

A V(III) Phosphate Built Up from Bioctahedral V_2O_{10} Units: $AgV_2(PO_4)P_2O_7$

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

Laboratoire CRISMAT, CNRS URA 1318 ISMRA, Université de Caen, Boulevard du Maréchal Juin, 14050 Caen Cedex, France

Received March 9, 1994; in revised form July 13, 1994; accepted July 21, 1994

Single crystals of a new V(III) phosphate $AgV_2(PO_4)(P_2O_7)$ have been isolated, and its structure was determined from X-ray diffraction data. This phase crystallizes in the space group $C2/c$ with $a = 11.546(1)$ Å, $b = 8.548(1)$ Å, $c = 8.779(1)$ Å, $\beta = 114.39(1)^\circ$, and $Z = 4$. The structure consists of monophosphate groups, diphosphate groups, and bioctahedral V_2O_{10} units of two edge-sharing octahedra. The $[V_2P_3O_{11}]_\infty$ framework results from the stacking along c of enantiomorphous $[V_2P_3O_{16}]_\infty$ layers. One $[V_2P_3O_{16}]_\infty$ layer can be described as built up either from $[V_2P_2O_{14}]_\infty$ chains of corner-sharing P_2O_7 and V_2O_{10} groups connected through monophosphate groups or from $[V_2PO_{12}]_\infty$ chains of corner-sharing V_2O_{10} and PO_4 units connected through diphosphate groups. This host lattice delimits cages where the silver ions are located with a distorted pentagonal bipyramidal coordination. This is to date the second V(III) phosphate involving V_2O_{10} units linked through PO_4 and P_2O_7 groups. © 1995 Academic Press, Inc.

INTRODUCTION

The crystal chemistry of V(III) phosphates has been extensively studied these past 10 years. In most of these compounds trivalent vanadium is present in the form of isolated VO_6 octahedra connected through single PO_4 tetrahedra like in the monophosphate $K_6V_2(PO_4)_4$ (1), in the diphosphates $AV_2(P_2O_7)$ with $A = Li, K, Rb, Cs$ (2–6) and $AV_2(P_2O_7)_2$ with $A = Ba, Sr, Cd$ (7–9), or in the polyphosphates $V(PO_3)_3$ and $Cs_3V_3P_{12}O_{36}$ (10–11). The tendency of VO_6 octahedra to share corners, edges, or faces in V(III) phosphates is rather rare. No compound with $V^{III}O_6$ corner-sharing octahedra has been isolated until now, to our knowledge, whereas only one diphosphate, $V_4(P_2O_7)_3$ (12), exhibits V_2O_9 bioctahedral units of face-sharing octahedra. The ability of V(III) octahedra to share edges is illustrated by the monophosphates VPO_4 (13), $AV_2O(PO_4)_2$ with $A = Cd, Ca$ (14, 15) that exhibit $[VO_2]_\infty$ rutile chains of edge-sharing octahedra by the monophosphates $Zn_3V_4(PO_4)_6$ (16) and $Cd_3V_4(PO_4)_6$ (17), and the polyphosphate $KV_4(PO_4)(P_2O_7)(P_4O_{13})$ (18) built up of V_2O_{10} bioctahedral units of edge-sharing octahedra.

Besides these structures, that of the monophosphate $K_{11}V_{15}O(PO_4)_{18}$ (19) which derives from the langbeinite is the most complicated since it forms “ V_3O ” clusters involving both V_2O_9 and V_2O_{10} bioctahedral units.

From the examination of these results, it appears clearly that the association of diphosphate groups with edge-sharing V(III) octahedra has rarely been observed to date. During the exploration of the Ag–V–W–P–O system, single crystals of a new phosphate of trivalent vanadium were isolated. The present paper deals with the crystal structure of this new phase, $AgV_2(PO_4)P_2O_7$, that is the second V(III) phosphate built up from monophosphate and diphosphate groups.

EXPERIMENTAL

Green crystals of $AgV_2P_3O_{11}$ were isolated as a minor product from a mixture of nominal composition $AgV_2WP_3O_{16}$. The growth of these crystals was performed in two steps. First, a mixture of $AgNO_3$, $H(NH_4)_2PO_4$, V_2O_5 , and WO_3 with the molar ratio 1:3:1:1 was heated to 653 K in order to eliminate CO_2 , NH_3 , NO_2 , NO , and H_2O . Second, the resulting finely ground product, placed in an alumina crucible was sealed in an evacuated silica ampoule. The mixture was then heated to 1223 K for 12 hr, cooled down to 873 K with a rate of 1 K/hr, and finally quenched to room temperature. Subsequent attempts to prepare a pure phase were unsuccessful.

A green crystal of $0.154 \times 0.154 \times 0.116$ mm was selected for the structure determination. The cell parameters reported in Table 1 were determined and refined by diffractometric techniques at 21°C with a least-squares refinement based upon 25 reflections with $18 < \theta < 22^\circ$. The systematic absences $h + k = 2n + 1$ for all the hkl , and $l = 2n + 1$ for $h0l$ are consistent with the space groups Cc and $C2/c$. The Harker peaks present in the Patterson function are characteristic of the centrosymmetric space group $C2/c$. The data were collected on an Enraf–Nonius CAD4 diffractometer with the conditions reported in Table 1. The reflections were corrected for

TABLE 1
Summary of Crystal Data Intensity, Measurements, and
Structure Refinement Parameters for $\text{AgV}_2(\text{PO}_4)(\text{P}_2\text{O}_7)$

Crystal data	
Space group	$C2/c$
Cell dimensions	$a = 11.546(1) \text{ \AA}$ $b = 8.548(1) \text{ \AA}$ $c = 8.779(1) \text{ \AA}$ $\beta = 114.39(1)^\circ$
Volume	$789.0(2) \text{ \AA}^3$
Z	4
$\rho_{\text{calc}} (\text{g cm}^{-3})$	4.03
Intensity measurements	
$\lambda (\text{MoK}\alpha)$	0.71073 \AA
Scan mode	$\omega - 2/3 \theta$
Scan width ($^\circ$)	$1.08 + 0.35 \tan \theta$
Slit aperture (mm)	$1.10 + \tan \theta$
Max (θ) ($^\circ$)	45
Standard reflections	3 measured every 3000 sec
Range	
h	$-23 \rightarrow 23$
k	$0 \rightarrow 17$
l	$0 \rightarrow 17$
Measured reflections	3529
Reflections with $I > 3 \sigma$	2483
$\mu (\text{mm}^{-1})$	5.35
Structure solution and refinement	
Parameters refined	84
Agreement factors	$R = 0.022, R_w = 0.024$
Weighting scheme	$w = F(\sin \theta/\lambda)$
Δ/σ max	< 0.004

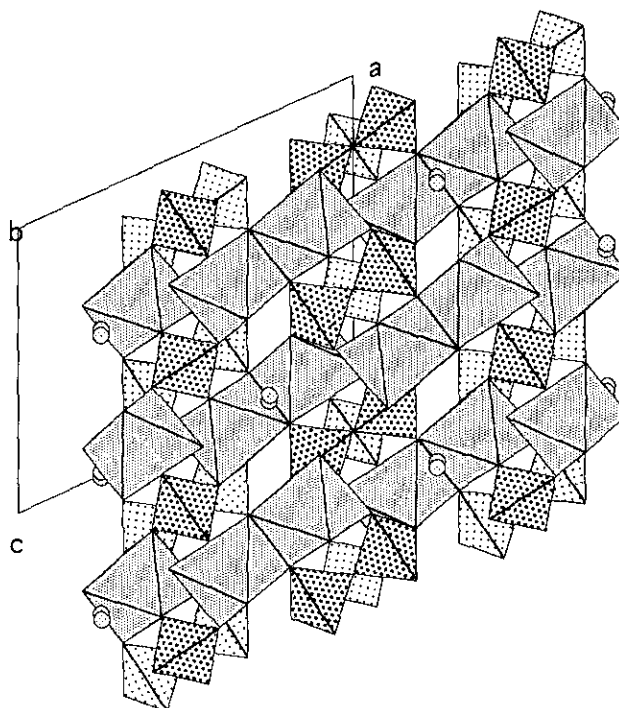


FIG. 1. Projection of the structure along b .

the Lorentz, polarization, absorption, and secondary extinction effects. The structure was solved by the heavy atom method. Initially, the Ag atoms were put on the $4c$ sites and the refinement increases its isotropic thermal factor to 3. At this stage the difference synthesis map shows strong electronic residues at $0.25 \ 0.22 \ 0.$, which allowed us to think that the four Ag atoms of the cell are spread randomly over eight positions. All these positions cannot be fully occupied at the same time because two positions related by a symmetry center are distant by only 0.33 \AA . The atomic coordinates and the anisotropic displacement factors were refined by a full matrix least-squares method which led to $R = 0.022$ and $R_w = 0.024$ and to the atomic coordinates listed in Table 2. All the calculations were performed on a micro-VAX II computer with the SDP system (20).

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

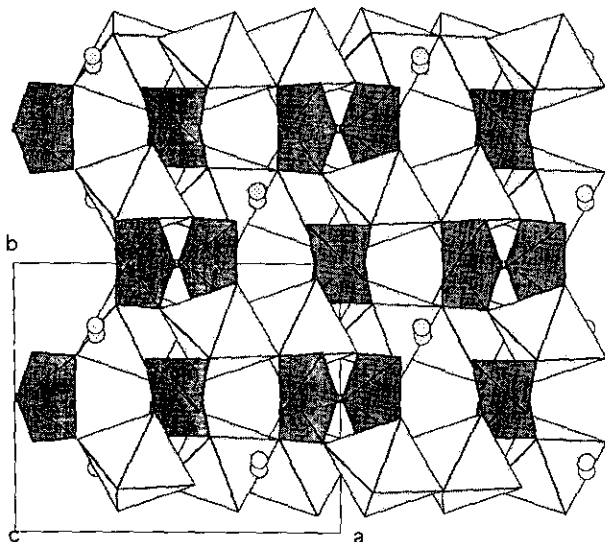
The projection of the structure along b (Fig. 1) shows that the $[\text{V}_2\text{P}_3\text{O}_{11}]_\infty$ framework consists of bioctahedral V_2O_{10} units, built up from two edge-sharing octahedra, connected through P_2O_7 diphosphate and PO_4 monophosphate groups.

In fact, the projection of the structure along c (Fig. 2) shows that it can be described as the stacking along b of pure octahedral layers and pure tetrahedral layers alternatively. In each of these (010) layers the V_2O_{10} units on one side and the PO_4 and P_2O_7 groups on the other side are isolated.

This structure is better described as the stacking along c of $[\text{V}_2\text{P}_3\text{O}_{16}]_\infty$ layers parallel to (001), two successive layers being enantiomorphic with respect to each other. The projection of half a cell of the structure along c includes one of these two enantiomorphic $[\text{V}_2\text{P}_3\text{O}_{16}]_\infty$ layers (Fig. 3). This layer consists of $[\text{V}_2\text{P}_2\text{O}_{14}]_\infty$ chains run-

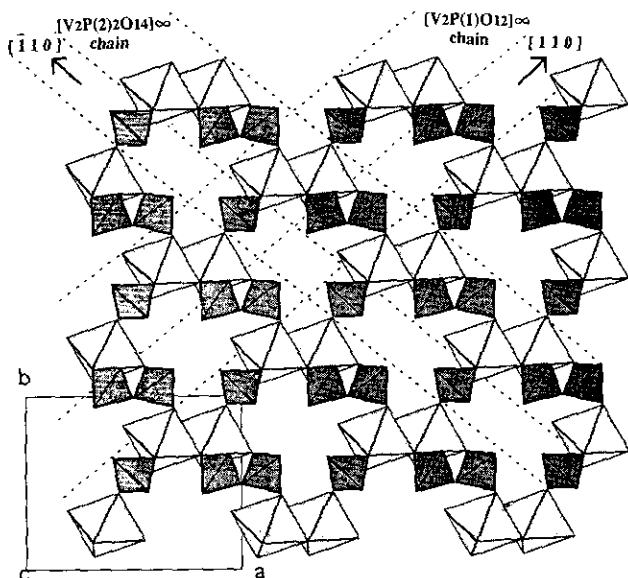
TABLE 2
Atomic Coordinates and Thermal Parameters and Their Estimated
Standard Deviations

Atom	x	y	z	$B_{\text{eq}} (\text{A}^2)$	Site	Occupancy
Ag	0.24953(4)	0.23351(5)	0.00917(4)	1.890(4)	8f	0.5
V	0.37502(1)	0.26201(2)	0.45937(2)	0.351(2)	8f	1.0
P(1)	0.5	0.45819(5)	0.25	0.354(4)	4e	1.0
P(2)	0.11174(2)	0.43723(3)	0.21437(3)	0.351(3)	8f	1.0
O(1)	0.39983(7)	0.3524(1)	0.2726(1)	0.61(1)	8f	1.0
O(2)	0.42887(9)	0.4448(1)	0.5941(1)	0.98(1)	8f	1.0
O(3)	0.55375(8)	0.1706(1)	0.5652(1)	0.68(1)	8f	1.0
O(4)	0.31348(7)	0.0714(1)	0.3104(1)	0.65(1)	8f	1.0
O(5)	0.18852(7)	0.3434(1)	0.3751(1)	0.54(1)	8f	1.0
O(6)	0.	0.5151(1)	0.25	0.57(1)	4e	1.0

FIG. 2. Projection of the structure along c .

ning along the $[1\bar{1}0]$ direction and built up from V_2O_{10} biotetrahedral units sharing their corners with P_2O_7 groups; laterally, these chains are interconnected through monophosphate groups. Another way to describe this layer is to consider the $[\text{V}_2\text{PO}_{12}]_\infty$ chains running along $[110]$ that are built up of corner-sharing V_2O_{10} and monophosphate groups; in that case, the $[\text{V}_2\text{PO}_{12}]_\infty$ chains are interconnected through disphosphate groups (Fig. 3).

Note that the symmetry of the structure results in the $[\text{V}_2\text{P}_2\text{O}_{14}]_\infty$ chains in two successive enantiomorphic layers being turned 106° with respect to each other.

FIG. 3. Projection of half a cell along c .TABLE 3
Main Distances (\AA) and Angles ($^\circ$) in the Polyhedra

V	O(1)	O(2)	O(3)	O(4)	O(5)	O(5')
O(1)	1.938(1)	2.814(1)	2.898(1)	2.673(1)	2.929(1)	4.001(1)
O(2)	94.2(1)	1.903(1)	2.818(2)	3.928(1)	2.783(1)	2.878(1)
O(3)	93.6(1)	91.26(1)	2.037(1)	2.880(1)	4.115(1)	3.054(1)
O(4)	84.8(1)	178.2(1)	90.3(1)	2.026(1)	2.913(1)	2.865(1)
O(5)	93.3(1)	88.3(1)	173.0(1)	90.2(1)	2.086(1)	2.608(2)
O(5')	168.5(1)	92.3(1)	95.6(1)	88.4(1)	77.4(1)	2.084(1)
P(1)	O(1)	O(1 ⁱⁱ)	O(2 ⁱⁱⁱ)	O(2 ^{iv})		
O(1)	1.544(1)	2.503(1)	2.525(1)	2.451(1)		
O(1 ⁱⁱ)	108.3(1)	1.544(1)	2.451(1)	2.525(1)		
O(2 ⁱⁱⁱ)	111.0(1)	106.3(1)	1.519(1)	2.545(1)		
O(2 ^{iv})	106.3(1)	111.0(1)	113.8(1)	1.519(1)		
P(2)	O(3 ^v)	O(4 ^{vi})	O(5)	O(6)		
O(3 ^v)	1.513(1)	2.537(1)	2.518(1)	2.524(1)		
O(4 ^{vi})	114.5(1)	1.504(1)	2.533(1)	2.468(1)		
O(5)	110.8(1)	112.37(1)	1.545(1)	2.475(1)		
O(6)	108.6(1)	105.6(1)	104.1(1)	1.593(1)		
Ag-O(1)	= 2.465(2)		Ag-O(3 ^v)	= 2.635(2)		
Ag-O(1 ⁱⁱ)	= 2.472(2)		Ag-O(4)	= 2.801(2)		
Ag-O(2 ⁱⁱⁱ)	= 3.100(2)		Ag-O(4 ^{vi})	= 3.081(2)		
Ag-O(3 ⁱⁱ)	= 2.664(2)					
P(2)-P(2)	= 2.895(1) \AA		P(2)-O(6) - P(2)	= 130.61(8) $^\circ$		

Note. Symmetry codes: (i) $1/2 - x, 1/2 - y, 1 - z$; (ii) $1 - x, y, 1/2 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $x, 1 - y, z - 1/2$; (v) $x - 1/2, 1/2 - y, z - 1/2$; (vi) $1/2 - x, 1/2 + y, 1/2 - z$; (vii) $1/2 - x, 1/2 - y, -z$; and (viii) $1/2 - x, y - 1/2, 1/2 - z$.

Each $[\text{V}_2\text{P}_3\text{O}_{16}]_\infty$ layer shares the corners of its PO_4 and P_2O_7 groups with those of the V_2O_{10} units of the enantiomorphic layer, with the result that each V_2O_{10} unit is linked to four diphosphate groups (Fig. 1): two apical oxygens are shared with two P_2O_7 groups, and four oxygens of the basal plane are shared with two P_2O_7 groups forming two triply bonded oxygen atoms (O(5) and O(5')). The remaining four apices of each V_2O_{10} unit are shared with monophosphate groups. The geometry of the VO_6 octahedra is rather close to that observed in V(III) phosphates characterized by V_2O_{10} units. One indeed observes (Table 3) two shorter V-O distances corresponding to the oxygen shared with the P(1) monophosphate groups (1.939–1.903 \AA), two intermediate distances corresponding to the oxygens shared between one P_2O_7 group (P(2)) and one VO_6 octahedron (2.026–2.037 \AA), and two longer V-O distances, characteristic of the triply bonded oxygen, between one P_2O_7 group and two VO_6 octahedra (2.084–2.086 \AA). The comparison of the average V-O, O-O, and V-V distances (Table 4), with other V(III) phosphates built up from biotetrahedral units V_2O_{10} shows that the size of these units does not vary significantly as well as the V-V distances (Table 4).

The P(1) O_4 tetrahedron exhibits an almost regular "O₄" tetrahedral geometry (Table 3) and is characterized

TABLE 4
The V-O, O-O, and V-V Average Distances in V_2O_{10} Units

MVPO	V_2O_{10} unit	V-O	O-O	V-V
$AgV_2P_3O_{11}$	VV	2.012	2.800	3.254
$Cd_3V_4(PO_4)_6$	VV	2.047	2.800	3.201
$Zn_3V_4(PO_4)_6$	V(1)V(1)	2.022	2.749	3.052
	V(2)V(2)	2.012	2.744	3.216
$KV_4(PO_4)(P_2O_7)(P_4O_{13})$	V(1)V(2)	1.996	2.820 V(1) 2.836 V(2)	3.199
	V(3)V(3)	2.009	2.842	3.210
	V(4)V(4)	2.003	2.827	3.244

by four very close P-O distances ranging from 1.519 to 1.544 Å.

The P(2) tetrahedron of the P_2O_7 unit exhibits one longer bond P(2)-O₍₆₎ of 1.593 Å, characteristic of the P-O-P bridging bond, an intermediate bond 1.545 Å corresponding to the O(5) triply bonded oxygen atom and two shorter distances (1.504-1.513 Å) characteristic of the P-O-V distances, close to those encountered in regular PO_4 tetrahedron.

CONCLUDING REMARKS

This study confirms the ability of V(III) to form phosphates with V_2O_{10} bioctahedral units. This is the second phosphate involving V_2O_{10} units and diphosphate groups simultaneously that has been obtained as yet besides the complicated phosphate $KV_4(PO_4)(P_2O_7)(P_4O_{13})$. Nevertheless, the difficulty in synthesizing a pure phase must be emphasized. Investigations are in progress in order to stabilize such a phase and to study its magnetic properties.

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