

## A New Vanadium(IV) Phosphate with a Tunnel Structure: $\text{Cs}_2\text{V}_3\text{P}_4\text{O}_{17}$

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A new  $\text{V}^{4+}$  phosphate,  $\text{Cs}_2\text{V}_3\text{P}_4\text{O}_{17}$ , has been synthesized and its structure was determined from single-crystal X-ray diffraction data. It crystallizes in the orthorhombic space group  $Pnma$  with  $a = 17.613(5)$ ,  $b = 7.328(2)$ ,  $c = 11.600(4)$  Å,  $V = 1497.1(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $R = 0.0272$ ,  $R_w = 0.0261$ , G.O.F. = 1.37 for 1402 unique reflections with  $I > 3.0 \sigma(I)$ . The structure contains tunnels where the  $\text{Cs}^+$  cations are located. The framework can be described as consisting of  $\text{V}_2\text{O}_{10}$  units formed from one  $\text{VO}_5$  square pyramid and one distorted  $\text{VO}_6$  octahedron sharing a corner, and infinite chains of distorted  $\text{VO}_6$  octahedra sharing opposite corners, which are linked in three dimensions through the pyrophosphate groups. © 1989 Academic Press, Inc.

### Introduction

Vanadium phosphorus oxides have shown a rich structural chemistry owing to the accessibility of more than one vanadium oxidation state and the ability of vanadium polyhedra and phosphate tetrahedra to form a variety of frameworks. In the system  $\text{V}-\text{P}-\text{O}$  several well-characterized phases have been reported. For example, in  $(\text{V}^{4+}\text{O})_2\text{P}_2\text{O}_7$ , double chains of edge-sharing octahedra are linked together via pyrophosphate groups (1). However,  $(\text{V}^{4+}\text{O})_2\text{H}_4\text{P}_2\text{O}_9$  adopts a layer structure and each layer contains pairs of face-sharing  $\text{VO}_6$  octahedra (2). Interestingly, the mixed-valence vanadium phosphate  $\text{V}_3\text{P}_4\text{O}_{15}$  consists of vanadium trimers composed of two trivalent va-

nadium atoms and one tetravalent vanadyl group (3).

To our knowledge, little structural work has been reported on the system  $M-\text{V}^{4+}-\text{P}-\text{O}$  ( $M =$  alkali metal cation). As part of our research project devoted to discovering novel mixed frameworks built up from corner-sharing octahedra and tetrahedra, the system  $\text{Cs}-\text{V}^{4+}-\text{P}-\text{O}$  was investigated. The present paper reports the synthesis and structure of a new cesium vanadium phosphate,  $\text{Cs}_2\text{V}_3\text{P}_4\text{O}_{17}$ .

### Experimental

#### Synthesis

$\text{Cs}_4\text{V}_2\text{O}_7$  (99.9%),  $\text{VO}_2$  (99.5%), V metal (99.5%), and  $\text{P}_2\text{O}_5$  (99.9%) were purchased

from Cerac. The title compound was first obtained as green needle-like crystals in an attempt to prepare "CsV<sub>2</sub>P<sub>3</sub>O<sub>12</sub>" in a sealed fused silica tube at 950°C. After identification by single-crystal X-ray structure analysis, a few reactions using proper amounts of the starting materials were conducted at several different temperatures ranging from 750 to 950°C. On the basis of powder X-ray analysis, Cs<sub>2</sub>V<sub>3</sub>P<sub>4</sub>O<sub>17</sub> was obtained as a major product with a small amount of unidentified phases.

### Single-Crystal X-Ray Structure Determination

A green crystal having the dimensions of 0.35 × 0.05 × 0.05 mm was selected for indexing and intensity data collection on a Nicolet R3/V diffractometer with a Mo X-ray source equipped with a graphite monochromator ( $\lambda = 0.71073 \text{ \AA}$ ). The orientation matrix and unit cell parameters were determined at room temperature by least-squares fit of 16 peak maxima with  $21^\circ < 2\theta < 34^\circ$ . The intensity data were collected up to  $2\theta = 55^\circ$  with a  $2\theta$ - $\theta$  scan. A periodic check of three standard reflections verified the stability of the sample. A total of 1402 unique reflections with  $I > 3.0 \sigma(I)$  were corrected for absorption, Lorentz, and polarization effects. Corrections for absorption effects were based on  $\psi$ -scans of a few suitable reflections with  $\chi$  values close to  $90^\circ$ . Based on the systematic absences, statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be *Pnma*. Crystal data: orthorhombic, space group *Pnma* (No. 62),  $a = 17.613(5)$ ,  $b = 7.328(2)$ ,  $c = 11.600(4) \text{ \AA}$ ,  $V = 1497.1(8) \text{ \AA}^3$ ,  $Z = 4$ ,  $D(\text{calc}) = 3.61 \text{ g/cm}^3$ ,  $F(000) = 1500$ ,  $\mu(\text{MoK}\alpha) = 70.5 \text{ cm}^{-1}$ .

The structure was solved by direct methods using SHELXTL PLUS program and refined by full-matrix least-squares refinement based on  $F$  values. The refinement of 136 parameters with the weighting scheme

$1/w = \sigma^2(F_o) + 0.000096 F_o^2$  converged at  $R = 2.72\%$ ,  $R_w = 2.61\%$ , goodness of fit = 1.37. In the final difference Fourier map the deepest hole was  $-0.84 \text{ e/\AA}^3$ , and the highest peak  $1.01 \text{ e/\AA}^3$ . Neutral atom scattering factors and anomalous dispersion terms were taken from "International Tables for X-Ray Crystallography" (4).

Cs1, Cs2, V1, V2, O2, O6, O9, O10, and O11 lie in mirror planes, P1, P2, and all other oxygen atoms are at general positions. V3, which was initially located at the 4b special position, exhibited very large  $U_{22}$  value ( $0.074 \text{ \AA}^2 = 10 \times U_{11}$  or  $U_{33}$ ), suggesting positional disorder. Therefore, a displacement of V3 from the inversion center was allowed with its occupancy factor fixed at 0.5. A few cycles of least-squares refinement converged at a slightly lower agreement factor (2.72 vs 2.83%) with reasonable thermal parameters. V3 shifted to (0.4991, 0.0312, 0.0000), indicating that disorder of the V atom is mainly along the  $b$ -axis.

Final atomic parameters are given in Table I. Selected bond distances and angles are listed in Table II.

TABLE I  
ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2 \times 10^3$ )

Atom	$x$	$y$	$z$	$U(\text{eq})^a$
Cs(1)	0.36527(3)	3/4	0.52696(5)	20.7(2)
Cs(2)	0.31313(3)	3/4	0.14859(5)	19.9(2)
V(1)	0.40609(7)	1/4	0.6605(1)	6.7(3)
V(2)	0.30608(7)	1/4	0.3268(1)	8.0(4)
V(3) <sup>b</sup>	0.4991(4)	0.0312(4)	0.0000(7)	6.5(9)
P(1)	0.16951(7)	0.5491(2)	0.3821(1)	7.0(4)
P(2)	0.46786(7)	0.0482(2)	0.2839(1)	6.9(4)
O(1)	0.3550(2)	0.4347(5)	0.7565(3)	11.2(10)
O(2)	0.1925(3)	3/4	0.4236(5)	17.1(17)
O(3)	0.2418(2)	0.4424(6)	0.3975(3)	14.2(11)
O(4)	0.3866(2)	0.4398(5)	0.3264(3)	11.6(10)
O(5)	0.4846(2)	0.4364(6)	0.6330(3)	13.1(11)
O(6)	0.5036(3)	1/4	0.2861(5)	11.7(15)
O(7)	0.3911(2)	0.9812(6)	-0.0378(3)	17.4(12)
O(8)	0.4722(2)	0.9737(6)	0.1633(3)	13.0(11)
O(9)	0.4907(3)	1/4	0.0103(5)	14.6(17)
O(10)	0.3571(3)	1/4	0.5456(4)	12.9(16)
O(11)	0.2778(3)	1/4	0.1976(5)	22.3(19)

<sup>a</sup> Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

<sup>b</sup> The occupancy factor for V(3) is 0.5.

TABLE II  
SELECTED BOND DISTANCES AND ANGLES FOR  
Cs<sub>2</sub>V<sub>3</sub>P<sub>4</sub>O<sub>17</sub>

Bond Distances (Å)			
Cs(1)–O(1)	3.530(4) (2×)	Cs(1)–O(2)	3.271(6)
Cs(1)–O(3)	3.473(4) (2×)	Cs(1)–O(4)	3.274(4) (2×)
Cs(1)–O(5)	3.349(4) (2×)	Cs(1)–O(5)	3.507(4) (2×)
Cs(1)–O(6)	3.167(5)	Cs(1)–O(11)	3.204(6)
Cs(2)–O(1)	3.489(4) (2×)	Cs(2)–O(3)	3.378(4) (2×)
Cs(2)–O(4)	3.332(4) (2×)	Cs(2)–O(7)	3.071(4) (2×)
Cs(2)–O(8)	3.251(4) (2×)	Cs(2)–O(10)	3.228(5)
V(1)–O(1)	1.970(4) (2×)	V(1)–O(5)	1.970(4) (2×)
V(1)–O(10)	1.589(5)	V(2)–O(3)	1.985(4) (2×)
V(2)–O(4)	1.986(4) (2×)	V(2)–O(11)	1.580(6)
V(2)–O(10)	2.692(5)	V(3)–O(7a)	1.986(8)
V(3)–O(7b)	1.986(8)	V(3)–O(8a)	1.997(9)
V(3)–O(8b)	1.960(9)	V(3)–O(9a)	1.615(3)
V(3)–O(9b)	2.072(3)	P(1)–O(1)	1.524(4)
P(1)–O(2)	1.601(3)	P(1)–O(3)	1.505(4)
P(1)–O(7)	1.500(4)	P(2)–O(4)	1.516(4)
P(2)–O(5)	1.516(4)	P(2)–O(6)	1.608(2)
P(2)–O(8)	1.504(4)		
Bond Angles (°)			
O(1)–V(1)–O(10)	103.1(2)	O(5)–V(1)–O(10)	104.2(2)
O(3)–V(2)–O(11)	102.2(2)	O(4)–V(2)–O(11)	102.9(2)
O(11)–V(2)–O(10)	178.9(2)	O(7a)–V(3)–O(9a)	96.4(4)
O(7b)–V(3)–O(9a)	96.8(4)	O(8a)–V(3)–O(9a)	96.8(4)
O(8b)–V(3)–O(9a)	96.5(4)	O(9a)–V(3)–O(9b)	179.0(5)
V(3)–O(9)–V(3)	167.3(4)	V(1)–O(10)–V(2)	166.6(3)
P(1)–O(2)–P(1)	133.7(4)	P(2)–O(6)–P(2)	133.8(3)

### Description of the Structure and Discussion

The crystal structure of Cs<sub>2</sub>V<sub>3</sub>P<sub>4</sub>O<sub>17</sub>, viewed along the *c*- and *b*-axis, is shown in Fig. 1 and Fig. 2, respectively, and contains intersecting tunnels where the Cs<sup>+</sup> cations are located. Figure 3 is a view of a tunnel along the *c*-axis and clearly shows how the building units are connected. The tunnel in Fig. 3 results from alternately stacking three types of rings. The first ring is formed by the edges of two V(2)O<sub>6</sub> octahedra, one V(1)O<sub>5</sub> square pyramid, and four PO<sub>4</sub> tetrahedra; the second ring by the edges of two V(1)O<sub>5</sub> pyramids, one V(2)O<sub>6</sub> octahedron, and four PO<sub>4</sub> tetrahedra; and the third ring by the edges of two corner-sharing V(3)O<sub>6</sub> octahedra, one V(2)O<sub>6</sub> octahedron, and two PO<sub>4</sub> tetrahedra. The second and third rings have a common edge of a V(2)O<sub>6</sub> octahedron. The framework can be described as consisting of V<sub>2</sub>O<sub>10</sub> units formed from one V(1)O<sub>5</sub> square pyramid and one V(2)O<sub>6</sub> octahedron sharing a corner, and chains of V(3)O<sub>6</sub> octahedra sharing opposite corners,

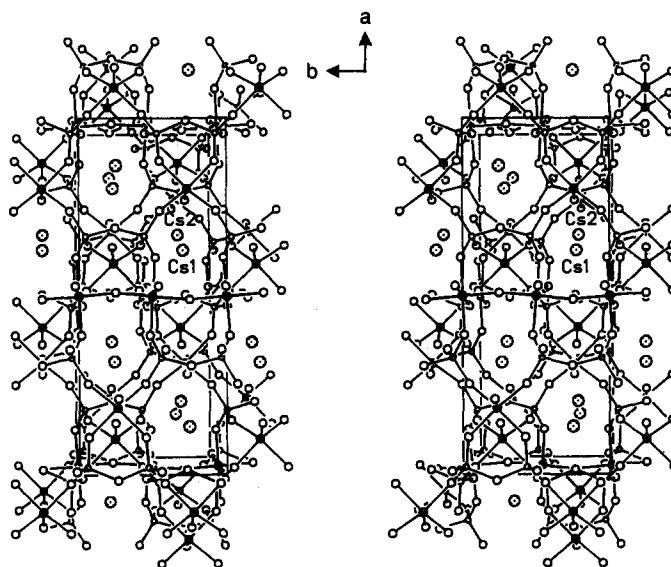


FIG. 1. A stereoscopic view of the Cs<sub>2</sub>V<sub>3</sub>P<sub>4</sub>O<sub>17</sub> structure along the *c*-axis. The Cs, V, P, and O atoms are represented by dotted, cross-hatched, small, and medium open circles, respectively.

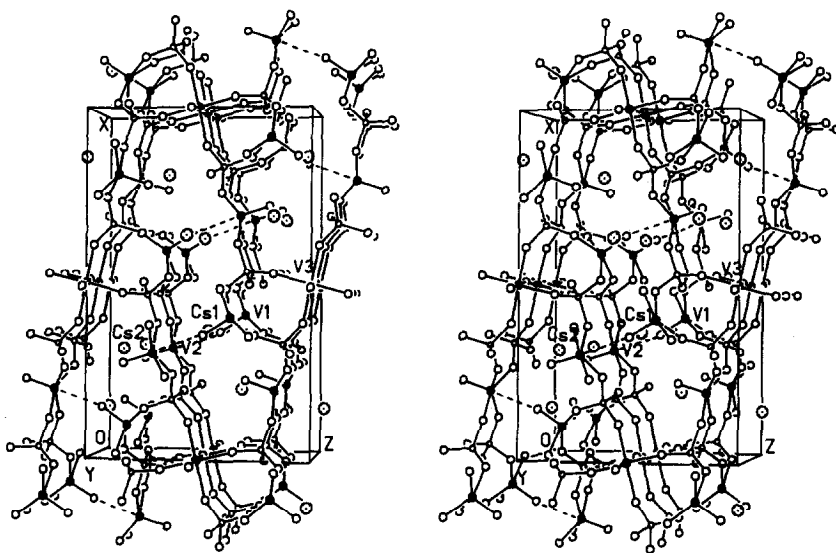


FIG. 2. A stereoscopic view of the  $\text{Cs}_2\text{V}_3\text{P}_4\text{O}_{17}$  structure along the  $b$ -axis. The Cs, V, P, and O atoms are represented by dotted, cross-hatched, small, and medium open circles, respectively. The weak  $\text{O}(10)\dots\text{V}(2)$  bonds are represented by dashed lines.

which are linked in three dimensions through  $\text{P}_2\text{O}_7$  groups. In  $\text{VO}_5$  square pyramids and in  $\text{VO}_6$  octahedra each vanadium atom is displaced from the center of the polyhedron, resulting in one short V–O bond. The short bond is typical of a  $\text{V}=\text{O}$  vanadyl group, involving both  $\sigma$  and  $\pi$

bondings. The structural formula is  $\text{Cs}_2(\text{VO})_3(\text{P}_2\text{O}_7)_2$ . V(1) is coordinated by five oxygen atoms in a square pyramid. However, the apical vanadyl oxygen (O(10)) of a  $\text{V}(1)\text{O}_5$  square pyramid is weakly coordinated to V(2) at a long  $\text{O}\dots\text{V}$  distance of  $2.692(5)$  Å, thus forming a  $\text{V}_2\text{O}_{10}$  unit. The

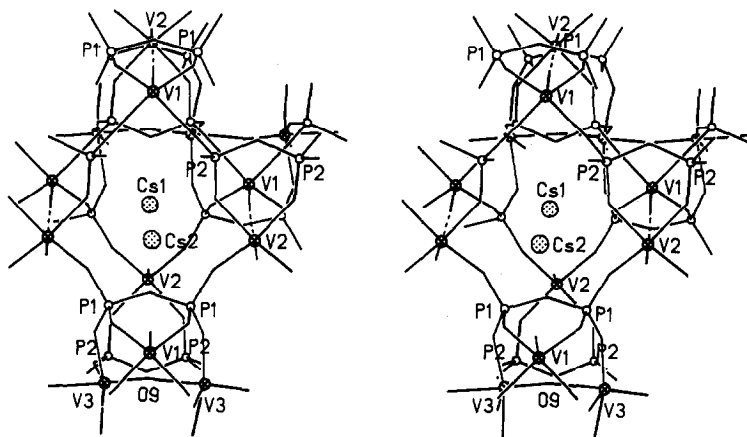


FIG. 3. A stereoscopic view of a tunnel in  $\text{Cs}_2\text{V}_3\text{P}_4\text{O}_{17}$ . For clarity, the radii for oxygen atoms are set equal to zero. The weak  $\text{O}(10)\dots\text{V}(2)$  bonds are represented by dashed lines.

$\text{O}(10)\dots\text{V}(2)=\text{O}(11)$  and  $\text{V}(1)=\text{O}(10)\dots\text{V}(2)$  bond angles are  $178.9(2)^\circ$  and  $166.6(3)^\circ$ , respectively. The  $\text{V}(2)\text{O}_6$  octahedron is much distorted as shown by the O–O distances ranging from 2.68 to 3.01 Å. The  $\text{V}=\text{O}$  units in  $\text{V}(3)\text{O}_6$  octahedra are arranged in chains running along the  $b$ -axis,  $\text{V}(3)=\text{O}(9)\dots\text{V}(3)=\text{O}(9)\dots\text{V}(3)=\text{O}(9)\dots$ , with alternately short and long distances of 1.615(3) and 2.072(3) Å and four equatorial V–O bonds (1.960(9)–1.997(9) Å) that complete the distorted octahedra. The  $\text{O}(9)=\text{V}(3)\dots\text{O}(9)$  and  $\text{V}(3)=\text{O}(9)\dots\text{V}(3)$  bond angles are  $179.0(5)$  and  $167.3(4)^\circ$ , respectively. The observed alternation in the  $\text{V}(3)=\text{O}(9)\dots\text{V}(3)$  distances depends entirely on the disorder model for V(3). The refinement to chemically reasonable distances indicates that it is a good disorder model, but the actual values of the bond distances themselves are not as reliable as the estimated deviations would indicate.

Each  $\text{V}(1)\text{O}_5$  square pyramid shares four corners with one bidentate  $\text{P}(1)_2\text{O}_7$  and two monodentate  $\text{P}(2)_2\text{O}_7$  ligands with the apical corner being weakly bonded to V(2). Each  $\text{V}(2)\text{O}_6$  shares four corners with one bidentate  $\text{P}(2)_2\text{O}_7$  and two monodentate  $\text{P}(1)_2\text{O}_7$  ligands with the apical oxygen atom (O(11)) being unshared.  $\text{V}(3)\text{O}_6$  octahedra form strings by sharing opposite corners with the equatorial positions being coordinated by two  $\text{P}(1)_2\text{O}_7$  and two  $\text{P}(2)_2\text{O}_7$  ligands.  $\text{P}(1)_2\text{O}_7$  and  $\text{P}(2)_2\text{O}_7$  groups have somewhat different coordination environments. Each  $\text{P}(1)_2\text{O}_7$  group is bonded to a  $\text{V}(1)\text{O}_5$  square pyramid as a chelate, bonded to two  $\text{V}(2)\text{O}_6$  octahedra as a monodentate ligand, and forms a bridge between two neighboring  $\text{V}(3)\text{O}_6$  octahedra. Each  $\text{P}(2)_2\text{O}_7$  group is bonded to a  $\text{V}(2)\text{O}_6$  octahedron as a chelate, bonded to two  $\text{V}(1)\text{O}_5$  square pyramids as a monodentate ligand, and also forms a bridge between two  $\text{V}(3)\text{O}_6$  octahedra. In the tetrahedra belonging to each pyrophosphate group the P atoms are, as usual, displaced away from the bridging oxygen atom

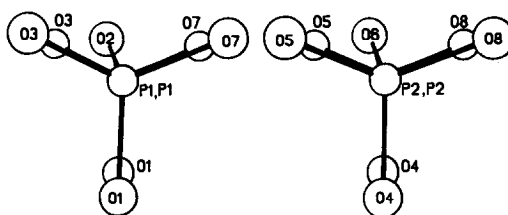


FIG. 4. Two  $\text{P}_2\text{O}_7$  groups in  $\text{Cs}_2\text{V}_3\text{P}_4\text{O}_{17}$  each in a direction parallel to the  $\text{P}\dots\text{P}$  vector.

giving three shorter and one longer P–O bonds. The P–O–P bond angle involving the bridging oxygen atom for  $\text{P}(1)_2\text{O}_7$  ( $133.7(4)^\circ$ ) is almost identical to that for  $\text{P}(2)_2\text{O}_7$  ( $133.8(3)^\circ$ ). The  $\text{PO}_4$  tetrahedra forming the  $\text{P}_2\text{O}_7$  groups exhibit an eclipsed configuration (Fig. 4) since the bridging oxygen atoms reside on mirror planes. The coordination number of  $\text{Cs}^+$  can be determined by the maximum bond distance for Cs–O using the procedure by Donnay and Allmann (5) with the revised radii of Shannon (6) leading to  $(\text{Cs}-\text{O})_{\text{max}} = 3.60$  Å. Accordingly, Cs(1) is surrounded by 13 oxygen atoms at distances ranging from 3.167(3) to 3.530(3) Å, and Cs(2) by 11 oxygen atoms at distances ranging from 3.071(4) to 3.489(4) Å.

This structural study of  $\text{Cs}_2\text{V}_3\text{P}_4\text{O}_{17}$  confirms the great ability of  $\text{PO}_4$  tetrahedra to form a variety of frameworks with vanadium polyhedra. There is good prospect for more novel structures in vanadium phosphorus oxides. Further research on these materials is in progress.

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