

A Vanadium(III) Monophosphate Built Up from Rutile Chains: $\text{CdV}_2\text{O}(\text{PO}_4)_2$

S. Boudin, A. Grandin, M. M. Borel, A. Leclaire, and B. Raveau

Laboratoire CRISMAT, Associé au CNRS, ISMRA/Université de Caen, Bd du Maréchal Juin 14050 Caen Cedex, France

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Single crystals of a new V(III) monophosphate $\text{CdV}_2\text{O}(\text{PO}_4)_2$ have been prepared and their structure has been determined by X-ray diffraction. The monophosphate crystallizes in the space group $Pnma$ with $a = 14.308(2)\text{Å}$, $b = 6.318(1)\text{Å}$, $c = 7.248(1)\text{Å}$. The tridimensional framework $[\text{V}_2\text{P}_2\text{O}_9]_\infty$ is built up from $[\text{VO}_2]_\infty$ rutile chains and $[\text{VPO}_8]_\infty$ chains of corner-sharing VO_6 octahedra and PO_4 tetrahedra that form $[\text{V}_2\text{PO}_7]_\infty$ infinite layers waving along (100). Two successive $[\text{V}_2\text{PO}_7]_\infty$ layers are connected along a through PO_4 tetrahedra. The latter share one edge with the VO_6 octahedra of one layer forming VPO_8 units, and the two opposite corners with two octahedra belonging to the rutile chain of the next layer. This framework delimits small tunnels running along b that are empty, and intersecting (011) tunnels where the cadmium ions are located with a distorted octahedral coordination. © 1994

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INTRODUCTION

A large number of vanadium phosphates have been discovered in recent years, with vanadium in various oxidation states. In all these phosphates, vanadium exhibits either a pyramidal or an octahedral coordination. In most of them, the VO_5 pyramids or VO_6 octahedra are isolated, i.e., linked to PO_4 tetrahedra only, or form units of two polyhedra. A number of vanadium phosphates exhibit $[\text{VO}_3]_\infty$ chains of corner-sharing VO_6 octahedra as in the orthorhombic form of $A(\text{VO})_2(\text{PO}_4)_2$ with $A = \text{Ca}, \text{Cd}$ (1, 2), in $A\text{VPO}_5$, A being Li (3), Na (4), K (5), Rb , Cs (6), and in $\text{K}(\text{VO})_3(\text{P}_2\text{O}_7)_2$ (7). On the contrary, the formation of infinite chains of edge-sharing octahedra is very rare in phosphates, the only example being VPO_4 (8).

Recent investigations of the system Cd-V-P-O have shown its large potential. Five vanadium phosphates have indeed been isolated up to now, characterized either by isolated VO_6 octahedra as in the $\text{Cd}_5\text{V}_3\text{O}(\text{PO}_4)_6$ phosphate (9), by $[\text{VO}_3]_\infty$ chains of corner-sharing VO_6 octahedra as in the orthorhombic $\text{Cd}(\text{VO})_2(\text{PO}_4)_2$ (2) structure, by V_4O_{20} octahedral units as in the monoclinic $\text{Cd}(\text{VO})_2(\text{PO}_4)_2$ (10), by V_2O_{10} units as in $\text{Cd}_3\text{V}_4(\text{PO}_4)_6$ (11), or by tetrahedra as in Cd_2VPO_7 (12). We report here on the structure of a

new V(III) monophosphate of this system $\text{CdV}_2\text{O}(\text{PO}_4)_2$ built up from $[\text{VO}_2]_\infty$ rutile chains and characterized by the presence of VPO_8 units made of one VO_6 octahedron and one PO_4 tetrahedron sharing one edge.

CRYSTAL GROWTH

During the study of the pseudoternary system $\text{V}_2\text{O}_3\text{-P}_2\text{O}_5\text{-CdO}$, black lamellar single crystals were obtained for the nominal $\text{CdV}_2\text{P}_2\text{O}_9$ composition from a mixture where $\text{Cd}_3\text{V}_4(\text{PO}_4)_6$ (11) was the major product. The crystal growth was performed in two steps. First, a mixture of CdO , $\text{H}(\text{NH}_4)_2\text{PO}_4$, and V_2O_5 with the molar ratio 10:20:6 was heated to 650 K in order to eliminate NH_3 and H_2O .

In a second step, the resulting finely ground powder mixed with an appropriate amount of vanadium was introduced in an alumina tube and sealed in an evacuated silica ampoule. This sample was heated to 1223 K for 24 hr, slowly cooled at the rate of 1 K hr^{-1} to 1123 K, and furnace cooled to room temperature.

The composition of this phase, deduced from the structural determination $\text{CdV}_2\text{O}(\text{PO}_4)_2$, was confirmed by microprobe analysis.

Subsequent attempts to prepare a pure phase were unsuccessful. Only the monoclinic monophosphate $\text{Cd}(\text{VO})_2(\text{PO}_4)_2$ (10) was obtained.

STRUCTURE DETERMINATION

A black crystal of $0.058 \times 0.019 \times 0.013\text{ mm}$ was selected for the structure determination. It was the greatest size of the single crystals with good diffraction patterns. The cell parameters reported in Table 1 were determined and refined by diffractometer techniques at 294 K, with a least-squares refinement based upon 25 reflections with $18 < \theta < 22^\circ$. The systematic absences $k + l = 2n + 1$ for $0kl$ and $h = 2n + 1$ for $hk0$ are consistent with the space groups $Pnma$ and $Pn2_1a$ (other setting of $Pna2_1$). The Harker peaks present in the Patterson function are characteristic of the centrosymmetric space group $Pnma$. The data were col-

TABLE 1
Summary of Crystal Data Intensity, Measurements, and
Structure Refinement Parameters for CdV₂O(PO₄)₂

Crystal data	
Space group	<i>Pnma</i>
Cell dimensions (Å)	<i>a</i> = 14.308(2) <i>b</i> = 6.318(1) <i>c</i> = 7.248(1)
Volume	655.2(2)
<i>Z</i>	4
Intensity measurements	
λ (MoK α) (Å)	0.71069
Scan mode	ω -2 θ
Scan width (°)	1 + 0.35 tan θ
Slit aperture (mm)	1.10 + tan θ
max θ (°)	45
Standard reflections	3 measured every 3000 s
Measured reflections	1168
Reflections with $I > 2.5\sigma$	412
μ (mm ⁻¹)	6.43
Structure solution and refinement	
Parameters refined	40
Agreement factors	$R = 0.038$ $R_w = 0.038$
Weighting scheme	$w = F(\sin \theta/\lambda)$
Δ/σ max	<0.004

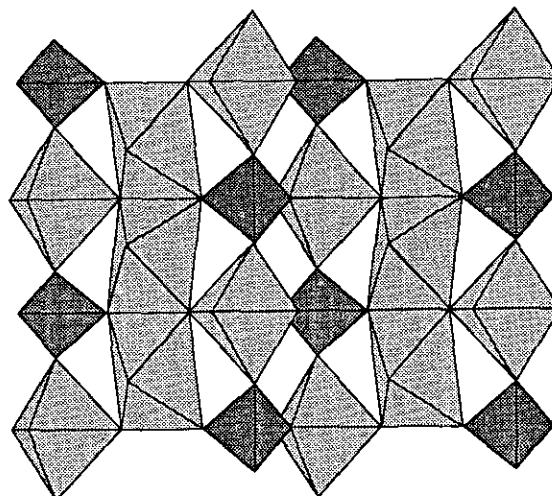


FIG. 1. Projection of the structure along *a*.

lected on a CAD-4 Enraf-Nonius automatic diffractometer with the measurement parameters reported in Table 1. The reflections were corrected for Lorentz and polarization. No absorption corrections were performed.

The structure was solved with the heavy atom method. The refinement of the atomic coordinates and the aniso-

tropic thermal factor for the Cd ions led to $R = 0.038$ and $R_w = 0.038$, and to the atomic parameters shown in Table 2. Owing to the limited number of observed reflections, it was not possible to refine the anisotropic thermal factor for other atoms.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The projection of half a cell of the structure along *a* (Fig. 1) shows that the [V₂P₂O₉]_∞ framework is characterized by two sorts of chains of polyhedra: [VO₂]_∞ chains of edge-sharing VO₆ octahedra running along *b*, similar to rutile

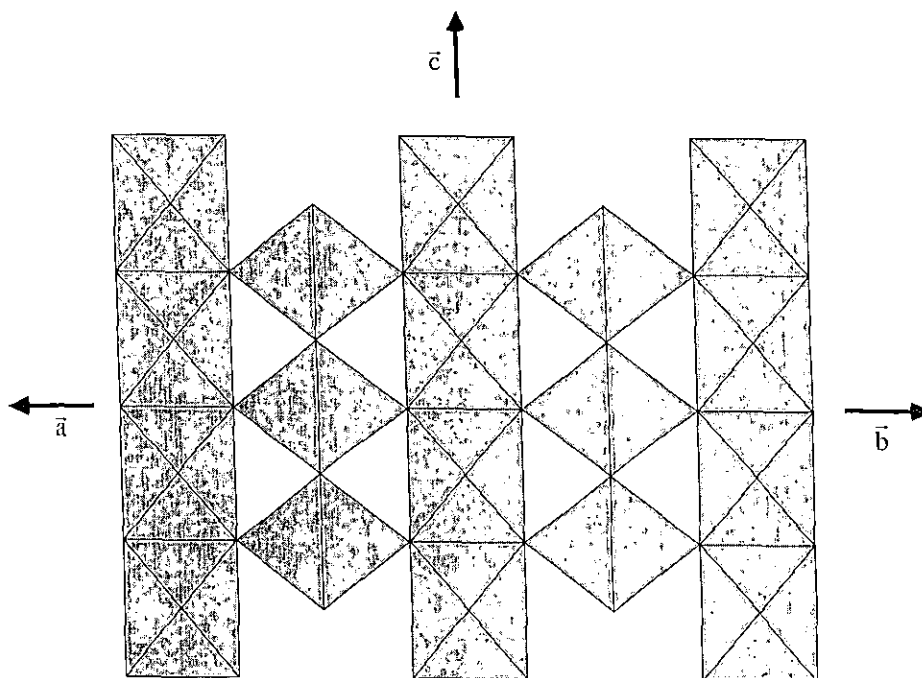


FIG. 2. The (011) plane in the rutile structure.

TABLE 2
Positional and Thermal Parameters with Their
Standard Deviations

Atom	x	y	z	B_{eq} (\AA^2)
Cd	0.22096(9)	0.25	0.1207(2)	0.74(2)
V(1)	0.3783(2)	0.75	0.1488(4)	0.34(4)*
V(2)	0.0	0.5	0.0	0.29(4)*
P(1)	0.1926(3)	0.75	0.1101(7)	0.43(7)*
P(2)	0.4309(3)	0.25	0.1317(7)	0.34(6)*
O(1)	0.3643(5)	0.439(1)	0.120(1)	0.6(1)*
O(2)	0.2636(8)	0.75	-0.047(2)	0.8(2)*
O(3)	0.496(1)	0.75	0.017(2)	0.9(2)*
O(4)	0.2531(8)	0.75	0.285(2)	0.4(2)*
O(5)	0.4480(7)	0.75	0.371(2)	0.5(2)*
O(6)	-0.0215(8)	0.25	0.180(2)	0.7(2)*
O(7)	0.1316(5)	0.549(1)	0.105(1)	0.6(1)*

Note. Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = 4/3 \sum_i \sum_j a_i \cdot a_j \cdot \beta_{ij}$.

and $[\text{VPO}_8]_\infty$ chains of corner-sharing VO_6 octahedra and PO_4 tetrahedra running also along that direction, already encountered in several monophosphates (1-5, 11). Along \mathbf{c} , the V(2) octahedra of the rutile chains share their corners with the V(1) octahedra and with the P(2) tetrahedra of the $[\text{VPO}_8]_\infty$ chains (Fig. 1) in a way very similar to that observed for the pure rutile structure (Fig. 2), so that the oxygens shared by one $[\text{VO}_2]_\infty$ chain and one $[\text{VPO}_8]_\infty$ chain are triply bonded. The $[\text{V}_2\text{P}_2\text{O}_9]_\infty$ framework can be described from $[\text{V}_2\text{PO}_7]_\infty$ layers parallel to (100), in which one rutile $[\text{VO}_2]_\infty$ chain alternates with two $[\text{VPO}_8]_\infty$ chains along \mathbf{c} (Fig. 1). Two successive $[\text{VPO}_8]_\infty$ chains share the corner of their polyhedra in such a way that the V(1)

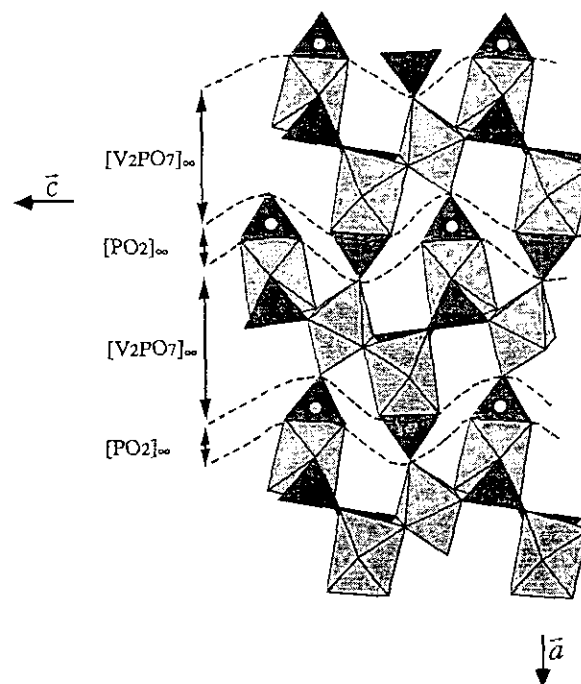


FIG. 3. Projection of the structure along \mathbf{b} .

octahedra of one chain can be linked to the P(2) tetrahedron of the adjacent chain. Note also that the two $[\text{VPO}_8]_\infty$ chains running between the rutile chains are not located at the same level as the basal plane of V(2) octahedra along \mathbf{a} : one of these two chains is located above the basal plane, whereas the second one runs below.

From the above description it appears that the $[\text{V}_2\text{PO}_7]_\infty$ layers are waving around the (100) plane. This is illustrated by the projection of the structure along \mathbf{b} (Fig. 3)

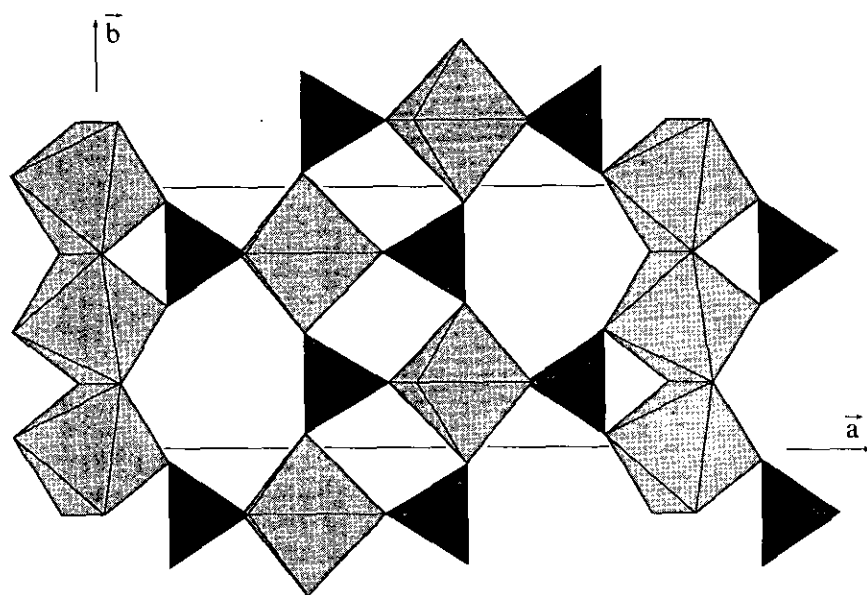


FIG. 4. Projection of half-cell along \mathbf{c} .

which shows that the [V₂PO₇]_∞ framework can be described by the stacking, along **a**, of identical [V₂PO₇]_∞ layers connected through [PO₂]_∞ layers of P(1) tetrahedra. Two successive [V₂PO₇]_∞ layers are shifted with respect to each other, one being deduced from the other by a "n" plane. At the junction between two [V₂PO₇]_∞ layers, each P(1) tetrahedron of the [PO₂]_∞ layer (Fig. 3) shares one edge with a V(1) octahedron of a [VPO₈]_∞ chain of one layer and its two other apices with two V(2) octahedra of a [VO₂]_∞ rutile chain of the next layer as schematized in Fig. 4; one recognizes at this junction the unusual VPO₈

units in which one PO₄ tetrahedron shares one edge with one octahedron, previously observed for some vanadium phosphates such as K₆V₂P₄O₁₆ (13).

It is worth pointing out the particular connection of PO₄ tetrahedra with VO₆ octahedra. Each P(1) tetrahedron is linked to three VO₆ octahedra and shares indeed one edge with one VO₆ octahedron, whereas each P(2) tetrahedron is linked to five VO₆ octahedra and exhibits a triply bonded oxygen O(6). In spite of this particularity the geometry of the PO₄ tetrahedra (Table 3) remains practically regular. This shows the great ability of the VO₆ octahedra to ac-

TABLE 3
Distances (Å) and Angles (°) in the Polyhedra

V(1)	O(1)	O(1 ⁱⁱⁱ)	O(2)	O(3)	O(4)	O(5)
O(1)	1.99(1)	3.94(2)	2.73(1)	2.83(1)	2.80(1)	2.94(1)
O(1 ⁱⁱⁱ)	163.4(6)	1.99(1)	2.73(1)	2.83(1)	2.80(1)	2.94(1)
O(2)	81.7(3)	81.7(3)	2.17(2)	3.36(2)	2.42(2)	4.02(2)
O(3)	92.1(3)	92.1(3)	109.6(6)	1.94(2)	3.98(2)	2.66(2)
O(4)	87.8(3)	87.8(3)	69.8(5)	179.3(7)	2.05(1)	2.86(2)
O(5)	98.1(3)	98.1(3)	162.6(5)	87.8(7)	92.8(5)	1.90(1)
V(2)	O(5 ^v)	O(5 ⁱⁱⁱ)	O(6)	O(6 ^{vi})	O(7 ^{vi})	O(7)
O(5 ^v)	1.98(1)	3.96(2)	3.21(2)	2.47(2)	2.78(1)	2.92(1)
O(5 ⁱⁱⁱ)	180.0(0)	1.98(1)	2.47(2)	3.21(2)	2.92(1)	2.78(3)
O(6)	104.9(4)	75.1(4)	2.07(1)	4.14(2)	2.89(1)	2.94(1)
O(6 ^{vi})	75.1(4)	104.9(4)	180.0(0)	2.07(1)	2.94(1)	2.89(1)
O(7 ^{vi})	92.9(4)	87.1(4)	91.0(4)	89.0(4)	2.06(1)	4.11(2)
O(7)	87.1(4)	92.9(4)	89.0(4)	91.0(4)	180.0(0)	2.05(1)
P(1)	O(2)	O(4)	O(7)	O(7 ^{iv})		
O(2)	1.53(1)	2.42(2)	2.53(1)	2.53(1)		
O(4)	104.0(6)	1.54(1)	2.52(1)	2.52(1)		
O(7)	111.0(5)	109.8(5)	1.54(1)	1.54(1)		
O(7 ^{iv})	111.0(5)	109.8(3)	111.1(6)	1.54(1)		
P(2)	O(1)	O(1 ⁱ)	O(3 ^{vii})	O(6 ^{viii})		
O(1)	1.53(1)	2.38(2)	2.53(2)	2.49(1)		
O(1 ⁱ)	102.4(6)	1.53(1)	2.53(2)	2.49(1)		
O(3 ^{vii})	113.3(5)	113.3(5)	1.50(2)	2.47(2)		
O(6 ^{viii})	109.1(5)	109.1(5)	109.4(8)	1.53(4)		
	Cd-O(1)	2.37(1)				
	Cd-O(1 ⁱ)	2.37(1)				
	Cd-O(2 ⁱⁱ)	2.42(1)				
	Cd-O(4 ⁱⁱⁱ)	2.46(1)				
	Cd-O(7)	2.28(1)				
	Cd-O(7 ⁱ)	2.28(1)				
Symmetry codes						
i	x	-y + 1/2	z			
ii	-x + 1/2	y - 1/2	z + 1/2			
iii	-x + 1/2	y - 1/2	z - 1/2			
iv	x	-y + 3/2	z			
v	x - 1/2	-y + 3/2	-z + 1/2			
vi	-x	-y + 1	-z			
vii	-x + 1	-y + 1	-z			
viii	x + 1/2	-y + 1/2	-z + 1/2			

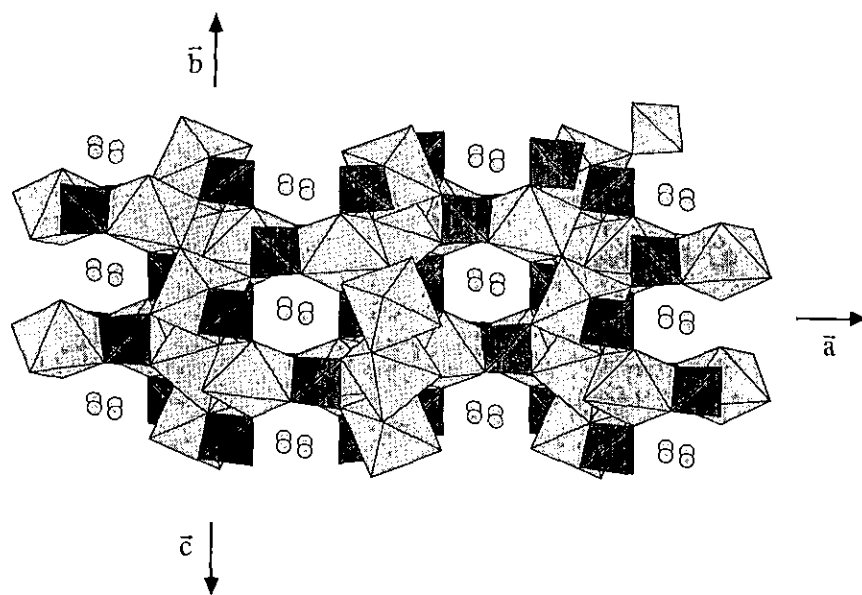


FIG. 5. Projection of the structure along (011) .

commodate the tetrahedral species. Although they are not dramatically distorted, the VO_6 octahedra show a great flexibility (Table 3) with V–O distances ranging from 1.90 to 2.17 Å. The V(1) octahedron of the VPO_8 unit is the most distorted; note that its shortest edge O(2)–O(4) of 2.42 Å corresponds to the edge it shares with the P(1) tetrahedron. The V(2) octahedron that belongs to the $[\text{VO}_2]_\infty$ rutile chain is less distorted with V–O distances ranging from 1.98 to 2.07 Å; note again that the shortest O–O distances of 2.47 Å, correspond to the edge shared by two V(2) octahedra.

The $[\text{V}_2\text{P}_2\text{O}_9]_\infty$ framework delimits two kinds of tunnels; the first kind, which run along **b**, (Fig. 3) are empty. Their section forms an elongated heptagonal window that is partially obstructed by cadmium. The second kind, which run along the (011) direction (Fig. 5), are occupied by cadmium. The Cd^{2+} cations that sit at the intersection of two (011) tunnels exhibit a distorted octahedral coordination with Cd–O distances ranging from 2.28 to 2.46 Å (Table 3).

CONCLUSION

This monophosphate is the second one after VPO_4 (10) that is characterized by trivalent vanadium-forming rutile

chains. Attempts will be made to synthesize bulk samples for the study of the magnetic and electrical properties of this phase.

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