The Diphosphovanadate Cd_2VPO_7: A Mixed Framework with Pseudo-Close-Packed Octahedral Layers Connected through Ditetrahedral VPO_7 Groups

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

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

A new vanadium (V) phosphate Cd_2VPO_7 has been synthesized by hydrothermal synthesis. It crystallizes in the space group $P2_{1/c}$ with $a = 4.712(1)$ Å, $b = 10.791(1)$ Å, $c = 5.620(1)$ Å, and $\beta = 97.34°(1)$. Refinement of the atomic parameters leads to $R = 0.032$ and $R_w = 0.037$. The structure is built from buckled $[Cd_2O_6]_\infty$ layers of edge-sharing CdO_6 octahedra parallel to (100), connected by layers of tetrahedral VPO_7 groups. A comparison with the divanadate $Cd_2V_2O_7$ shows that both structures exhibit $[Cd_2\square O_6]_\infty$ layers derived from the close-packed $[Cd_3O_6]_\infty$ layers observed in the rock salt CdO structure by elimination of one Cd atom out of three in an ordered way. It results in distorted six-sided windows, which are oriented differently in Cd_2VPO_7 and in $Cd_2V_2O_7$ so that the V_2O_7 and VPO_7 that block these windows are displayed differently. The distribution of V and P is discussed. The idea of a random distribution of V and P is discarded in favor of the existence of VPO_7 groups oriented at random. © 1994 Academic Press, Inc.

INTRODUCTION

The ability of vanadium to form phosphates characterized by a mixed framework has been aptly demonstrated for various oxidation states of vanadium, i.e., single valences (III, IV, V) and mixed valences (III–IV and IV–V). In all these different phosphates, vanadium adopts various coordination states ranging from strongly distorted octahedral to pyramidal. Although it is currently observed in many vanadates, the tetrahedral coordination of pentavalent vanadium is rather rare in phosphates. Moreover, several vanadates are found to be isotypic with phosphates, but the substitution of vanadium (V) by phosphorus is generally not observed owing to the size difference between these two species. However, a partial substitution of phosphorus for tetrahedral vanadium (V) in the oxides $NaVO_3$ (1) and $Zn_3V_2O_8$ (2) has been observed. The existence of the oxide $Cd_2V_2O_7$ (3), built up from tetrahedral divanadate groups, induced us to explore the possibility

of replacement of V(V) by P. The present work deals with the synthesis and crystal structure of the diphosphovanadate Cd_2VPO_7.

SYNTHESIS

Yellow crystals of the title compound were obtained through hydrothermal synthesis. A mixture of 0.350 g of CdO, 0.507 g of V_2O_5, 0.028 g of V, 0.22 ml of 85% H_3PO_4 (molar ratio Cd : V : P = 5 : 3 : 6) was added to 1.35 ml of water and sealed in a 7-cm-long, 0.4-cm-diameter gold tube. The latter was heated to 873 K under an external atmosphere of 2 kbar for 24 hr, then cooled at a rate of 1 K hr^{-1} to 773 K and finally cooled in the furnace to room temperature. The mixture of crystals was filtered, washed with water, rinsed with acetone, and dried in air at room temperature. Some yellow single crystals were selected. The composition Cd_2VPO_7, deduced from the structural determination, was confirmed by microprobe analysis.

Subsequent attempts to prepare pure Cd_2VPO_7 were made under the same conditions by heating hydrothermally a stoichiometric mixture of CdO, V_2O_5, V, and H_3PO_4. The Cd_2VPO_7 phase was obtained as a major product in a mixture of two kinds of crystals. Additional attempts to synthesize Cd_2VPO_7 by heating the mixture of CdO, V_2O_5, P_2O_5, and vanadium in stoichiometric ratio at 873 K in an evacuated silica ampoule for 24 hr were unsuccessful; $Cd_2V_2O_7$ was obtained as the major product.

STRUCTURE DETERMINATION

A yellow crystal with dimensions 0.116 × 0.051 × 0.031 mm was selected for the structure determination. The cell parameters were determined and refined by diffractometric techniques at 294 K with a least-squares refinement based upon 25 reflections with $18 < \theta < 20°$. The data were collected on a CAD-4 Enraf–Nonius

TABLE 1
Summary of Crystal Data Intensity, Measurements, and Structure Refinement Parameters for Cd_2VPO_7

Crystal data	
Space group	$P2_{1/c}$
Cell dimensions	$a = 4.712(1)$ Å, $b = 10.791(1)$ Å,
	$c = 5.620(1)$ Å, $\beta = 97.34(1)°$
Volume	$283(1)$ Å^3
Z	2
Intensity measurements	
λ (Mo$K\alpha$)	0.71073 Å
Scan mode	$\omega - 2/3\theta$
Scan width (°)	$1 + 0.35 \tan \theta$
Slit aperture (mm)	$1 + \tan \theta$
Max $\theta(°)$	45
Standard reflections	3 measured every 3000 sec
Reflections with $I > 3\sigma$	1169
μ (mm^{-1})	9.25
Structure solution and refinement	
Parameters refined	53
Agreement factors	$R = 0.032 \ R_w = 0.037$
Weighting scheme	$w = f(\sin \theta/\lambda)$
Δ/σ max	0.004
$\Delta\rho(e$Å$^{-3})$	2.8

TABLE 2
Positional Parameters and their Estimated Standard Deviations

Atom	x	y	z	B (Å^2)
Cd	0.88849(9)	0.15111(3)	0.59457(6)	1.434(4)
VP	0.3559(2)	0.39044(8)	0.6494(2)	1.08(1)
O(1)	0.1202(9)	0.3213(3)	0.4708(7)	1.50(5)
O(2)	0.6006(9)	0.2983(4)	0.7556(7)	1.55(5)
O(3)	0.2137(8)	0.4518(3)	0.8654(7)	1.57(5)
O(4)	0.5	0.5	0.5	3.2(1)

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

single crystal diffractometer using the parameters from Table 1.

The reflections were corrected for Lorentz polarizations and secondary extinction effects. No absorption corrections were performed. The structure was solved by the heavy atom method. In the unit cell, only one independent tetrahedral site was found for both vanadium and phosphorus. The refinement of the occupation of this tetrahedral site filled with only vanadium atom led to a number of electrons compatible with 0.5 V + 0.5 P. Attempts to refine the structure in the noncentrosymmetric space group Pc with the vanadium and the phosphorus atoms ordered on two different sites all failed. Therefore, the two vanadium and two phosphorus atoms are spread randomly over the four equivalent positions of the $P2_{1/c}$ space group. Then, for this tetrahedral site, we used diffraction factors which are the average of those of vanadium and phosphorus. The refinement of the atomic coordinates and the anisotropic thermal factors gave $R = 0.032$ and $R_w = 0.037$ and the parameters in the Table 2.
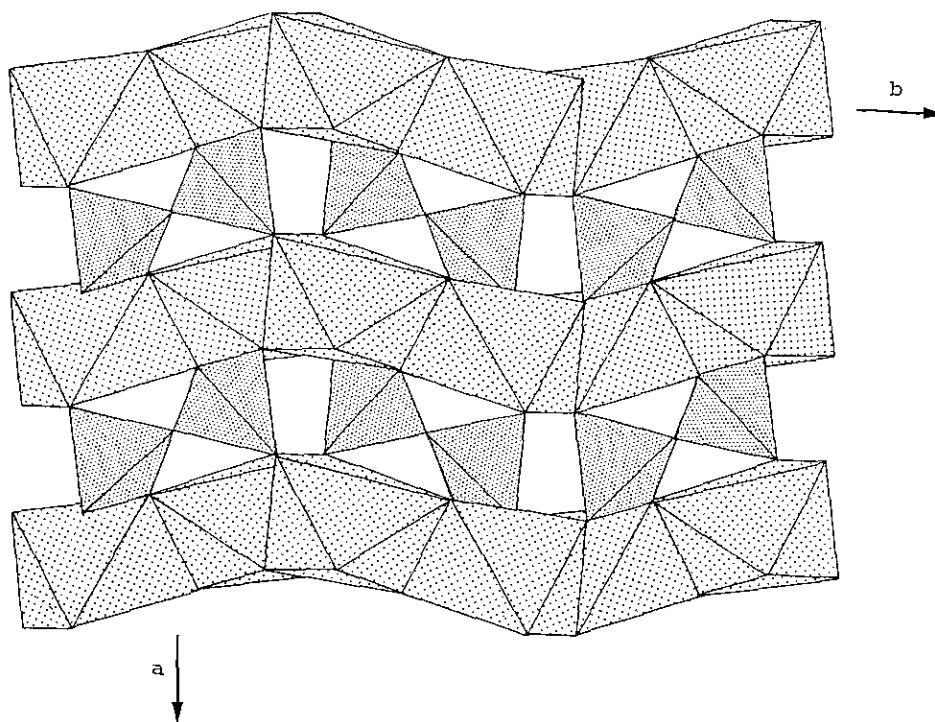

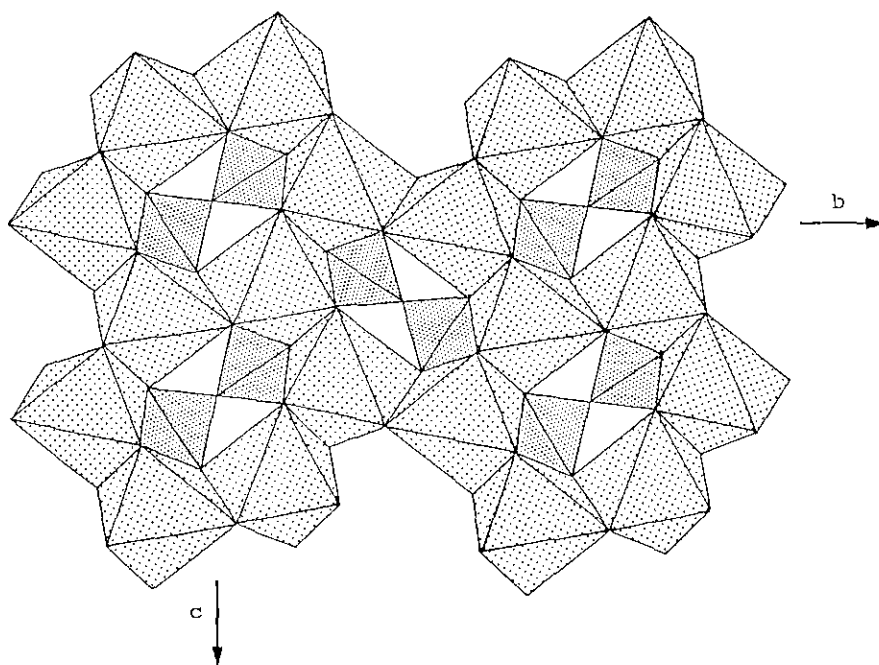FIG. 1. Projection of the structure onto the (001) plane.

FIG. 2. Projection of the structure onto the (100) plane.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The projections of the structure of Cd₂(VPO₇) onto the (001) plane (Fig. 1) and onto the (100) plane (Fig. 2) show that it consists of layers of edge-sharing CdO₆ octahedra parallel to (100) connected by layers of diphosphovanate groups VPO₇. The structure of this phase is very closely related to that of the divanadate Cd₂(V₂O₇) (3) whose structure (Fig. 3) is also built up from layers of edge-sharing CdO₆ octahedra connected through divanadate groups. In both structures the PVO₇ and V₂O₇ groups share their six corners with two different buckled layers of CdO₆ octahedra. However, the important difference between the two structures lies in the relative orientations of the ditetrahedral groups: the V₂O₇ groups are all parallel in Cd₂V₂O₇ (Fig. 3), whereas the VPO₇ groups form a herringbone array with respect to the c direction in Cd₂VPO₇ (Fig. 2).

In fact, both structures are governed by the tendency of cadmium to form close-packed layers of edge-sharing CdO₆ octahedra such as those in the rock salt structure of CdO. Starting from an anionic packed layer of CdO₆ octahedral [CdO₆/₃]∞ or [Cd₃O₆]∞ observed in the CdO structure (Fig. 4a), one can form cadmium deficient oxygen close-packed layers [Cd₂□O₆]∞ by eliminating one cadmium ion out of three in an ordered way (Fig. 4b); this results in regular six-sided windows forming into a hexagonal array. Similarly distorted hexagonal arrays of six-sided windows are observed for the [Cd₂□O₆]∞ octahedral layers of Cd₂(VPO₇) (Fig. 4c) and

Cd₂V₂O₇ (Fig. 4d). Note that, in both structures, the six-sided windows are similarly shaped (Fig. 4c–4d). Each is elongated with respect to the ideal hexagonal window (Fig. 4b). In the two structures, the largest dimensions of the six-sided windows are oriented differently, i.e., parallel in Cd₂V₂O₇ (Fig. 4d) and in a herringbone array in Cd₂VPO₇ (Fig. 4c). This large deformation of the windows is related to the buckling of the [Cd₂□O₆]∞ layers (Fig. 1) and is due to the great ability

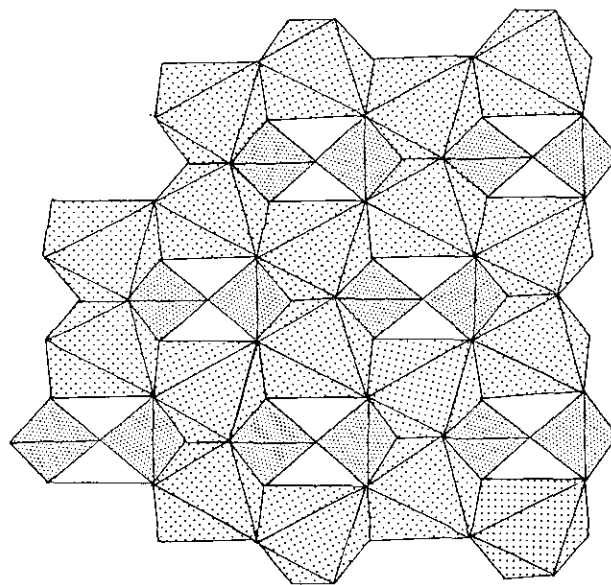FIG. 3. Projection of the Cd₂V₂O₇ structure along c.
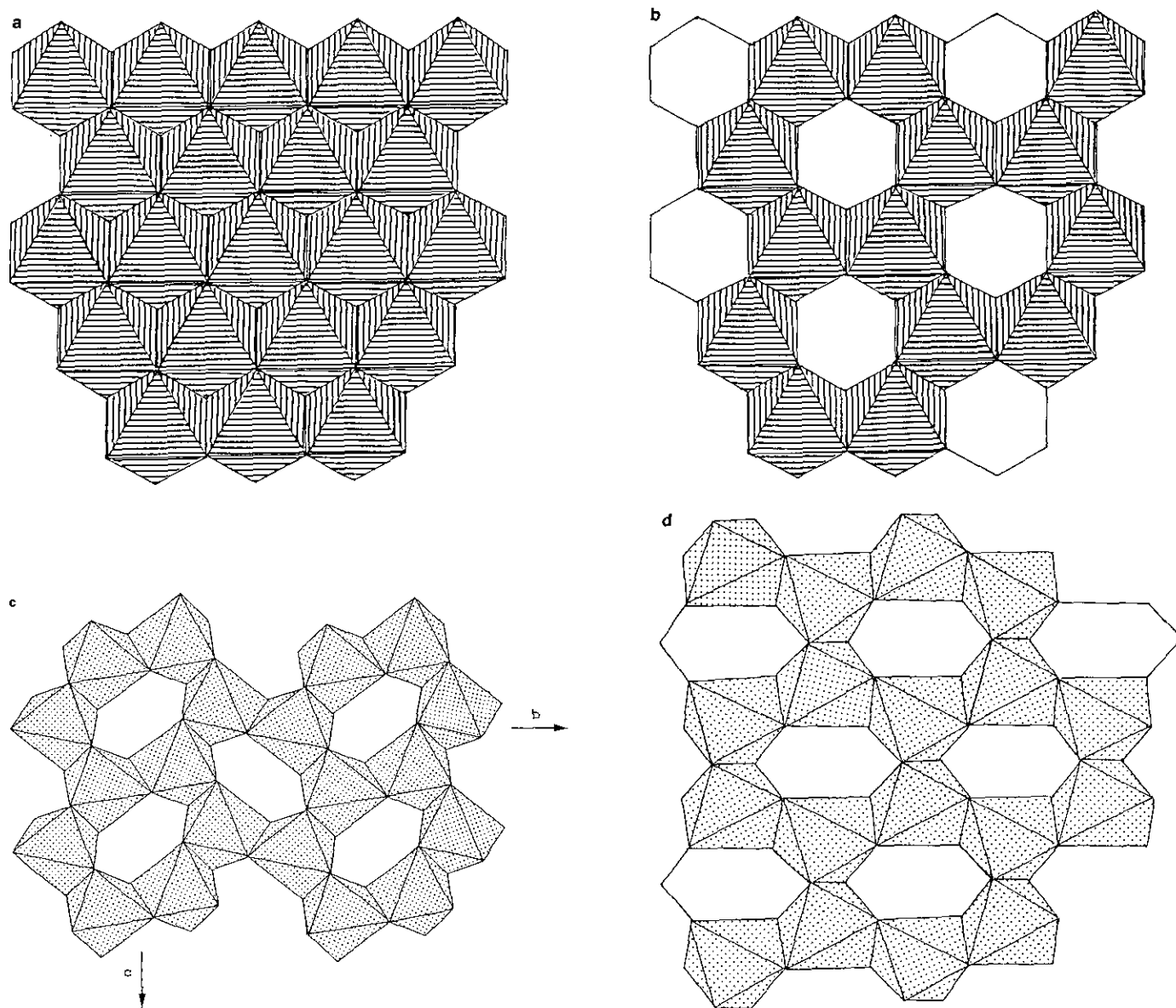
FIG. 4. (a) An anionic close-packed layer of edge-sharing CdO_6 octahedra $[CdO_{6/3}]$ or $[Cd_3O_6]$ observed in the CdO structure. (b) A cadmium deficient, oxygen close-packed layer $[Cd_2\square O_6]_x$ by elimination of one cadmium out of three in an ordered way. (c) The distorted hexagonal arrays of six-sided windows observed for the $[Cd_2\square O_6]$ octahedral layers of $Cd_2(VPO_7)$. (d) The distorted hexagonal arrays of six-sided windows observed for the $[Cd_2\square O_6]$ octrahedral layers of $Cd_2V_2O_7$.

of Cd(II) to accommodate very distorted CdO_6 octahedra. Indeed, one observes, for Cd_2VPO_7, O–O distances ranging from to 2.86 to 3.92 Å and O–Cd–O angles ranging from 76.6 to 118.3°, whereas the Cd–O bond lengths do not vary dramatically, ranging from 2.22 to 2.39 Å (Table 2). Similar phenomena are observed for $Cd_2V_2O_7$ (3).

The "V_2O" or "VPO" groups of the V_2O_7 (Fig. 3) or VPO_7 (Fig. 2) groups block the six-sided windows. They are oriented in such a way that the P–O–P bond is directed along the largest dimension of the window. Note also their staggered configuration in both structures.

The presence of vanadium and phosphorus on the same crystallographic site is rather rare and is unexpected owing to the significant size difference between these two cations. Nevertheless, it has been previously observed for (Na, K)(V, P)O$_3$ (4) and $Zn_3V_{0.5}P_{1.5}O_8$ (5). As noted above, all attempts to order V and P on two different sites in the noncentrosymmetric space group Pc were unsuccessful. Moreover, the edge (V, P)–O distances (Table 1) are very close to those expected from the average calculated for the P–O and V–O distances in diphosphate and divanadate groups, i.e., showing a significantly longer

(V, P)–O–(V, P) bridging bond and three shorter (V, P)–O–Cd distances. However, it is most probable that this observation is not due to a completely statistical distribution of V and P over the tetrahedral sites. One can indeed admit that the structure does not consist of V$_2$O$_7$ and P$_2$O$_7$ groups, but only of VPO$_7$ groups. The larger size of one V(V) atom in one tetrahedron of this group is compensated by the smaller size of P in the second tetrahedral site. The values of the B factors of (V, P)

and O(4) of 1.08 and 3.2 Å^2, respectively (Table 3), which correspond to amplitudes of 0.13 and 0.25 compared with the difference between the V–O and P–O distances in VO$_4$ and PO$_4$ tetrahedra (about 0.10 Å), are in agreement with this point of view. Thus, the observation of only one site for V and P may be the result of a random orientation of the VPO$_7$ group in the structure.

CONCLUDING REMARKS

This study shows the ability of diphosphovanadate groups to accommodate pseudo-close-packed layers of CdO$_6$ octahedra. The great flexibility of CdO$_6$ octahedra and the close relationship between the divanadate Cd$_2$V$_2$O$_7$ and the diphosphovanadate Cd$_2$VPO$_7$ suggest the possibility of synthesizing other original mixed frameworks in Cd–V–P–O-based systems.

TABLE 3
Bond Distances (Å) and Angles (°) in the Cd$_2$VPO$_7$ Structure

VP	O(1)	O(2)	O(3)	O(4)
O(1)	1.585(4)	2.612(5)	2.616(6)	2.621(4)
O(2)	111.2(2)	1.581(4)	2.595(5)	2.617(4)
O(3)	110.3(2)	109.2(2)	1.603(4)	2.649(4)
O(4)	108.4(2)	108.4(2)	109.2(2)	1.646(1)

Cd	O(1^i)	O(1^{ii})	O(2)	O(2^{ii})	O(3^{iv})	O(3^v)
O(1^i)	2.290(4)	3.204(6)	3.102(6)	2.893(6)	4.426(6)	3.050(6)
O(1^{ii})	89.2(1)	2.272(4)	2.893(6)	4.438(6)	3.358(6)	3.760(6)
O(2)	84.0(2)	77.6(1)	2.345(4)	2.997(6)	3.920(6)	4.697(6)
O(2^{ii})	79.0(1)	156.7(1)	81.2(1)	2.259(4)	3.478(6)	3.319(6)
O(3^{iv})	157.7(1)	96.7(1)	118.3(1)	101.8(2)	2.222(4)	2.864(6)
O(3^v)	81.2(1)	107.2(1)	164.3(1)	90.9(1)	76.6(2)	2.397(4)

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