

Fig. 2. Projection along the a direction of the atomic arrangement of $\text{Te}(\text{OH})_6 \cdot (\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$. Hatched octahedra represent the $\text{Te}(\text{OH})_6$ groups and empty circles are the NH_4 groups. H atoms have been omitted for clarity.

as an almost regular octahedron with, in the present study, $\text{Te}-\text{O}$ distances ranging from 1.909 to 1.919 Å and $\text{Te}-\text{O}-\text{H}$ angles varying from 106 to 112°. As shown by Fig. 2 these $\text{Te}(\text{OH})_6$ groups are located in planes $y = 0$ and $\frac{1}{2}$ and so form layers alternating with the phosphoric ones.

The $(\text{NH}_4)\text{O}_n$ polyhedra. The two NH_4 groups appear as moderately distorted tetrahedra with $\text{N}-\text{H}$ distances ranging from 0.78 to 0.87 Å in $\text{N}(1)\text{H}_4$ and from 0.85 to 1.03 Å in $\text{N}(2)\text{H}_4$. $\text{H}-\text{N}-\text{H}$ angles spread from 96 to 127° in the first group and from 96 to 133° in the second with, in

both cases, an average value of 109°. Within a range of 3.50 Å $\text{N}(1)\text{H}_4$ has ten O neighbours while $\text{N}(2)\text{H}_4$ has only six.

The hydrogen bonds. Among the main geometrical features of the hydrogen-bond network reported in Table 2 it must be noted that all the hydrogen bonds involving H atoms of the $\text{Te}(\text{OH})_6$ or NH_4 groups are classical with $\text{N}-\text{O}$ or $\text{O}-\text{O}$ distances ranging from 2.628 to 3.029 Å, while those connecting the $\text{P}_2\text{O}_7\text{H}_2^{2-}$ groups correspond to much shorter distances (2.523 and 2.594 Å), comparable to the $\text{O}-\text{O}$ distances inside a PO_4 tetrahedron. This fact explains the formation of $[\text{P}_2\text{O}_7\text{H}_2^{2-}]_n$ chains or ribbons commonly observed in the dihydrogendifosphates. Such entities are today sometimes designated as 'macroanions'.

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Hydrothermal Synthesis and Structures of Two Layered Dioxovanadium(V) Phosphates $A(\text{VO}_2)\text{PO}_4$ ($A = \text{Ba, Sr}$)

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Abstract. Barium dioxovanadium(V) phosphate, $\text{Ba}(\text{VO}_2)\text{PO}_4$, $M_r = 315.256$, monoclinic, $P2_1/c$, $a =$

5.616 (2), $b = 10.062 (1)$, $c = 8.727 (1)$ Å, $\beta = 90.90 (2)$ °, $V = 493.1 (2)$ Å³, $Z = 4$, $D_x = 4.247$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70930$ Å, $\mu = 100.49$ cm⁻¹, $F(000) = 568$, $T = 297$ K, $R = 0.0239$

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for 2025 unique reflections. Strontium dioxovanadium(V) phosphate, Sr(VO₂)PO₄, $M_r = 265.536$, monoclinic, $P2_1/c$, $a = 5.430$ (1), $b = 9.846$ (2), $c = 8.517$ (2) Å, $\beta = 90.60$ (2)°, $V = 455.3$ (2) Å³, $Z = 4$, $D_x = 3.873$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 136.45$ cm⁻¹, $F(000) = 496$, $T = 297$ K, $R = 0.0288$ for 844 unique reflections. Single crystals of the title compounds were grown hydrothermally at 503 K. Their structures contain layers of phosphate tetrahedra and edge-sharing biotahedra, that contain two distorted VO₆ octahedra, with the divalent metal cations between the layers. Within a layer windows are formed by the edges of four octahedra and four tetrahedra.

Introduction. Although a large number of new compounds have been synthesized and structurally characterized in the system A –V–P–O (A = metal cation) containing V in the oxidation states less than + 5 (Wang, Kang, Cheng & Lii, 1991), little structural work has been reported on the system A –V⁵⁺–P–O. To our knowledge, A (VO₂)HPO₄ (A = NH₄⁺, K⁺, Rb⁺, Tl⁺) were essentially the only structurally well characterized examples (Amoros, Beltran-Porter, Le Bail, Ferey & Villeneuve, 1988; Huan, Johnson, Jacobson, Corcoran & Goshorn, 1991). The structure consists of isolated chains of VO₅ square pyramids. Adjacent VO₅ units in each chain are bridged by HPO₄ groups. Attempts to add new members to the A –V⁵⁺–P–O series of compounds have yielded the layered dioxovanadium(V) phosphates A (VO₂)PO₄ (A = Ba, Sr) which adopt a new structure type. The present work describes the hydrothermal synthesis and single-crystal X-ray structure determinations of these new compounds.

Experimental. V₂O₅ (99.9%) came from Cerac and reagent grade H₃PO₄ (85%), Ba(OH)₂·8H₂O and Sr(OH)₂·8H₂O from Merck, and were used as received. A suitable reaction condition for the crystal growth of the Ba compound consisted of a mixture of 0.244 g of V₂O₅, 0.846 g of Ba(OH)₂·8H₂O, 0.6 mL of 85% H₃PO₄, and 10 mL of H₂O in a 23 mL Teflon-lined autoclave. The reaction vessel was maintained at 503 K and autogenous pressure for 4 d before slow cooling at 5 K h⁻¹ to room temperature. The yellow product was filtered off, washed with water, rinsed with ethanol, and dried in a desiccator at ambient temperature. The X-ray powder pattern of the product compared well with that calculated from the single-crystal data. The crystal growth of the Sr compound was achieved under similar conditions. However, powder X-ray diffraction showed that the product was contaminated with a small amount of unidentified materials.

Ba(VO₂)PO₄. Yellow prismatic crystal of approximate dimensions 0.15 × 0.20 × 0.25 mm, density not

Table 1. *Positional parameters and equivalent isotropic thermal parameters (Å² × 100)*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ba(VO₂)PO₄				
Ba	0.16138 (3)	0.68667 (2)	0.08426 (2)	1.014 (8)
V	0.6591 (1)	0.58669 (6)	0.41399 (6)	0.75 (1)
P	0.3445 (2)	0.38096 (8)	0.22217 (9)	0.80 (2)
O(1)	0.7156 (5)	0.6716 (3)	0.6145 (3)	1.40 (6)
O(2)	0.4840 (5)	0.5142 (2)	0.2332 (3)	1.07 (6)
O(3)	0.4956 (4)	0.7727 (2)	0.3490 (3)	1.20 (6)
O(4)	0.9109 (5)	0.6255 (3)	0.3384 (3)	1.47 (6)
O(5)	0.3043 (4)	0.5668 (2)	0.5152 (3)	1.03 (5)
O(6)	0.1236 (5)	0.4105 (3)	0.1281 (3)	1.47 (6)
Sr(VO₂)PO₄				
Sr	0.83958 (8)	0.68435 (4)	0.07688 (5)	0.65 (1)
V	0.3352 (1)	0.58865 (8)	0.41072 (9)	0.39 (2)
P	0.6674 (2)	0.3882 (1)	0.2166 (1)	0.43 (3)
O(1)	0.2549 (6)	0.6646 (3)	0.6173 (4)	0.7 (1)
O(2)	0.5279 (6)	0.5264 (3)	0.2287 (4)	0.67 (9)
O(3)	0.5058 (6)	0.7789 (3)	0.3549 (4)	0.74 (9)
O(4)	0.0763 (6)	0.6280 (3)	0.3278 (4)	0.8 (1)
O(5)	0.6949 (6)	0.5735 (3)	0.5306 (4)	0.67 (9)
O(6)	0.8880 (6)	0.4159 (4)	0.1158 (4)	1.1 (1)

measured. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. 25 reflections ($7.5 < \theta < 20$ °) for refining unit-cell parameters. $\omega/2\theta$ scan, scan width ($0.70 + 0.35\tan\theta$)°, scan speed 8.2° min⁻¹. The space group was determined to be $P2_1/c$ from systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). The hkl data ranged from $-9, 0, 0$ to $9, 16, 14$; $2\theta_{\text{max}} = 70$ °. Three intensity control reflections measured every 1 h did not exhibit any significant variation. 2336 reflections were collected of which 2025 were unique [$I > 3\sigma(I)$] and were corrected for Lorentz and polarization effects. The data were corrected for absorption ($T_{\text{min}} = 0.829$, $T_{\text{max}} = 0.997$). Calculations were performed on a MicroVAX II computer with the *SHELXTL-Plus* system (Sheldrick, 1990).

Sr(VO₂)PO₄. Yellow prismatic crystal of approximate dimensions 0.16 × 0.18 × 0.24 mm, density not measured. Nicolet R3m/V diffractometer, graphite monochromator. 16 reflections ($6 < \theta < 16$ °) for refining unit-cell parameters. $\omega/2\theta$ scan, scan width 1.0°, variable scan speed 3–14.6° min⁻¹. The space group was determined to be $P2_1/c$ from systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). The hkl data ranged from $0, 0, -12$ to $8, 13, 12$; $2\theta_{\text{max}} = 55$ °. Three intensity control reflections measured every 50 reflections did not exhibit any significant variation. 1299 reflections were collected of which 844 were unique [$I > 3\sigma(I)$] and were corrected for Lorentz and polarization effects. The data were corrected for absorption ($T_{\text{min}} = 0.350$, $T_{\text{max}} = 0.877$). Calculations were also performed using the *SHELXTL-Plus* system.

The two structures were solved using the same strategy: heavy atoms located by direct methods and successive Fourier syntheses. Anisotropic full-matrix least-squares refinement (on F) for all atoms. Scat-

Table 2. Selected bond lengths (Å), bond valence sums ($\sum s$) and bond angles ($^\circ$) for $\text{Ba}(\text{VO}_2)\text{PO}_4$

$\text{Ba}—\text{O}(1')$	2.897 (3)	$\text{V}—\text{O}(1)$	1.968 (3)
$\text{Ba}—\text{O}(2)$	2.813 (3)	$\text{V}—\text{O}(2)$	1.985 (3)
$\text{Ba}—\text{O}(3)$	3.078 (3)	$\text{V}—\text{O}(3)$	2.157 (3)
$\text{Ba}—\text{O}(3'')$	2.833 (3)	$\text{V}—\text{O}(4)$	1.617 (3)
$\text{Ba}—\text{O}(4')$	3.171 (3)	$\text{V}—\text{O}(5)$	2.202 (3)
$\text{Ba}—\text{O}(4'')$	2.716 (3)	$\text{V}—\text{O}(5'')$	1.675 (2)
$\text{Ba}—\text{O}(5'')$	2.679 (2)	$\sum s(\text{V}—\text{O})$	= 5.03
$\text{Ba}—\text{O}(6)$	2.814 (3)	$\text{P}—\text{O}(1')$	1.562 (3)
$\text{Ba}—\text{O}(6'')$	2.619 (3)	$\text{P}—\text{O}(2)$	1.555 (3)
$\sum s(\text{Ba}—\text{O})$	= 2.17	$\text{P}—\text{O}(3'')$	1.548 (3)
		$\text{P}—\text{O}(6)$	1.507 (3)
		$\sum s(\text{P}—\text{O})$	= 4.90

$\text{O}(1)—\text{V}—\text{O}(2)$	159.6 (1)	$\text{O}(3)—\text{V}—\text{O}(5'')$	161.2 (1)
$\text{O}(1)—\text{V}—\text{O}(3)$	85.4 (1)	$\text{O}(4)—\text{V}—\text{O}(5)$	171.2 (1)
$\text{O}(1)—\text{V}—\text{O}(4)$	97.4 (1)	$\text{O}(4)—\text{V}—\text{O}(5'')$	105.7 (1)
$\text{O}(1)—\text{V}—\text{O}(5)$	79.5 (1)	$\text{O}(5)—\text{V}—\text{O}(5'')$	82.8 (1)
$\text{O}(1)—\text{V}—\text{O}(5'')$	93.1 (1)	$\text{O}(1')—\text{P}—\text{O}(3'')$	105.3 (1)
$\text{O}(2)—\text{V}—\text{O}(3)$	84.6 (1)	$\text{O}(2)—\text{P}—\text{O}(1')$	110.6 (1)
$\text{O}(2)—\text{V}—\text{O}(4)$	100.9 (1)	$\text{O}(2)—\text{P}—\text{O}(3'')$	109.7 (1)
$\text{O}(2)—\text{V}—\text{O}(5)$	81.1 (1)	$\text{O}(2)—\text{P}—\text{O}(6)$	105.9 (1)
$\text{O}(2)—\text{V}—\text{O}(5'')$	90.6 (1)	$\text{O}(6)—\text{P}—\text{O}(1')$	112.1 (2)
$\text{O}(3)—\text{V}—\text{O}(4)$	93.1 (1)	$\text{O}(6)—\text{P}—\text{O}(3'')$	113.4 (1)
$\text{O}(3)—\text{V}—\text{O}(5)$	78.5 (1)		

Symmetry code: (i) $-1 + x, 1.5 - y, -0.5 + z$; (ii) $x, 1.5 - y, -0.5 + z$; (iii) $-1 + x, y, z$; (iv) $-x, 1 - y, -z$; (v) $1 - x, 1 - y, 1 - z$; (vi) $1 - x, -0.5 + y, 0.5 - z$.

tering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV). 83 parameters refined, $R = 0.0239$, $wR = 0.0321$, $S = 1.708$, $w = 1/[\sigma^2(F) + 0.0005F^2]$, $\Delta\rho < 1.54 \text{ e \AA}^{-3}$, $(\Delta/\sigma)_{\text{max}} = 0.001$ for $\text{Ba}(\text{VO}_2)\text{PO}_4$; 83 parameters refined, $R = 0.0288$, $wR = 0.0300$, $S = 0.955$, $w = 1/[\sigma^2(F) + 0.0010F^2]$, $\Delta\rho < 1.21 \text{ e \AA}^{-3}$, $(\Delta/\sigma)_{\text{max}} = 0.001$ for $\text{Sr}(\text{VO}_2)\text{PO}_4$. The largest residual electron densities are near the divalent metal cations. Both structures have a near orthorhombic metric cell. This is just accidental since the axial oscillation photographs taken along the a and c axis do not show a mirror plane symmetry.

Discussion. The atomic coordinates, thermal parameters, selected bond lengths, bond angles, and bond-valence sums (Brown & Altermatt, 1985) are given in Tables 1–3.* The bond-valence sums for the cations in both structures are in good accord with their formal oxidation states. Both compounds adopt a new structure type.

The structure of $\text{Ba}(\text{VO}_2)\text{PO}_4$, viewed approximately parallel to the c axis, is shown in Fig. 1 and contains layers of dioxovanadium phosphate with the Ba^{2+} ions between the layers. Each layer is built up from distorted VO_6 octahedra and PO_4 tetrahedra. Within a layer windows are formed by the edges of four octahedra and four tetrahedra. The Ba^{2+}

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54898 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR0009]

Table 3. Selected bond lengths (Å), bond valence sums ($\sum s$) and bond angles ($^\circ$) for $\text{Sr}(\text{VO}_2)\text{PO}_4$

$\text{Sr}—\text{O}(1')$	2.720 (3)	$\text{V}—\text{O}(1)$	1.965 (3)
$\text{Sr}—\text{O}(2)$	2.646 (3)	$\text{V}—\text{O}(2)$	1.977 (3)
$\text{Sr}—\text{O}(3)$	3.138 (3)	$\text{V}—\text{O}(3)$	2.146 (3)
$\text{Sr}—\text{O}(3'')$	2.630 (3)	$\text{V}—\text{O}(4)$	1.614 (3)
$\text{Sr}—\text{O}(4')$	3.102 (3)	$\text{V}—\text{O}(5)$	2.199 (3)
$\text{Sr}—\text{O}(4'')$	2.544 (3)	$\text{V}—\text{O}(5'')$	1.681 (3)
$\text{Sr}—\text{O}(5'')$	2.540 (3)	$\sum s(\text{V}—\text{O})$	= 5.07
$\text{Sr}—\text{O}(6)$	2.677 (4)		
$\text{Sr}—\text{O}(6'')$	2.430 (4)		
$\sum s(\text{Sr}—\text{O})$	= 2.11		
$\text{P}—\text{O}(1')$	1.562 (3)	$\text{P}—\text{O}(1')$	1.561 (4)
$\text{P}—\text{O}(2)$	1.555 (3)	$\text{P}—\text{O}(2)$	1.560 (3)
$\text{P}—\text{O}(3'')$	1.548 (3)	$\text{P}—\text{O}(3'')$	1.550 (4)
$\text{P}—\text{O}(6)$	1.507 (3)	$\text{P}—\text{O}(6)$	1.506 (4)
$\sum s(\text{P}—\text{O})$	= 4.90	$\sum s(\text{P}—\text{O})$	= 4.88

Symmetry code: (i) $1 + x, 1.5 - y, -0.5 + z$; (ii) $x, 1.5 - y, -0.5 + z$; (iii) $1 + x, y, z$; (iv) $2 - x, 1 - y, -z$; (v) $1 - x, 1 - y, 1 - z$; (vi) $1 - x, -0.5 + y, 0.5 - z$.

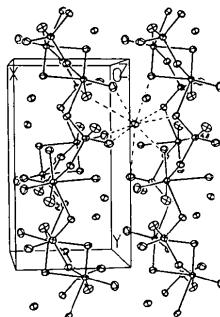
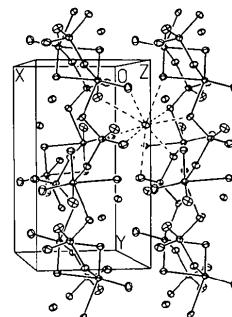


Fig. 1. Stereoscopic view of the $\text{Ba}(\text{VO}_2)\text{PO}_4$ structure in a direction approximately parallel to the c axis. The $\text{Ba}—\text{O}$ bonds are represented by dashed lines. Thermal ellipsoids are shown at the 60% probability level.

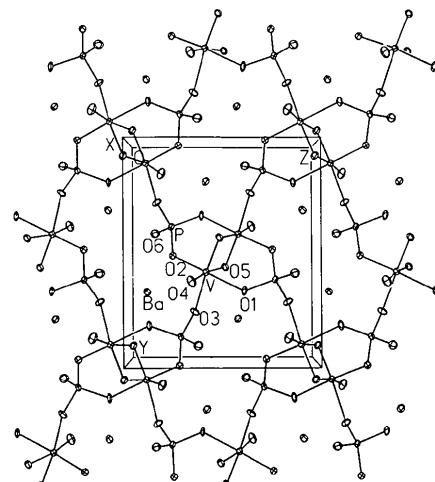


Fig. 2. View of the $\text{Ba}(\text{VO}_2)\text{PO}_4$ structure along the a axis. Thermal ellipsoids are shown at the 60% probability level.

ions are located above as well as below each window which align the windows so that straight tunnels are formed running along the *a* axis (see Fig. 2).

Two neighbouring VO₆ octahedra form an edge-sharing bioctahedron with a V···V distance of 2.928 (1) Å. Each distorted VO₆ octahedron consists of two very short, two medium and two long V—O bond distances with one of the O atoms, O(4), not being shared with P and coordinated to the Ba²⁺ ions only. The two very short V—O bonds are *cis* to each other and the bonds *trans* to them have long V—O distances. Atoms O(1) and O(2), which are *trans* to each other, have two medium-length V—O bond distances. Each PO₄ group has two O atoms that bridge the nonbonding V···V contact within a bioctahedron, one O atom being coordinated to a neighbouring bioctahedron, and one O atom to the Ba²⁺ ions only. The P tetrahedron is slightly distorted as shown by three long P—O distances of ~1.55 Å and a short one of 1.507 Å. Atom O(6), which is not shared with V, shows the shortest P—O bond. The Ba²⁺ ions are nine coordinated by O atoms from adjacent layers. The coordination number is determined on the basis of the maximum gap in the Ba—O distances ranked in increasing order.

The Sr phase is isostructural with Ba(VO₂)PO₄. It should be noted that the Pb analogue can also be obtained under similar reaction conditions. Preliminary work on a crystal of Pb(VO₂)PO₄ of reasonable quality showed that it was isostructural with the Ba compound. The indexed cell dimensions of the Pb compound are *a* = 5.505 (2), *b* = 9.913 (3), *c* = 8.511 (3) Å, β = 90.50 (3)° and *V* = 464.4 (3) Å. However, the Ca and Mg analogues have not been obtained under similar reaction conditions.

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Structure of KYF₄

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Abstract. Potassium yttrium tetrafluoride, KYF₄, *M*, = 204.0, trigonal, *P*3₁, *a* = 14.060 (10), *c* = 10.103 (10) Å, *V* = 1729 (5) Å³, *Z* = 18, *D*_x = 3.49 g cm⁻³, λ (Ag *K* α) = 0.5594 Å, μ = 87.93 cm⁻¹, *F*(000) = 753, room temperature, final *R* = 0.038 for 3045 independent reflections. KYF₄ is a fluorite-related superstructure. Cations are distributed on three layers perpendicular to the *c* axis. In each layer,

chains of YF₁₂ groups formed by two F pentagonal bipyramids surrounding the Y atoms alternate with chains of F edge-shared distorted cubes surrounding the K atoms.

Introduction. In an initial study (Le Fur, 1977; Aléonard, Le Fur, Pontonnier, Gorius & Roux, 1978), we have shown that the hexagonal lattices of the phases