The Original Structure of $Zn_3V_4(PO_4)_6$ Involving Bioctahedral V_2O_{10} Units and ZnO_5 Trigonal Bipyramids

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A new monophosphate of trivalent vanadium and zinc $Zn_3V_4(PO_4)_6$ was isolated and its structure has been determined from a single crystal X-ray diffraction study. It crystallizes in the space group $P\bar{1}$ with $a = 6.349(2)$ Å, $b = 7.869(1)$ Å, $c = 9.324(2)$ Å, $\alpha = 105.32(1)°$, $\beta = 108.66(2)°$, and $\gamma = 101.23(2)°$. This tridimensional framework consists of bioctahedral V_2O_{10} units of two edge-sharing octahedra, monophosphate groups, distorted ZnO_6 octahedra, and distorted ZnO_5 trigonal bipyramids. In fact, the $[V_4P_6O_{24}]_\infty$ framework can be described as a stacking along b of $[V_4P_4O_{24}]_\infty$ layers parallel to the (a, c) plane, interconnected through layers of PO_4 tetrahedra. The $[V_4P_4O_{24}]_\infty$ layers are themselves built up from two kinds of $[V_2P_2O_{14}]_\infty$ ribbons running along a; the latter are obtained by the assemblage of two $[VPO_8]_\infty$ single chains sharing the edges of their octahedra in two different ways. The ZnO_5 bipyramids share two edges with two different V_2O_{10} units, whereas the ZnO_6 octahedra share their apices with the VO_6 octahedra, the PO_4 tetrahedra, and the ZnO_5 bipyramids. A remarkable feature of this structure deals with the presence of numerous triply bonded oxygen atoms. © 1995 Academic Press, Inc.

INTRODUCTION

The recent investigations of the system Cd–V–P–O have shown the great ability of cadmium to form vanadophosphates with original structures characterized by different vanadium valences. One V(V) monophosphate Cd_2VPO_7 (1) which involves VO_4 tetrahedra was synthesized. Two vanadium (IV) monophosphates Cd-$(VO)_2(PO_4)_2$ are known; one form (2) with the monoclinic symmetry consists of V_4O_{20} octahedra units, whereas the second form (3), which is orthorhombic, is built up from $[VO_3]_\infty$ octahedral chains. One mixed valent V(III)–V(IV) monophosphate $Cd_5V_3O(PO_4)_6$ (4) was obtained which exhibits isolated VO_6 octahedra and VO5 pyramids. Besides these compounds, three V(III) phosphates were isolated; two of them are monophosphates, $Cd_3V_4(PO_4)_6$ (5) and $CdV_2O(PO_4)_2$ (6), characterized by octahedral units V_2O_{10} and rutile chains $[VO_4]_\infty$, respectively, whereas the third one, $CdV_2(P_2O_7)_2$ (7), is a diphosphate involving isolated VO_6 octahedra.

Zinc, owing to its d^{10} electronic configuration similar to that of cadmium, is susceptible to generate, as this cation, new vanadophosphates. Nevertheless, its significantly smaller size suggests that it should lead to different original structures. This is the case of the V(V) monophosphate $Zn_3(V_{0.5}P_{1.5})O_8$ (8) and of the V(IV) monophosphate $Zn_2VO(PO_4)_2$ (9) in which vanadium exhibits tetrahedral and square pyramidal coordination, respectively. No V(III) zinc phosphate has been synthesized up to now to our knowledge. We report here on the crystal structure of the first V(III) zinc phosphate, $Zn_3V_4(PO_4)_6$, we have isolated recently.

EXPERIMENTAL

Khaki-green crystals were isolated from a mixture having the composition of the title compound. The synthesis of these crystals was performed in two steps. First, a mixture of $Zn(CH_3COO)_2 \cdot 2H_2O$, V_2O_5 and $(NH_4)_2HPO_4$ with the molar ratio 5 : 2 : 10 was heated to 893 K for 2 hr. In the second step, the finely ground powder was mixed with an appropriate amount of vanadium according to stoichiometry, placed in an alumina crucible, and sealed in an evacuated silica ampoule. This sample was heated at 1223 K for 24 hr, cooled at a rate of 1°/hr to 1023 K, and quenched to room temperature. The composition of the crystals was confirmed by microprobe analysis.

In order to obtain the polycrystalline powder of this phase, the same process is used, but instead of slow cooling, the sample is quenched to room temperature. The X-ray powder diffractogram was recorded on a Philips diffractometer with $CuK\alpha$ radiation and was indexed (Table 1) in a triclinic cell, in agreement with the cell parameters obtained from the single crystal study.

STRUCTURE DETERMINATION

A parallelepipedic khaki-green crystal of $Zn_3V_4(PO_4)_6$ with dimensions $0.051 \times 0.051 \times 0.039$ mm was selected for the structure determination. The triclinic cell parameters reported in Table 2 were determined and refined, by diffractometric techniques, at 294 K with a least-squares

TABLE 1
Intereticular Distances

h	k	l	d obs(Å)	d calc(Å)	I obs	h	k	l	d obs(Å)	d calc(Å)	I obs
0	1	0	7.225	7.226	4	2	0	1	2.427	2.427	4
0	1	-1	6.738	6.740	6	0	3	0	2.409	2.409	4
1	0	-1	5.917	5.921	3	2	-2	-2	2.362	2.366	6
1	0	0	5.725	5.527	6	2	-1	-3		2.364	
1	-1	0	5.351	5.356	1	1	1	2		2.360	
1	-1	-1	4.729	4.712	8	1	-3	2		2.360	
1	1	-1	4.441	4.442	2	1	-1	3	2.351	2.351	5
0	1	-2	4.293	4.299	14	1	1	-4	2.322	2.325	1
1	-1	1		4.291		0	1	3		2.319	
0	0	2	4.136	4.136	3	1	0	-4	2.246	2.247	2
1	0	1	4.026	4.027	3	0	3	-3		2.247	
1	1	0	3.940	3.940	4	1	3	-2	2.223	2.225	3
1	1	-2	3.885	3.903	2	2	2	-2		2.221	
0	2	-1	3.842	3.843	2	2	-3	0	2.203	2.205	3
0	2	0	3.613	3.613	5	0	1	-4		2.203	
1	-2	0	3.589	3.591	4	0	2	-4	2.149	2.150	10
1	-1	-2	3.456	3.456	2	2	2	-3	2.135	2.136	3
1	-2	1	3.423	3.426	4	0	3	1	2.118	2.121	8
0	2	-2	3.369	3.370	2	2	-3	-1		2.120	
1	-1	2	3.112	3.116	15	1	3	-3		2.117	
2	0	-1		3.110		2	0	-4		2.117	
1	1	1	3.052	3.052	4	1	-2	-3	2.085	2.085	2
1	1	-3	2.994	3.001	10	2	1	1		2.084	
1	2	-1		2.990		3	-1	-2	2.075	2.077	4
2	-1	0		2.992		3	0	-2	2.067	2.070	7
1	0	-3		2.983		0	0	4		2.068	
2	0	-2	2.951	2.960	100	1	-3	3		2.067	
0	2	1		2.952		2	-2	-3	2.032	2.032	6
1	2	-2		2.950		2	0	2	2.012	2.013	2
0	1	-3		2.943		1	3	0		2.011	
2	0	0	2.861	2.864	12	3	-2	-1	1.995	1.997	4
1	0	2		2.862		1	-3	-2	1.982	1.983	2
1	-2	2		2.861		2	2	-4	1.942	1.943	3
2	-1	-2	2.802	2.803	21	0	3	-4		1.942	
1	2	0	2.706	2.705	2	3	-1	-3	1.935	1.936	3
2	1	-2	2.674	2.679	10	0	4	-1	1.908	1.910	19
2	-2	0		2.678		3	0	0		1.909	
2	1	-1		2.669		1	2	2		1.906	
2	-1	1	2.601	2.603	11	1	-4	2		1.906	
1	2	-3		2.600		2	-2	3	1.826	1.826	4
2	0	-3	2.545	2.548	4	0	1	4		1.826	
1	-3	1		2.544		1	2	-5	1.821	1.821	3
1	-3	0	2.511	2.512	2	3	-1	1		1.820	
0	3	-2	2.497	2.498	6	0	4	0	1.805	1.807	4
2	-2	1	2.470	2.471	3	2	-1	3		1.804	

refinement based upon 25 reflections with $18° < \theta < 22°$. The data were collected with an Enraf–Nonius CAD4 diffractometer with the parameters reported in Table 2. The reflections were corrected for Lorentz, polarization, and secondary extinction effects. No absorption correction was performed. The structure was solved by the heavy-atom method and refined successfully in the centrosymmetric space group $P\bar{1}$. The final refinement of the atomic coordinates and of the anisotropic thermal factors of all the atoms lead to $R = 0.036$ and $R_w = 0.037$. The atomic parameters are reported in Table 3.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The projection of the $[V_4P_6O_{24}]_\infty$ framework along **a** (Fig. 1) shows that the latter consists of V_2O_{10} bioctahedral units built up by two edge-sharing octahedra connected through single PO_4 tetrahedra. Two sorts of V_2O_{10}

TABLE 2
Summary of Crystal Data, Intensity Measurements and Structure Refinement Parameters for $Zn_3V_4(PO_4)_6$

Crystal data		
Space group	$P\bar{1}$	
Cell dimensions	$a = 6.349(2)$ Å	$\alpha = 105.32(1)°$
	$b = 7.869(1)$ Å	$\beta = 108.66(1)°$
	$c = 9.324(2)$ Å	$\gamma = 101.23(2)°$
Volume	405(4) Å³	
Z	1	
ρ_{calc} (g cm^{-3})	3.98	
Intensity measurements		
λ (MoKα)	0.71073 Å	
Scan mode	$\omega - 2/3\ \theta$	
Scan width (°)	$1.05 + 0.35\ tg\ \theta$	
Slit aperture (mm)	$1.03 + tg\ \theta$	
Max θ (°)	45	
Standard reflections	3 measured every 3000 sec	
Measured reflections		
h	$-12 \rightarrow 12$	
k	$-15 \rightarrow 15$	
l	$0 \rightarrow 18$	
Reflections with $I > 3\ \sigma$	1952	
μ (mm^{-1})	7.36	
Structure solution and refinement		
Parameters refined	170	
Agreement factors	$R = 0.036$	$R_w = 0.037$
Weighting scheme	$w = F(\sin \theta/\lambda)$ [Hamilton scheme]	
Δ/σ max	<0.004	

TABLE 3
Positional Parameters and their Estimated Standard Deviations

Atom	x	y	z	B (Å²)
Zn(1)	0.	0.	0.	0.97(1)
Zn(2)	0.2855(1)	−0.18538(8)	0.29056(7)	0.613(9)
V(1)	0.3890(1)	0.4610(1)	0.11579(9)	0.31(1)
V(2)	0.9548(1)	0.2846(1)	0.47813(9)	0.39(1)
P(1)	0.9128(2)	0.4095(2)	0.1663(1)	0.33(2)
P(2)	0.3954(2)	0.2312(2)	0.3683(1)	0.43(2)
P(3)	0.2262(2)	0.1423(2)	−0.2312(1)	0.41(2)
O(1)	0.6909(6)	0.4581(4)	0.0820(4)	0.56(5)
O(2)	0.5439(6)	0.7372(5)	0.2272(4)	0.60(5)
O(3)	0.1238(6)	0.5404(5)	0.1624(4)	0.58(5)
O(4)	0.4514(7)	0.3686(5)	0.2877(5)	0.97(6)
O(5)	0.2257(6)	0.1962(5)	−0.0583(4)	0.69(6)
O(6)	0.0159(6)	0.1811(5)	0.6579(4)	0.59(5)
O(7)	0.2464(6)	0.2786(5)	0.4623(5)	0.90(6)
O(8)	0.9376(6)	0.4566(4)	0.3455(4)	0.49(5)
O(9)	0.6297(6)	0.2320(5)	0.4924(4)	0.79(6)
O(10)	0.7868(6)	0.0575(5)	0.2924(4)	0.67(6)
O(11)	0.8948(6)	0.2127(5)	0.0857(5)	0.85(6)
O(12)	0.2707(7)	0.0371(5)	0.2336(4)	0.80(6)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B = 4/3$ $[\beta_{11}a^{*2} + \beta_{22}b^{*2} + \beta_{33}c^{*2} + \beta_{12}a^* \cdot b^*\cos \gamma^* + \beta_{13}a^*b^* \cdot \cos^* \beta + \beta_{23}b^* \cdot c^* \cdot \cos \alpha^*]$.

units must be distinguished that correspond to two crystallographically independent vanadium atoms labeled V(1) and V(2), respectively. The V(1)–V(1) pairs are oriented transversally to the (**b**, **c**) plane, whereas the V(2)–V(2) pairs are parallel to **b** (Fig. 1).
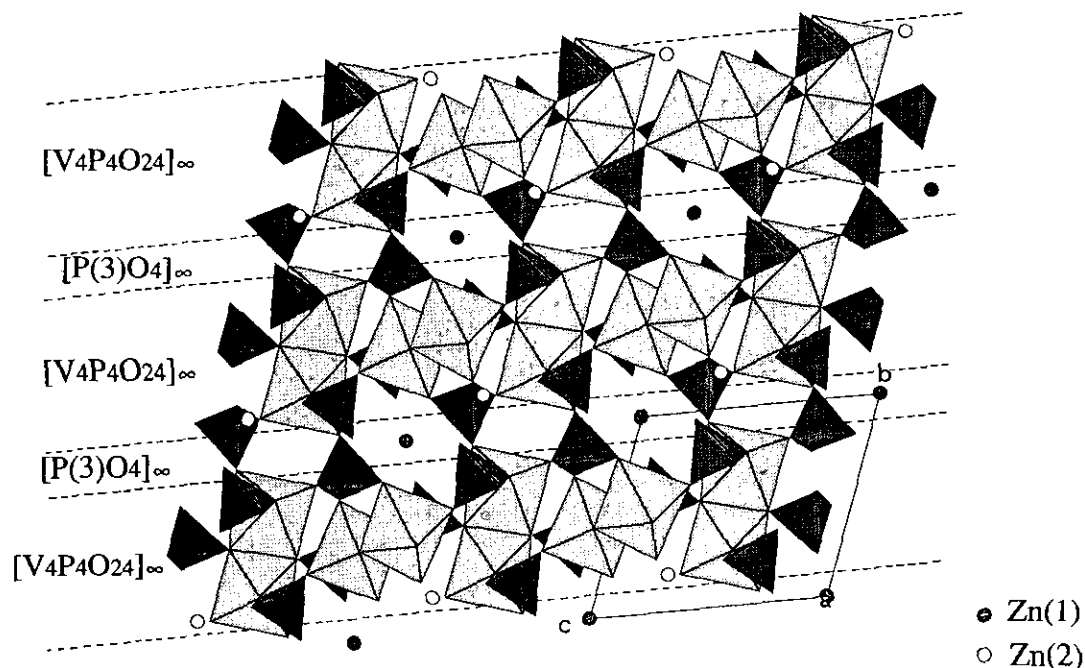

$[V_4P_4O_{24}]_\infty$

$[P(3)O_4]_\infty$

$[V_4P_4O_{24}]_\infty$

$[P(3)O_4]_\infty$

$[V_4P_4O_{24}]_\infty$

⊘ Zn(1)

○ Zn(2)

FIG. 1.   Projection of $Zn_3V_4(PO_4)_6$ along **a**.
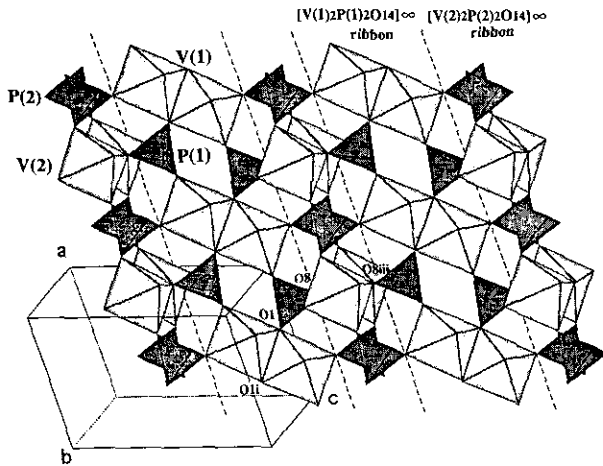
FIG. 2. Projection of the $[V_4P_4O_{28}]_\infty$ layer perpendicular to the (a, c) plane.

In fact, this structure can be described by the stacking along **b** of identical $[V_4P_4O_{24}]_\infty$ layers parallel to the (a, c) plane interconnected through layers of P(3) monophosphate groups (Fig. 1). The view of one $[V_4P_4O_{24}]_\infty$ layer along the perpendicular of (010) plane (Fig. 2) shows that it consists of two kinds of $[V_2P_2O_{14}]_\infty$ ribbons running along **a**. The first type of ribbon corresponds to the V(1)–V(1) units that are interconnected with P(1) tetrahedra in such a way that each bioctahedral unit shares the two apices of its communal edge with two different P(1) tetrahedra, i.e., forms two triply bonded oxygens; as a result, one observes a geometry characterized by diamond-shaped windows similar to those observed in the diphosphate (VO)₂P₂O₇ (10). In the second kind of ribbon, each V(2)–V(2) unit shares its four apical corners with four P(2) tetrahedra. In fact, both ribbons can be described by the association of $[VPO_8]_\infty$ chains in which one PO₄ tetrahedron alternates with one VO₆ octahedron, by sharing the edges of their VO₆ octahedra in two different manners (Fig. 3). The connection between the "V(1)–V(1)" and the "V(2)–V(2)" ribbons is ensured by the P(1) and P(2) tetrahedra as shown in Fig. 2: each P(1) tetrahedron of the V(1)–V(1) ribbons shares one apex with a V(2)–V(2) bioctahedral unit forming a triply bonded oxygen atom, whereas each P(2) tetrahedron of the V(2)–V(2) ribbons shares one apex with one V(1) octahedron. Thus, each V(1)–V(1) unit is linked to four P(1) tetrahedra and two P(2) tetrahedra in its basal plane [i.e., parallel to (010)] and shares its four apical corners with two P(3) tetrahedra, so that it exhibits two triply bonded oxygen atoms O(1) and O(1^i). In the same way, each V(2)–V(2) unit is linked to two P(1) tetrahedra and four P(3) tetrahedra in its basal plane [i.e., parallel to (100)], and shares its four apical corners with four P(2) tetrahedra, so that it exhibits also two triply bonded oxygens O(8) and O(8^{iii}).

Note that these two triply bonded oxygens belong to the same phosphate group.

This tridimensional framework $[V_4P_6O_{24}]_\infty$ shows small tunnels running along **a** (Fig. 1). Zn(1) cations are located in the center of these tunnels on a symmetry center forming distorted ZnO₆ octahedra. As a result, the monophosphate Zn₃V₄(PO₄)₆ cannot be considered as a tunnel structure. Moreover, the second zinc atom labeled Zn(2) is located on the border of the tunnel forming a very distorted trigonal bipyramid ZnO₅. The connection between the ZnO₅ and ZnO₆ polyhedra and the other polyhedra of the structure is very complex. For instance, each ZnO₅ bipyramid shares two opposite edges with two different bioctahedral units, V(1)–V(1) and V(2)–V(2), forming infinite undulating ribbons $[V_4Zn_2O_{22}]_\infty$ running along [101] (Fig. 4). The connections between the Zn(1)O₆ octahedra and the other polyhedra are still more complicated. One indeed observes (Fig. 5) that for each Zn(1) octahedron two opposite apices O(2) are triply bonded, i.e., shared with a Zn(2) bipyramid and a P(2) tetrahedron; two other apices O(5) are also triply bonded,
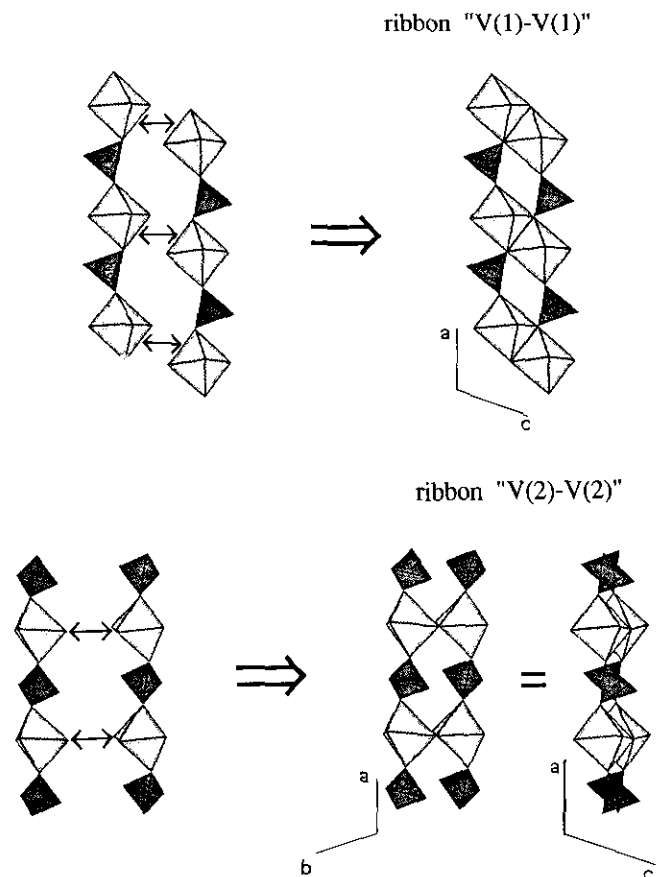
ribbon "V(1)-V(1)"

ribbon "V(2)-V(2)"

FIG. 3. (a) Assemblage of the "V1–V1" ribbon. (b) Assemblage of the "V2–V2" ribbon.
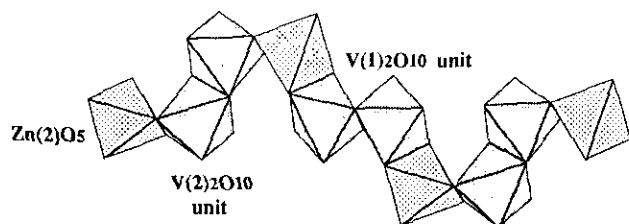
FIG. 4. Infinite corrugated ribbon: $[V_4Zn_2O_{22}]_\infty$ along [101].

i.e., shared with a V(1) octahedron and a P(3) tetrahedron, whereas the two other O(11) apices are shared with a single P(1) tetrahedron.

The geometry of the VO_6 octahedra is easily explained by their mode of connection with the other polyhedra. The largest interatomic V–O distances (Table 4) correspond to triply bonded oxygens; this is the case of the V(1)–O(1), V(1)–O(1^i), V(2)–O(8), and V(2)–O(8^{iii}) bonds ranging from 2.04 to 2.07 Å, whose oxygen atoms are shared between two VO_6 octahedra and one PO_4 tetrahedron; similarly, the V(1)–O(2), V(1)–O(3), V(1)–O(5), V(2)–O(6), and V(2)–O(9) bonds, whose oxygen atoms are shared between a VO_6 octahedron, a ZnO_x polyhedron, and a PO_4 tetrahedron, ranging from 2.01 to 2.08 Å. Coherently, for the shortest V–O bonds, V(1)–O(4), V(2)–O(7), and V(2)–O(10) ranging from 1.89 to 1.94 Å, the oxygen atoms are only shared between a VO_6 octahedron and a PO_4 tetrahedron.

Although they are not strongly distorted, the PO_4 tetrahedron exhibits similar behavior. The shortest P–O distances correspond to oxygen atoms shared between one PO_4 tetrahedron and one MO_6 octahedron only, as shown for the P(1)–O(11), P(2)–O(4), P(2)–O(7), and P(3)–O(10) distances that range from 1.50 to 1.52 Å; the other P–O bonds that correspond to triply bonded oxygen are significantly longer, ranging from 1.54 to 1.56 Å (Table 4).
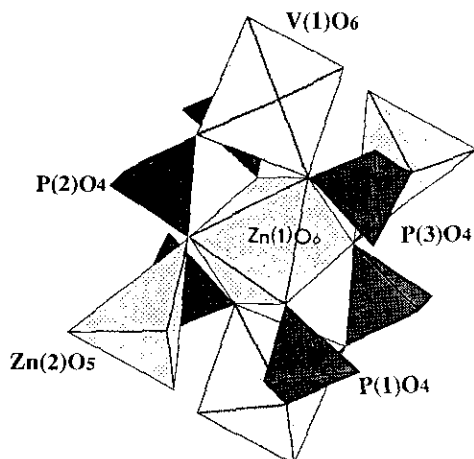

FIG. 5. Polyhedra around Zn(1)O6 octahedron.

TABLE 4
Distances (Å) and Angles (°) in the Polyhedra

V(1)	O(1^i)	O(1)	O(2)	O(3)	O(4)	O(5)
O(1^i)	2.053(4)	2.727(8)	2.629(6)	2.881(6)	3.941(8)	2.750(6)
O(1)	83.5(2)	2.043(4)	2.750(5)	4.040(8)	2.941(6)	2.901(6)
O(2)	80.4(2)	85.1(2)	2.023(4)	2.597(5)	3.080(8)	4.063(8)
O(3)	89.6(2)	164.0(2)	79.5(2)	2.037(4)	2.810(6)	3.252(8)
O(4)	175.9(2)	96.7(2)	103.8(2)	91.3(2)	1.891(5)	2.876(8)
O(5)	83.3(2)	89.3(2)	163.2(2)	104.2(2)	92.6(2)	2.084(4)

V(2)	O(6^{ii})	O(7^{ii})	O(8)	O(8^{iii})	O(9)	O(10)
O(6^{ii})	2.013(4)	2.840(6)	4.033(8)	2.818(6)	2.616(5)	3.033(8)
O(7^{ii})	92.7(2)	1.912(5)	2.739(6)	3.039(8)	3.968(8)	2.767(6)
O(8)	164.6(2)	87.2(2)	2.056(4)	2.585(8)	3.236(8)	2.954(6)
O(8^{iii})	87.3(2)	99.4(2)	77.6(2)	2.071(5)	2.932(5)	3.984(8)
O(9)	79.5(2)	167.6(2)	103.0(2)	89.9(2)	2.079(4)	2.594(6)
O(10)	100.2(2)	91.8(2)	95.2(2)	166.3(2)	80.3(2)	1.942(4)

P(1)	O(1)	O(3^{ii})	O(8)	O(11)
O(1)	1.551(4)	2.503(5)	2.459(6)	2.527(5)
O(3^{ii})	108.2(2)	1.540(4)	2.516(6)	2.485(5)
O(8)	104.4(2)	108.5(2)	1.561(4)	2.558(5)
O(11)	112.0(2)	109.9(2)	113.6(2)	1.496(4)

P(2)	O(4)	O(7)	O(9)	O(12)
O(4)	1.520(5)	2.540(6)	2.501(6)	2.479(6)
O(7)	113.6(2)	1.516(5)	2.470(6)	2.523(6)
O(9)	108.4(2)	106.7(2)	1.563(4)	2.556(5)
O(12)	107.5(2)	110.5(2)	110.2(2)	1.554(4)

P(3)	O(2^i)	O(5)	O(6^{iv})	O(10^v)
O(2^i)	1.562(4)	2.551(6)	2.528(6)	2.485(6)
O(5)	109.8(2)	1.556(5)	2.511(6)	2.506(6)
O(6^{iv})	108.9(2)	108.2(2)	1.545(4)	2.513(6)
O(10^v)	108.5(2)	110.2(2)	111.2(2)	1.500(4)

Zn(1)–O(5)	2.194(4)
Zn(1)–O(5^{vi})	2.194(4)
Zn(1)–O(11^{vii})	1.989(4)
Zn(1)–O(11^v)	1.989(4)
Zn(1)–O(12^{vi})	2.204(4)
Zn(1)–O(12)	2.204(4)
Zn(2)–O(2^{viii})	2.057(4)
Zn(2)–O(3^{viii})	2.032(4)
Zn(2)–O(6^{ix})	2.121(4)
Zn(2)–O(9^x)	2.072(4)
Zn(2)–O(12)	1.970(4)

Note. The V–O or P–O distances are on the diagonal; above it are the $O_i \cdots O_j$ distances and under it are the O_i–V–O_j or O_i–P–O_j angles. Symmetry codes (i) $1 - x, 1 - y, -z$; (ii) $1 + x, y, z$; (iii) $2 - x, 1 - y$, $1 - z$; (iv) $x, y, z - 1$; (v) $1 - x, -y, -z$; (vi) $-x, -y, -z$; (vii) $x - 1, y, z$; (viii) $x, y - 1, z$; (ix) $-x, -y, 1 - z$; and (x) $1 -x, -y, 1 - z$.

The distorted octahedral coordination of Zn(1), with Zn–O distances ranging from 1.99 to 2.20 Å (Table 4) is usually observed in ternary zinc oxides; with Zn(2)–O distances, ranging from 1.97 to 2.07 Å (Table 4) the bipyramidal coordination of Zn(2) is quite unusual. Neverthe-

less, fivefold coordination of zinc has previously been observed in zinc phosphates such as γ $(Zn_{0.7}Ni_{0.3})_3(PO_4)_2$ (11) that contains ZnO_5 trigonal bipyramids and Zn_2 $VO(PO_4)_2$ (9) that exhibits ZnO_5 square pyramids and both coordinations have been observed by Hawthorne (12) in the same structure in adamite, $Zn_2(OH)AsO_4$.

CONCLUDING REMARKS

A zinc vanadophosphate built up by bioctahedral V_2O_{10} units has been synthesized for the first time. This is to be compared with the cadmium vanadophosphate $Cd_3V_4(PO_4)_6$ (5) that exhibits similar V_2O_{10} bioctahedral units. However, the most remarkable features of this existence for zinc atoms of two coordinations, octaheral and trigonal bipyramidal, the second being unusual. This study suggests that zinc, owing to its great flexibility, should allow many other vanadium phosphates with original frameworks to be generated.

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