>O<sub>7</sub> according to the X-ray powder pattern.

### Crystal data

(NH<sub>4</sub>)<sub>2</sub>(VO)(VP)O<sub>7</sub>  
 $M_r = 296.9$   
 Tetragonal  
*P4bm*  
 $a = 8.6233$  (6) Å  
 $c = 5.6384$  (7) Å  
 $V = 419.28$  (8) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 2.35$  Mg m<sup>-3</sup>  
 $D_m$  not measured

Mo K $\alpha$  radiation  
 $\lambda = 0.71073$  Å  
 Cell parameters from 25 reflections  
 $\theta = 18$ –22°  
 $\mu = 2.44$  mm<sup>-1</sup>  
 $T = 294$  K  
 Cubic  
 0.33 × 0.33 × 0.33 mm  
 Brown–black

### Data collection

CAD-4 diffractometer  
 $\omega$ -4/ $\theta$  scans  
 Absorption correction:  
 Gaussian  
 $T_{\min} = 0.438$ ,  $T_{\max} = 0.531$   
 1759 measured reflections  
 1759 independent reflections

1386 observed reflections  
 $[I > 3\sigma(I)]$   
 $\theta_{\max} = 45^\circ$   
 $h = 0 \rightarrow 21$   
 $k = 0 \rightarrow 21$   
 $l = 0 \rightarrow 13$   
 3 standard reflections  
 frequency: 50 min  
 intensity decay: 0.77%

### Refinement

Refinement on  $F$   
 $R = 0.046$   
 $wR = 0.046$   
 $S = 0.612$   
 1386 reflections  
 42 parameters  
 H atoms not located  
 Unit weights applied  
 $(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 1.87$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.92$  e Å<sup>-3</sup>  
 Extinction correction:  
 Zachariasen (1968)  
 Extinction coefficient: 0.06  
 Atomic scattering factors  
 from *International Tables*  
 for X-ray Crystallography  
 (1974, Vol. IV, Tables  
 2.2B and 2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	<i>U</i> <sub>eq</sub>
P†	0.36969 (4)	-x + 1/2	0.06353	0.0097 (5)
V2‡	0.36969 (4)	-x + 1/2	0.06353	0.0135 (5)
V1	0	0	0.0593 (4)	0.01329 (9)
O1	1/2	1/2	0.3436 (9)	0.0279 (9)
O2	0.3699 (3)	-x + 1/2	0.3440 (6)	0.0218 (5)
O3	0.7019 (2)	0.4169 (3)	-0.0402 (5)	0.0261 (5)
O4	1/2	0	-0.035 (1)	0.045 (1)
N	0.1701 (3)	-x + 1/2	0.585 (1)	0.0420 (9)

† Site occupancy = 0.51 (1). ‡ Site occupancy = 0.49 (1).

Table 2. Selected geometric parameters (Å, °)

P/V2—O2	1.582 (3)	O1 <sup>iii</sup> —O3 <sup>v</sup>	2.868 (5)
P/V2—O3 <sup>i</sup>	1.613 (2)	O3 <sup>i</sup> —O3 <sup>iii</sup>	3.765 (3)
P/V2—O3 <sup>ii</sup>	1.613 (2)	O3 <sup>i</sup> —O3 <sup>iv</sup>	2.662 (3)
P/V2—O4	1.683 (2)	O3 <sup>i</sup> —O3 <sup>v</sup>	2.662 (3)
O2—O3 <sup>i</sup>	2.638 (4)	O3 <sup>iii</sup> —O3 <sup>iv</sup>	2.662 (3)
O2—O3 <sup>ii</sup>	2.638 (4)	O3 <sup>iii</sup> —O3 <sup>v</sup>	2.662 (3)
O2—O4	2.660 (5)	O3 <sup>iv</sup> —O3 <sup>v</sup>	3.765 (3)
O3 <sup>i</sup> —O3 <sup>ii</sup>	2.623 (3)	N—O2	2.789 (4)
O3 <sup>i</sup> —O4	2.669 (2)	N—O2 <sup>i</sup>	2.942 (4)
O3 <sup>ii</sup> —O4	2.669 (2)	N—O2 <sup>ii</sup>	2.942 (4)
V1—O1 <sup>iii</sup>	1.603 (6)	N—O4 <sup>iii</sup>	2.986 (6)
V1—O3 <sup>i</sup>	1.964 (2)	N—O3 <sup>viii</sup>	3.014 (5)
V1—O3 <sup>iii</sup>	1.964 (2)	N—O3 <sup>ix</sup>	3.014 (5)
V1—O3 <sup>iv</sup>	1.964 (2)	N—O3 <sup>x</sup>	3.235 (5)
V1—O3 <sup>v</sup>	1.964 (2)	N—O3 <sup>xi</sup>	3.235 (5)
O1 <sup>iii</sup> —O3 <sup>i</sup>	2.868 (5)	N—O1	3.477 (4)
O1 <sup>iii</sup> —O3 <sup>ii</sup>	2.868 (5)	N—O1 <sup>iii</sup>	3.477 (4)
O1 <sup>iii</sup> —O3 <sup>iv</sup>	2.868 (5)		
O2—P/V2—O3 <sup>i</sup>	111.3 (1)	O1 <sup>iii</sup> —V1—O3 <sup>i</sup>	106.6 (1)
O2—P/V2—O3 <sup>ii</sup>	111.3 (1)	O3 <sup>i</sup> —V1—O3 <sup>iii</sup>	146.8 (2)
O2—P/V2—O4	109.1 (2)	O3 <sup>i</sup> —V1—O3 <sup>iv</sup>	85.3 (1)
O3 <sup>i</sup> —P/V2—O3 <sup>ii</sup>	108.8 (1)	O3 <sup>i</sup> —V1—O3 <sup>v</sup>	85.3 (1)
O3 <sup>i</sup> —P/V2—O4	108.1 (1)	O3 <sup>iii</sup> —V1—O3 <sup>iv</sup>	85.3 (1)
O3 <sup>ii</sup> —P/V2—O4	108.1 (1)	O3 <sup>iii</sup> —V1—O3 <sup>v</sup>	85.3 (1)
O1 <sup>iii</sup> —V1—O3 <sup>i</sup>	106.6 (1)	O3 <sup>iv</sup> —V1—O3 <sup>v</sup>	146.8 (2)
O1 <sup>iii</sup> —V1—O3 <sup>ii</sup>	106.6 (1)	P/V2—O3 <sup>i</sup> —V1	141.6 (2)
O1 <sup>iii</sup> —V1—O3 <sup>iv</sup>	106.6 (1)		

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

The site occupancy for N was refined to take account of the NH<sub>4</sub><sup>+</sup> group, giving an occupancy of 1.23 (1). Structure solution and refinement used *Xtal3.2* (Hall, Flack & Stewart, 1992).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1160). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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