

## Synthesis and Crystal Structure of $Zn_2VO(PO_4)_2$ , a Vanadyl(IV) Orthophosphate Containing a Dimer of Edge-Sharing $ZnO_5$ Square Pyramids

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Reactions in the  $ZnO-VO_2-P_2O_5$  system afford the new phase  $Zn_2VO(PO_4)_2$ , the structure of which was determined by the single-crystal X-ray diffraction method ( $I4cm$ ,  $a = 8.9227(13)$ ,  $c = 9.039(3)$  Å,  $Z = 4$ ,  $R = 0.026$  for 228 unique reflections). The structure consists of infinite chains of corner-sharing  $VO_6$  octahedra along the  $c$ -axis and finite chains of edge-sharing  $ZnO_5$  and  $PO_4$  polyhedra parallel to the  $\langle 110 \rangle$  directions. The  $VO_6$  octahedra are distorted such that alternately long and short V-O bonds along the axis of the infinite chain are formed. The  $Zn^{2+}$  ions exhibit a square pyramidal coordination. © 1991 Academic Press, Inc.

### Introduction

We recently reported the crystal structures of a number of alkali metal vanadium phosphates containing vanadium in the oxidation states less than +5 (1-7). These vanadium phosphates often adopt tunnel or layer structures with the alkali metal cations located in the tunnels or between the layers. The nature of alkali metal cations plays an important role in the crystal structures of these phosphates. For example,  $A_2V_3P_4O_{17}$  ( $A = Cs, Rb$ ) are isomorphous (1), but the corresponding potassium compound is polymorphic (6, 8).  $AVP_2O_7$  ( $A = Cs-Li$ ) crystallize in three different structure types (3-5). Although these compounds can be structurally characterized by X-ray diffraction, our predictive ability of the structures as a function of the nature of counter cations is almost nonexistent. However, this lack of predictive ability is

often a source of great challenge in synthetic solid state chemistry. Therefore, it would be interesting to synthesize and characterize vanadium phosphates with divalent counter cations. Our efforts to synthesize vanadium phosphates containing alkaline earth metals have been unsuccessful. The divalent cation  $Zn^{2+}$  was considered since there is no ligand field stabilization effect in  $Zn^{2+}$  and zinc shows similarities with the main-group element magnesium. The complexes of Zn commonly have coordination numbers of 4, 5, or 6. Tetrahedral and trigonal bipyramidal coordination of zinc are especially common. Interestingly, the zinc ions in the title compound exhibit a square pyramidal coordination. The present work deals with the synthesis and crystal structure of  $Zn_2VO(PO_4)_2$ , a vanadyl(IV) orthophosphate containing a dimer of edge-sharing  $ZnO_5$  square pyramids.

TABLE I  
CRYSTAL DATA, INTENSITY MEASUREMENT, AND  
REFINEMENT PARAMETERS FOR  $Zn_2VO(PO_4)_2$

Crystal data	
Crystal system	Tetragonal
Space group	$I4cm$ (No. 108)
Cell constants	$a = 8.9227(13)$ , $c = 9.039(3)$ Å $V = 719.62(22)$ Å <sup>3</sup>
Z	4
Density (calcd)	3.578 g/cm <sup>3</sup>
Intensity Measurement	
$\lambda$ (MoK $\alpha$ )	0.70930 Å
Scan mode	$\theta/2\theta$
Scan rate	5.5°/min
Scan width	$0.65^\circ + 0.35^\circ \tan \theta$
Maximum $2\theta$	55°
Unique reflections measured	244
Structure solution and refinement	
Reflections included	228
Parameters refined	40
Agreement factors <sup>a</sup>	$R = 0.026$ , $R_w = 0.025$
$(\Delta\rho)_{\max}$ ; $(\Delta\rho)_{\min}$	1.65 e/Å <sup>3</sup> ; -0.82 e/Å <sup>3</sup>

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ , where  $w = 1/\sigma^2(F)$ .

## Experimental

### Synthesis

Blue chunky crystals of  $Zn_2VO(PO_4)_2$  were first discovered in a reaction product by heating a mixture of ZnO,  $V_2O_3$ , and  $P_2O_5$  (mole ratio 3:2:3) in a sealed silica tube at 950°C for 1 day. The exact stoichiometry was not known until its single-crystal X-ray structure was solved. Subsequently, the title compound was obtained as a single-phase material by heating a mixture of ZnO,  $VO_2$ , and  $P_2O_5$  in a 2:1:1 molar ratio in a sealed silica tube at 850°C for 2 days with an intermediate grinding. The powder X-ray pattern of the blue polycrystalline product compared well with that calculated from the single-crystal data.

### Single-Crystal X-Ray Diffraction Study

A blue crystal having the dimensions of  $0.10 \times 0.10 \times 0.07$  mm was selected for intensity data collection on an Enraf-Nonius CAD4 diffractometer at room temperature. The orientation matrix and unit cell parameters were determined by least-

squares fit of 24 peak maxima with  $17 < 2\theta < 29^\circ$ . The intensity data were corrected for Lorentz and polarization effects, but no absorption correction has been applied. Direct methods (NRCVAX) were used to locate the metal atoms, with the remaining nonmetal atoms being found from a successive difference Fourier map (9). Neutral-atom scattering factors and corrections for anomalous dispersion were taken from common sources (10). The final cycle of full-matrix least-squares refinement gave  $R$  and  $R_w$  values of 0.026 and 0.025, respectively. A final difference synthesis showed a residual peak of 1.65 e/Å<sup>3</sup> at 0, 0, 0.207, which is at a distance of 0.80 Å from the vanadium site. Some crystallographic and refinement data for the title compound are summarized in Table I.

## Results and Discussion

Final atomic coordinates and thermal parameters are given in Table II. Interatomic distances and bond angles appear in Table

TABLE II  
POSITIONAL AND THERMAL PARAMETERS FOR  
 $Zn_2VO(PO_4)_2$

Atom	x	y	z	$B_{iso}^a$		
Zn	0.61810(9)	0.11810	0.26348	0.71(4)		
V	0	0	0.1011(5)	0.77(8)		
P	0.30665(21)	0.19335	0.1204(4)	0.50(8)		
O(1)	0.8271(6)	0.1355(5)	0.1548(6)	0.71(20)		
O(2)	0.6518(8)	0.1518	0.4690(10)	2.0(3)		
O(3)	0	0	0.4275(17)	1.7(4)		
O(4)	0.3960(6)	0.1040	0.2369(10)	1.0(3)		
Anisotropic thermal parameters (Å <sup>2</sup> × 100) <sup>b</sup>						
	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Zn	0.85(4)	0.85	1.01(6)	-0.25(5)	-0.03(4)	-0.03
V	0.45(9)	0.45	2.04(17)	0	0	0
P	0.59(8)	0.59	0.73(14)	0.04(9)	-0.04(8)	-0.04
O(1)	0.39(23)	0.42(24)	1.9(3)	-0.05(21)	0.30(25)	-0.08(25)
O(2)	3.1(4)	3.1	1.5(6)	-0.5(4)	-0.7(3)	-0.7
O(3)	2.1(5)	2.1	2.4(8)	0	0	0
O(4)	1.18(24)	1.18	1.4(6)	-0.1(3)	-0.05(25)	-0.05

<sup>a</sup>  $B_{iso}$  is the mean of the principal axes of the thermal ellipsoid.

<sup>b</sup> Anisotropic temperature factors are of the form:  $\text{Temp} = \exp[-2\pi^2(h^2U_{11}a^{*2} + \dots + 2hkU_{12}a^*b^* + \dots)]$ .

TABLE III  
INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR  $Zn_2VO(PO_4)_2$

Zn square pyramid						
Zn	O(1)	O(1a)	O(2)	O(4)	O(4)b	
O(1)	2.113(5)	2.417(9)	3.245(7)	3.927(7)	3.014(4)	
O(1a)	69.76(18)	2.113(5)	3.245(7)	3.014(4)	3.927(7)	
O(2)	107.6(3)	107.6(3)	1.906(10)	3.129(11)	3.129(11)	
O(4)	145.4(3)	94.2(2)	106.5(3)	2.000(5)	2.625(15)	
O(4)b	94.2(2)	145.4(3)	106.5(3)	82.0(2)	2.000(5)	
VO <sub>6</sub> octahedron						
V	O(1)	O(1c)	O(1d)	O(1e)	O(3)	O(3)f
O(1)	2.019(5)	2.772(7)	3.921(10)	2.772(7)	3.149(13)	2.840(12)
O(1c)	86.7(2)	2.019(5)	2.772(7)	3.921(10)	3.149(13)	2.840(12)
O(1d)	152.2(3)	86.7(2)	2.019(5)	2.772(7)	3.149(13)	2.840(12)
O(1e)	86.7(2)	152.2(3)	86.7(2)	2.019(5)	3.149(13)	2.840(12)
O(3)	76.1(2)	76.1(2)	76.1(2)	76.1(2)	2.950(16)	4.520(13)
O(3)f	103.9(2)	103.9(2)	103.9(2)	103.9(2)	180	1.570(16)
PO <sub>4</sub> tetrahedron						
P	O(1g)	O(1h)	O(2)i	O(4)		
O(1g)	1.569(4)	2.417(9)	2.541(10)	2.516(8)		
O(1h)	100.8(3)	1.569(4)	2.541(10)	2.516(8)		
O(2)i	113.7(4)	113.7(3)	1.466(8)	2.496(11)		
O(4)	107.9(4)	107.9(2)	112.1(5)	1.543(11)		

Note. Symmetry codes are *a*:  $0.5 + y, -0.5 + x, z$ ; *b*:  $1 - x, -y, z$ ; *c*:  $1 - y, -1 + x, z$ ; *d*:  $2 - x, -y, z$ ; *e*:  $1 + y, 1 - x, z$ ; *f*:  $2 - x, y, -0.5 + z$ ; *g*:  $y, 1 - x, z$ ; *h*:  $-0.5 + x, 0.5 - y, z$ ; *i*:  $0.5 - y, -0.5 + x, -0.5 + z$ .

III. The motif of the mutual adjunction (11) is given in Table IV. The refined ellipsoids all appear to have reasonable shapes except for V and O(1). Their very large  $U_{33}$  values could be attributed to the positional disorder along the *c*-axis. A similar phenomenon occurs in  $\alpha$ -VPO<sub>5</sub> (12). It is noted that both

TABLE IV  
MOTIVES OF MUTUAL ADJUNCTION AND COORDINATION NUMBER (C.N.) IN  $Zn_2VO(PO_4)_2$

	4 O(1)	2 O(2)	O(3)	2 O(4)	C.N.
V	4/1		2/2		6
2 Zn	2/1	1/1		2/2	5
2 P	2/1	1/1		1/1	4
C.N.	3	2	2	3	

structures contain infinite chains of distorted VO<sub>6</sub> octahedra involving alternately long and short V–O bonds parallel to the axis of the chain. The coordination octahedron formed by the O atoms around the V atom in  $Zn_2VO(PO_4)_2$  has  $C_{4v}$  symmetry, with the rotation axis passing through the V atom and the vanadyl oxygen O(3) (see Fig. 1). The V atom is displaced 0.485 Å out of the basal plane along the fourfold axis toward O(3). The V–O(3) distances are 1.570(16) and 2.950(16) Å while the equatorial V–O bond lengths are 2.019(5) Å. The sum of bond valences for V–O bonds using the empirical formula derived by Brown and Altermatt (13) is +3.94, which is in agreement with the formal oxidation state +4 based on the stoichiometry. The very

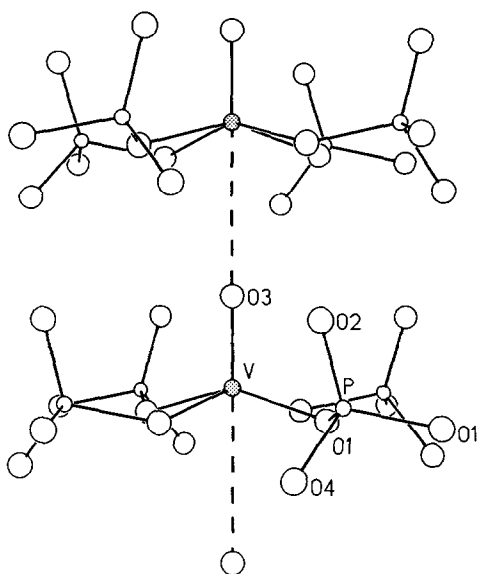


FIG. 1. A section of the infinite chain of distorted  $\text{VO}_6$  octahedra in  $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ .

short V–O bond is characteristic of the vanadyl ion  $\text{VO}^{2+}$ , which has a strong bond with both  $\sigma$  and  $\pi$  character.

The framework of  $\text{Zn}_2\text{VO}(\text{PO}_4)_2$  consists of infinite chains of corner-sharing  $\text{VO}_6$  octahedra along the  $c$ -axis and finite chains of edge-sharing  $\text{ZnO}_5$  and  $\text{PO}_4$  polyhedra parallel to the  $\langle 110 \rangle$  directions. The finite chain in  $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ , shown in Fig. 2, is similar to the grouping found in  $\alpha\text{-CaZn}_2(\text{PO}_4)_2$  (14) except that the apices of two square pyramids in the latter point in opposite directions. As shown in Fig. 3 each finite chain

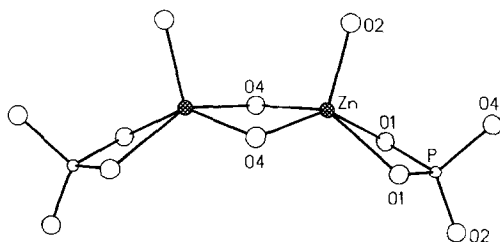


FIG. 2. The finite chain in  $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ .

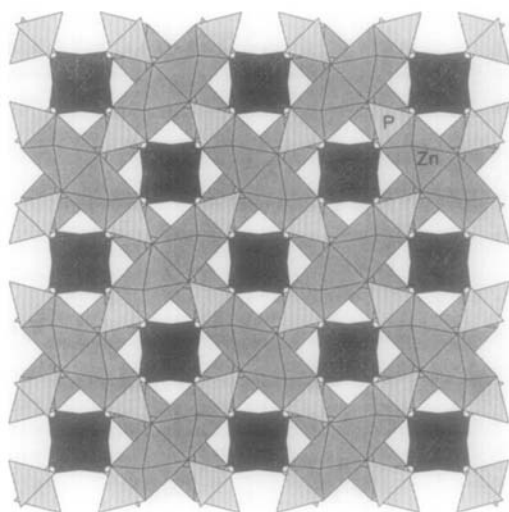


FIG. 3. A polyhedron representation of the  $\text{Zn}_2\text{VO}(\text{PO}_4)_2$  structure along  $[001]$ .

of edge-sharing Zn and P polyhedra shares its eight corners (four O(2) and four O(4)) with eight others to form square tunnels where the vanadyl groups,  $\text{VO}^{2+}$ , are located. Four of the eight finite chains are in a parallel direction and the other four are in an orthogonal direction. The remaining four corners (four O(1)) of the finite chain are shared with four separate infinite chains of  $\text{VO}_6$  octahedra and each of the equatorial oxygen atoms of a  $\text{VO}_6$  octahedron is shared with a different finite chain. The Zn–O bond distances in the title compound range from 1.906(10) to 2.113(5) Å. The shortest Zn–O distance involves the apical oxygen, O(2), which is strongly bonded only to one Zn and one P atom. The Zn ion is displaced 0.60 Å from the plane of four basal oxide ligands. A bond-strength analysis of the Zn–O bonds in the title compound gives a value of +2.14, which is close to the formal oxidation state +2 for Zn. As indicated by the  $\text{O} \cdots \text{O}$  distances (2.417(9)–3.245(7) Å), the  $\text{ZnO}_5$  square pyramid is strongly distorted because of edge sharing. The common edge of two Zn polyhedra is

shortened (2.624(15) Å) and the edges parallel to the chain direction are elongated (3.014(4) Å). The common edges of Zn polyhedra and P tetrahedra are markedly shortened (2.417(9) Å). The Zn ··· Zn and Zn ··· P distances across the shared edges are 2.980(2) and 2.708(4) Å, respectively. The  $PO_4$  tetrahedron is also distorted because of edge-sharing. The four P–O bonds can be divided into two groups: three longer distances at 1.543(11)–1.569(5) Å, and a very short one at 1.466(8) Å. The shortest P–O bond involves the apical oxygen O(2). It is also observed that the coordination around O(1) is nearly planar, i.e., the oxygen atom lies in the plane formed by 1 P, 1 V, and 1 Zn atom. Atom O(4) is 0.40 Å off the plane formed by 1 P and 2 V atoms. Both O(2) and O(3) are two-coordinated.

As a conclusion, the synthesis of  $Zn_2VO(PO_4)_2$  shows the ability of zinc to participate in the octahedral–tetrahedral network. It is likely that many additional mixed frameworks containing divalent metals will be synthesized in the future.

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