

Octaèdres NbO₆

Nb—O(3) × 2	1,928 (4)	O(3)··O(2) × 2	2,79 (1)
Nb—O(4) × 2	2,000 (9)	O(3)··O(2) × 2	2,86 (1)
Nb—O(2) × 2	2,0099 (8)	O(4)··O(4)	2,77 (2)
O(3)··O(3)	2,78 (3)	O(4)··O(2) × 2	2,85 (1)
O(3)··O(4) × 2	2,79 (2)	O(4)··O(2) × 2	2,73 (2)
O(3)··O(4) × 2	3,92 (1)	O(2)··O(2)	4,016 (2)
O(3)—Nb—O(3)	92,1 (8)	O(4)—Nb—O(4)	87,5 (7)
O(4)—Nb—O(3) × 2	90,3 (5)	O(2)—Nb—O(4) × 2	90,7 (5)
O(4)—Nb—O(3) × 2	175,4 (4)	O(2)—Nb—O(4) × 2	85,7 (5)
O(2)—Nb—O(3) × 2	90,2 (5)	O(2)—Nb—O(2)	175,1 (9)
O(2)—Nb—O(3) × 2	93,2 (4)		

Polyèdres KO₁₂

K··O(4) × 2	2,84 (1)	K··O(2)	3,19 (2)
K··O(3) × 2	2,85 (1)	K··O(2)	3,24 (2)
K··O(4) × 2	2,93 (1)	K··O(4) × 2	3,25 (1)
K··O(1)	2,990 (5)	K··O(4) × 2	3,48 (1)
K··O(2)	3,08 (2)		

Programme(s) pour la solution de la structure: *MULTAN80* (Main *et al.*, 1980). Programme(s) pour l'affinement de la structure: *ORXFLS* (Busing, 1971) modifié par P. Laruelle. Les dessins ont été obtenus à l'aide de *MOLVIEW* (Cense, 1990). Programme(s) pour la préparation du manuscrit: *ORFFE* (Busing, Martin & Levy, 1964).

Les auteurs remercient M. A. Mazurier (Laboratoire de Physique de la Faculté de Pharmacie de Paris) qui a réalisé l'enregistrement des intensités diffractées aux rayons X.

Les listes des facteurs de structure et des facteurs d'agitation thermique anisotrope ont été déposées au dépôt d'archives de l'UICr (Référence: DU1095). On peut en obtenir des copies en s'adressant à: The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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Acta Cryst. (1995). **C51**, 796–798

CaV₂O(PO₄)₂, Isotypic with the Cd Phase

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(Received 16 September 1994; accepted 14 October 1994)

Abstract

The new V^{III} monophosphate, calcium divanadium oxodiphosphate, CaV₂O(PO₄)₂, is isotypic with the Cd phase. Its structure consists of [V₂PO₇]_∞ layers, built up from [VO₄]_∞ rutile chains and [VPO₈]_∞ chains, interconnected through PO₄ tetrahedra. This framework delimits tunnels running along ⟨011⟩, at the intersection of which the calcium ions are located in a '6 + 1' coordination mode.

Comment

Investigations of vanadium(III) phosphates performed in the last ten years have shown that it is possible to generate original mixed frameworks with [VO₄]_∞ rutile chains. Nevertheless, the formation of such infinite chains remains rare since only two examples, VPO₄ (Kinomura, Muto & Koizumi, 1982) and CdV₂O(PO₄)₂ (Boudin, Grandin, Borel, Leclaire & Raveau, 1994), are known as yet. Calcium, owing to the similarity of its crystal chemistry with that of cadmium, should be considered for the generation of such structures. Two compounds, CaV₂P₂O₁₀ (Lii, Chen, Kang & Wang, 1992) and CaV₂(P₂O₇)₂ (Hwu & Willis, 1991), which are isotypic with the Cd phases CdV₂P₂O₁₀ (Leclaire, Chardon, Grandin, Borel & Raveau, 1993) and CdV₂(P₂O₇)₂ (Boudin, Grandin, Leclaire, Borel & Raveau, 1994), respectively, have already been synthesized, whereas Ca₂V(PO₄)(P₂O₇) (Lii, Wen, Su & Chueh, 1992) does not exhibit structural relationships with the Cd phase. We have investigated the system Ca–V^{III}–P–O, and we report here the synthesis and crystal structure of a new V^{III} monophosphate, CaV₂O(PO₄)₂, isotypic with the cadmium phase.

The results (Table 1) clearly show that CaV₂O(PO₄)₂ is isotypic with CdV₂O(PO₄)₂. Thus, its structure is built up from [V₂P(1)O₇]_∞ infinite waving layers parallel to (100) in which one [V(2)O₄]_∞ rutile chain of edge-sharing octahedra running along *b* alternates with two [V(1)PO₈]_∞ chains of corner-sharing V(1)O₆ octahedra and P(1)O₄ tetrahedra (Fig. 1). Along *a*, the [V₂PO₇]_∞ layers are connected through P(2)O₄ tetrahedra in such

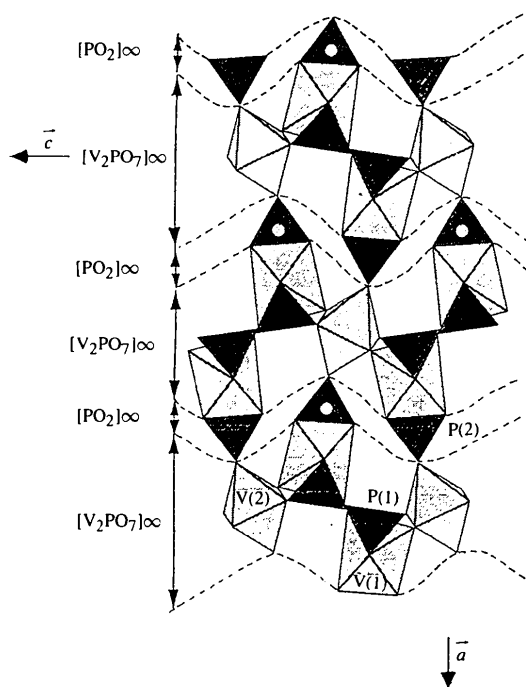


Fig. 1. Projection of the structure of $\text{CaV}_2\text{O}(\text{PO}_4)_2$ along b showing the stacking of the $[\text{V}_2\text{PO}_7]_\infty$ and $[\text{PO}_2]_\infty$ layers.

a way that one $\text{P}(2)\text{O}_4$ tetrahedron shares one edge with one $\text{V}(2)\text{O}_6$ octahedron of one layer and two apices with two $\text{V}(2)\text{O}_6$ octahedra of the next layer.

In this framework, as in the cadmium vanadium phosphate, the VO_6 octahedra are not strongly distorted; this can be seen for the $\text{V}(1)$ octahedra which form the $[\text{VPO}_8]_\infty$ chains and exhibit $\text{V}(1)\text{—O}$ distances ranging from 1.898 (4) to 2.164 (4) Å (Table 2) compared with 1.90–2.17 Å for the Cd phase (Boudin, Grandin, Borel, Leclaire & Raveau, 1994). Note, however, that the $\text{V}(2)$ octahedra of the rutile chains, in spite of their identical ranges of bond lengths in the Ca and Cd phases [2.008 (2)–2.071 (3) Å in the Ca phase and 1.98–2.07 Å in Cd], show different behaviour. In the Ca compound, one observes four short bonds (average 2.011 Å) and two longer ones [2.071 (3) Å], while in the Cd compound one observes two short bonds (1.98 Å) and four longer ones (average 2.07 Å). The geometries of the PO_4 tetrahedra are very similar in both structures, *i.e.* the $\text{P}(1)$ tetrahedra of the $[\text{VPO}_8]_\infty$ chains are very regular with four P—O distances close to 1.54 Å, whereas the $\text{P}(2)$ tetrahedra that share one edge with VO_6 octahedra exhibit three longer P—O distances (1.53–1.54 Å) and a shorter one of 1.50 Å.

Like cadmium, calcium is located at the intersection of small tunnels running along the $\langle 011 \rangle$ directions. This cation, like cadmium, exhibits distorted octahedral coordination, with Ca—O distances ranging from 2.342 (3) to 2.519 (5) Å (Table 2), which are greater than

the Cd—O distances (2.28–2.46 Å), consistent with the larger size of calcium. Note, however, that calcium has a seventh neighbour at 2.911 (4) Å, whereas for cadmium the seventh oxygen neighbour is much further away (more than 3 Å). Taking into consideration this seventh neighbour leads to an electrostatic valence of 1.92 using the Brown & Altermatt (1985) curves, instead of 1.84 with six oxygen neighbours. This difference between calcium and cadmium is easily understood on the basis of the larger ionicity of calcium with respect to cadmium. In conclusion, $\text{CaV}_2\text{O}(\text{PO}_4)_2$ represents the third example presently known of a V^{III} monophosphate with rutile chains.

Experimental

A single crystal of $\text{CaV}_2\text{O}(\text{PO}_4)_2$ was extracted from a mixture of composition ' $\text{CaV}_2\text{P}_2\text{O}_8$ '. The latter was prepared by first heating CaCO_3 , V_2O_5 and $\text{H}(\text{NH}_4)_2\text{PO}_4$ at 1073 K in air for 2 h and then adding to the intermediate mixture the appropriate amount of metallic V. The final mixture was placed in an alumina crucible, heated in an evacuated silica ampoule at 1453 K for 24 h, slowly cooled at a rate of 4 K h^{-1} to 1253 K and finally quenched to room temperature. The composition of the black lamellar single crystal was confirmed by microprobe analysis.

Crystal data

$\text{CaV}_2\text{O}(\text{PO}_4)_2$
 $M_r = 347.9$
 Orthorhombic
Pnma
 $a = 14.192(1) \text{ \AA}$
 $b = 6.424(1) \text{ \AA}$
 $c = 7.317(1) \text{ \AA}$
 $V = 667.1(1) \text{ \AA}^3$
 $Z = 4$
 $D_x = 3.46 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 18\text{--}22^\circ$
 $\mu = 3.968 \text{ mm}^{-1}$
 $T = 294 \text{ K}$
 Lamellar
 $0.077 \times 0.051 \times 0.039 \text{ mm}$
 Black

Data collection

Enraf–Nonius CAD-4 diffractometer
 Bisect scans
 Absorption correction: none
 3133 measured reflections
 3133 independent reflections
 914 observed reflections
 $[I > 3\sigma(I)]$

$\theta_{\text{max}} = 45^\circ$
 $h = 0 \rightarrow 28$
 $k = 0 \rightarrow 12$
 $l = 0 \rightarrow 14$
 3 standard reflections
 frequency: 50 min
 intensity decay: none

Refinement

Refinement on F
 $R = 0.030$
 $wR = 0.032$
 $S = 0.999$
 914 reflections
 79 parameters
 $w = F \sin(\theta/\lambda)$

$(\Delta/\sigma)_{\text{max}} < 0.004$
 $\Delta\rho_{\text{max}} = 0.841 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.251 \text{ e \AA}^{-3}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	x	y	z	B _{eq}
Ca	0.21979 (7)	1/4	0.1149 (2)	0.70 (1)
V(1)	0.37954 (5)	3/4	0.1489 (1)	0.321 (9)
V(2)	0	1/2	0	0.404 (9)
P(1)	0.18974 (8)	3/4	0.1134 (2)	0.46 (2)
P(2)	0.43270 (8)	1/4	0.1366 (2)	0.36 (2)
O(1)	0.3662 (2)	0.4378 (4)	0.1278 (4)	0.65 (3)
O(2)	0.2632 (3)	3/4	-0.0424 (6)	0.77 (6)
O(3)	0.4929 (3)	3/4	0.0081 (7)	1.23 (6)
O(4)	0.2514 (3)	3/4	0.2875 (5)	0.59 (5)
O(5)	0.4442 (2)	3/4	0.3759 (5)	0.59 (5)
O(6)	-0.0186 (3)	1/4	0.1750 (5)	0.77 (6)
O(7)	0.1283 (2)	0.5533 (4)	0.1084 (4)	0.79 (4)

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

Table 2. Selected geometric parameters (Å, °)

Ca—O(7)	2.342 (3)	O(5 ⁱⁱ)—O(6)	2.430 (5)
Ca—O(7 ⁱ)	2.342 (3)	O(5 ⁱⁱ)—O(6 ^{vi})	3.276 (1)
Ca—O(1)	2.405 (3)	O(5 ⁱⁱ)—O(7 ^{vi})	2.905 (4)
Ca—O(1 ⁱ)	2.405 (3)	O(5 ⁱⁱ)—O(7)	2.784 (4)
Ca—O(4 ⁱⁱ)	2.430 (4)	V(2)—O(6)	2.071 (3)
Ca—O(2 ⁱⁱ)	2.519 (5)	O(6 ⁱ)—O(6 ^{vi})	4.142 (7)
Ca—O(5 ⁱⁱ)	2.911 (4)	O(6 ⁱ)—O(7 ^{vi})	2.884 (5)
V(1)—O(1)	2.020 (3)	O(6 ⁱ)—O(7)	2.895 (4)
O(1)—O(1 ^{iv})	4.011 (7)	V(2)—O(6 ^{vi})	2.071 (3)
O(1)—O(2)	2.777 (4)	O(6 ^{vi})—O(7 ^{vi})	2.895 (4)
O(1)—O(3)	2.832 (4)	O(6 ^{vi})—O(7)	2.884 (5)
O(1)—O(4)	2.836 (4)	V(2)—O(7 ^{vi})	2.015 (3)
O(1)—O(5)	2.922 (4)	O(7 ^{vi})—O(7)	4.031 (5)
V(1)—O(1 ^{iv})	2.020 (3)	V(2)—O(7)	2.015 (3)
O(1 ^{iv})—O(2)	2.777 (4)	P(1)—O(2)	1.545 (4)
O(1 ^{iv})—O(3)	2.832 (4)	O(2)—O(4)	2.420 (6)
O(1 ^{iv})—O(4)	2.836 (4)	O(2)—O(7)	2.545 (4)
O(1 ^{iv})—O(5)	2.922 (4)	O(2)—O(7 ^{iv})	2.545 (4)
V(1)—O(2)	2.164 (4)	P(1)—O(4)	1.545 (4)
O(2)—O(3)	3.281 (6)	O(4)—O(7)	2.523 (4)
O(2)—O(4)	2.420 (6)	O(4)—O(7 ^{iv})	2.523 (4)
O(2)—O(5)	3.995 (7)	P(1)—O(7)	1.536 (3)
V(1)—O(3)	1.911 (5)	O(7)—O(7 ^{iv})	2.527 (6)
O(3)—O(4)	3.992 (7)	P(1)—O(7 ^{iv})	1.536 (3)
O(3)—O(5)	2.779 (7)	P(2)—O(1)	1.533 (3)
V(1)—O(4)	2.083 (4)	O(1)—O(1 ⁱ)	2.413 (5)
O(4)—O(5)	2.811 (5)	O(1)—O(3 ^{vii})	2.537 (5)
V(1)—O(5)	1.898 (4)	O(1)—O(6 ^{viii})	2.491 (4)
V(2)—O(5 ^v)	2.008 (2)	P(2)—O(1 ⁱ)	1.533 (3)
O(5 ^v)—O(5 ⁱⁱ)	4.016 (5)	O(1 ⁱ)—O(3 ^{vii})	2.537 (5)
O(5 ^v)—O(6)	3.276 (1)	O(1 ⁱ)—O(6 ^{viii})	2.491 (4)
O(5 ^v)—O(6 ^{vi})	2.430 (5)	P(2)—O(3 ^{vii})	1.495 (5)
O(5 ^v)—O(7 ^{vi})	2.784 (4)	O(3 ^{vii})—O(6 ^{viii})	2.464 (7)
O(5 ^v)—O(7)	2.905 (4)	P(2)—O(6 ^{viii})	1.542 (4)
V(2)—O(5 ⁱⁱ)	2.008 (2)		
O(1 ^{iv})—V(1)—O(1)	166.2 (2)	O(7 ^{vi})—V(2)—O(5 ^v)	87.6 (1)
O(2)—V(1)—O(1)	83.1 (1)	O(7 ^{vi})—V(2)—O(5 ⁱⁱ)	92.4 (1)
O(2)—V(1)—O(1 ^{iv})	83.1 (1)	O(7 ^{vi})—V(2)—O(6)	89.8 (1)
O(3)—V(1)—O(1)	92.2 (1)	O(7 ^{vi})—V(2)—O(6 ^{vi})	90.2 (1)
O(3)—V(1)—O(1 ^{iv})	92.2 (1)	O(7 ^{vi})—V(2)—O(5 ^v)	92.4 (1)
O(3)—V(1)—O(2)	107.1 (2)	O(7 ^{vi})—V(2)—O(5 ⁱⁱ)	87.6 (1)
O(4)—V(1)—O(1)	87.5 (1)	O(7 ^{vi})—V(2)—O(6)	90.2 (1)
O(4)—V(1)—O(1 ^{iv})	87.5 (1)	O(7 ^{vi})—V(2)—O(6 ⁱ)	89.8 (1)
O(4)—V(1)—O(2)	69.4 (2)	O(7 ^{vi})—V(2)—O(7 ^{iv})	180.0
O(4)—V(1)—O(3)	176.5 (2)	O(4)—P(1)—O(2)	103.1 (2)
O(5)—V(1)—O(1)	96.4 (1)	O(7)—P(1)—O(2)	111.5 (1)
O(5)—V(1)—O(1 ^{iv})	96.4 (1)	O(7)—P(1)—O(4)	109.9 (2)
O(5)—V(1)—O(2)	159.2 (2)	O(7 ^{iv})—P(1)—O(2)	111.5 (1)
O(5)—V(1)—O(3)	93.7 (2)	O(7 ^{iv})—P(1)—O(4)	109.9 (2)
O(5)—V(1)—O(4)	89.8 (2)	O(7 ^{iv})—P(1)—O(7)	110.8 (2)
O(5 ⁱⁱ)—V(2)—O(5 ^v)	180.0	O(1 ⁱ)—P(2)—O(1)	103.9 (2)
O(6)—V(2)—O(5 ^v)	106.9 (1)	O(3 ^{vii})—P(2)—O(1)	113.9 (2)
O(6)—V(2)—O(5 ⁱⁱ)	73.1 (1)	O(3 ^{vii})—P(2)—O(1 ⁱ)	113.9 (2)
O(6 ^{vi})—V(2)—O(5 ^v)	73.1 (1)	O(6 ^{viii})—P(2)—O(1)	108.3 (2)
O(6 ^{vi})—V(2)—O(5 ⁱⁱ)	106.9 (1)	O(6 ^{viii})—P(2)—O(1 ⁱ)	108.3 (2)
O(6 ^{vi})—V(2)—O(6)	180.0	O(6 ^{viii})—P(2)—O(3 ^{vii})	108.5 (3)

Symmetry codes: (i) $x, \frac{1}{2} - y, z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$; (iv) $x, \frac{3}{2} - y, z$; (v) $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} - z$; (vi) $-x, 1 - y, -z$; (vii) $1 - x, 1 - y, -z$; (viii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$.

Data were collected with ω -4/3 θ scans of width $(1 + 0.35 \tan \theta)^\circ$ and with and a slit aperture of $(1 + \tan \theta)$ mm. The refinements in $Pn2_1a$ (other setting of $Pna2_1$) failed. Calculations were performed using a MicroVAXII computer with the SDP system (B. A. Frenz & Associates, Inc., 1982).

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1094). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 798–800

Hydroxylammonium Sulfate

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(Received 26 July 1994; accepted 18 November 1994)

Abstract

The structure of $(\text{NH}_3\text{OH})_2\text{SO}_4$ consists of sulfate and hydroxylammonium ions, which are connected by O—H...O and N—H...O hydrogen bonds. The bond distances fall within normal limits. All O atoms of the sulfate group are involved in two hydrogen bonds.