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$RbVOPO_4$ and $CsVOPO_4$, Two Vanadyl(IV) Orthophosphates with an Intersecting Tunnel Structure and Discrete VO_5 Pyramids

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Two new ternary vanadyl(IV) orthophosphates, $RbVOPO_4$ and $CsVOPO_4$, have been prepared and their structures have been determined from single-crystal X-ray diffraction data. They crystallize in the orthorhombic space group $P2_12_12_1$ with $a = 7.8669(9)$, $b = 7.5848(8)$, $c = 8.3771(10)$ Å, $V = 499.8(1)$ Å^3, $Z = 4$, and $R = 0.029$ for $RbVOPO_4$, and $a = 7.3665(15)$, $b = 7.6146(15)$, $c = 9.8035(17)$ Å, $V = 549.9(2)$ Å^3, $Z = 4$, and $R = 0.029$ for $CsVOPO_4$. These two compounds consist of intersecting tunnels running along each axis, and the alkali metal cations are located at the intersection of these tunnels. Unlike other $AMOPO_4$ structures (A = alkali metals; M = Ti, V), the frameworks of the title compounds are built up from discrete VO_5 pyramids and PO_4 tetrahedra. Each VO_5 pyramid shares its four basal oxygen atom vertices with three different PO_4 tetrahedra. One of the phosphate groups is coordinated to the V atom as a bidentate ligand. These two closely related structures are not isomorphous, differing in the orientation of vanadyl oxygens. © 1993 Academic Press, Inc.

Introduction

Phosphates of stoichiometry $AMOPO_4$ (A = alkali metals, M = Ti or V) exhibit several structure types. The lithium compounds β-$LiVOPO_4$ (*1*) and $LiTiOPO_4$ (*2*) are isostructural. α-$LiVOPO_4$ (*3*), $NaVOPO_4$ (*4*), and α-$NaTiOPO_4$ (*5*) are structurally similar to the naturally occurring mineral $CaTiOSiO_4$ (*6*). These phosphates contain infinite chains of *trans*-corner-sharing MO_6 octahedra with alternating short and long M–O bonds. Adjacent octahedra in the chain of β-$LiVOPO_4$ have an eclipsed configuration in contrast to the staggered configuration in α-$LiVOPO_4$. All the above-mentioned phosphates crystallize in centrosymmetric space groups. The polymorph of $NaTiOPO_4$ isomorphous with $KTiOPO_4$ (KTP) (*7*) and $KVOPO_4$ (*8*), β-$NaTiOPO_4$, can be prepared in powder or single-crystal form by treating KTP powder or crystals with a molten $NaNO_3$ flux at 350°C (*5*). The structure of KTP is very interesting, since KTP is a well known second-harmonic generation (SHG) crystal for transforming infrared radiation from Nd : YAG lasers ($\lambda = 1.06$ μm) into the green part of the optical spectrum ($\lambda = 532$ nm). It possesses a high χ_{ijk} coefficient as well as mechanical strength and temperature stability and is phase-matchable for doubling 1.06-μm radiation (*9*, *10*). With respect to SHG, the crystals of interest are confined to the 20 noncentrosymmetric crystal classes. KTP crystallizes in the noncentrosymmetric orthorhombic space group $Pna2_1$ and is characterized by helices of TiO_6 octahedra. The octahedra in these helices are alternately *cis* and *trans* vertex sharing, building up a long–

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short–long chain of Ti–O bonds. The KTP structure is particularly accommodating with respect to isomorphous substitution. For example, Rb and Cs can be substituted for K in KTP.

To our knowledge, the two compounds that remain in this family, $CsVOPO_4$ and $RbVOPO_4$, have not been reported. The study of their crystal structures potentially allows for a better understanding of the structural chemistry of $AMOPO_4$. In this work, we present the synthesis and single-crystal X-ray structures of the title compounds, which are noncentrosymmetric and adopt a new structure type.

Experimental

Synthesis

$Rb_4V_2O_7$ (99.9%), $Cs_4V_2O_7$ (99.9%), V_2O_3 (99.9%), and P_2O_5 (99.9%), obtained from Cerac Inc., were used as received. Loading of the reactants was carried out in a glovebox which was flushed with nitrogen. Air-stable, small green crystals of $RbVOPO_4$ and $CsVOPO_4$ were obtained by heating pressed pellets of $Rb_4V_2O_7$ (or $Cs_4V_2O_7$), V_2O_3, and P_2O_5 (mole ratio 1 : 1 : 2) in sealed silica tubes at 785°C for 48 hr and then cooled to room temperature over 20 hr. Based on powder X-ray diffraction, single-phase polycrystalline $RbVOPO_4$ was prepared by heating the reaction mixture at 700°C for 48 hr with an intermediate grinding. The X-ray powder patterns were recorded at room temperature using a Rigaku powder diffractometer with filtered Cu radiation. Single-phase $CsVOPO_4$ has not been obtained under similar reaction conditions.

Single-Crystal X-Ray Diffraction

Two green crystals of dimensions 0.05 × 0.05 × 0.05 mm for $RbVOPO_4$ and 0.10 × 0.08 × 0.06 mm for $CsVOPO_4$ were selected for indexing and intensity data collection on an Enraf Nonius CAD4 diffractometer with κ-axis geometry using graphite-monochromated Mo$K\alpha$ radiation. Unit-cell parameters and orientation matrices were determined by a least-squares fit of 25 peak maxima (2θ = 12°–32°) for $RbVOPO_4$, and 24 peak maxima (2θ = 11°–25°) for $CsVOPO_4$. Axial oscillation photographs were taken to check the symmetry properties and unit-cell parameters. The intensity data were corrected for Lp and absorption effects. Corrections for absorption effects were based on ψ scans of a few suitable reflections with χ values close to 90°. On the basis of the systematic absences, statistical analyses of the intensity data, and successful solution and refinement of the structures, the space groups for both structures were determined to be $P2_12_12_1$. Both structures were solved by direct methods and successive Fourier synthesis, and were refined by full-matrix least-squares refinement based on F values. The absolute configurations of both structures were established by adding to the least-squares refinement one additional parameter, η (*11*). Refinement of η tended strongly to +1, indicating that the configurations were correct. The multiplicities of Rb and Cs were allowed to refine but did not deviate significantly from full occupancy. Therefore, the alkali metal sites were considered fully occupied in subsequent calculations. The final cycle of refinement including atomic coordinates, anisotropic thermal parameters, and a secondary extinction coefficient converged at R = 0.029 for both $RbVOPO_4$ and $CsVOPO_4$. Calculations were performed on a DEC MicroVAX 3600 computer system using NRCVAX programs (*12*). Neutral-atom scattering factors were used in the calculations and corrections for anomalous dispersion were applied. The crystallographic data are listed in Table I.

Description of the Structures and Discussion

Final atomic coordinates and thermal parameters are listed in Table II. Selected in-

TABLE I

CRYSTALLOGRAPHIC DATA FOR $RbVOPO_4$ AND $CsVOPO_4$

	$RbVOPO_4$	$CsVOPO_4$
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a	7.8669(9) Å	7.3665(15) Å
b	7.5848(8) Å	7.6146(15) Å
c	8.3771(10) Å	9.8035(17) Å
V	499.8(1) Å^3	549.9(2) Å^3
Z	4	4
ρ_{calcd}	3.287 g/cm^3	3.561 g/cm^3
Absorption coefficient	125.73 cm^{-1}	87.51 cm^{-1}
Trans coefficient	0.780–0.993	0.910–0.998
T	24°C	24°C
λ(Mo$K\alpha$)	0.7093 Å	0.7093 Å
$2\theta_{max}$	55°	55°
No. of unique reflections	527 ($I > 2.5\sigma(I)$)	663 ($I > 2.5\sigma(I)$)
No. of parameters refined	74	74
R	0.029	0.029
R_w	0.027	0.026
GOF	1.45	1.53
$(\Delta\rho)_{max}$; $(\Delta\rho)_{min}$	0.64; −0.77 e/Å^3	0.73; −0.90 e/Å^3

TABLE II

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR $RbVOPO_4$ AND $CsVOPO_4$

	x	y	z	B_{iso} (Å^2)[a]
		$RbVOPO_4$		
Rb	0.70553(12)	0.12829(12)	−0.02083(11)	1.41(3)
V	0.71277(20)	0.63765(21)	−0.12580(16)	0.98(6)
P	0.5686(3)	0.6245(4)	0.1552(3)	0.87(8)
O(1)	0.5825(8)	0.4806(7)	0.0252(8)	1.1(2)
O(2)	0.5812(8)	0.6801(9)	−0.2632(8)	1.7(3)
O(3)	0.8904(9)	0.8129(8)	−0.1847(8)	1.3(3)
O(4)	0.6766(9)	0.7711(7)	0.0743(7)	1.2(2)
O(5)	0.8561(9)	0.4363(8)	−0.1847(8)	1.2(2)
		$CsVOPO_4$		
Cs	0.87100(9)	0.13496(9)	0.16473(7)	1.73(3)
V	0.8878(3)	0.57196(22)	−0.04166(15)	1.1(6)
P	0.6580(3)	0.6306(4)	0.15445(25)	1.07(9)
O(1)	0.6585(10)	0.4860(10)	0.0418(7)	1.4(3)
O(2)	1.0506(9)	0.4611(11)	0.0202(8)	1.8(3)
O(3)	0.9840(9)	0.7616(10)	−0.1575(8)	1.6(3)
O(4)	0.8233(9)	0.7407(9)	0.1086(6)	1.4(3)
O(5)	0.8054(9)	0.4496(10)	−0.2053(7)	1.8(3)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

TABLE III

BOND DISTANCES AND BOND VALENCE SUMS (Σs) FOR $RbVOPO_4$ AND $CsVOPO_4$

		$RbVOPO_4$	
Rb–O(1)	2.868(6)	Rb–O(1)a	3.078(6)
Rb–O(2)c	2.918(7)	Rb–O(2)f	3.096(7)
Rb–O(3)e	3.118(7)	Rb–O(3)f	2.949(7)
Rb–O(4)e	2.833(6)	Rb–O(5)	2.957(7)
Rb–O(5)b	3.280(7)		
Σs(Rb–O) = 1.27			
V–O(1)	2.018(6)	V–O(2)	1.581(7)
V–O(3)	1.991(7)	V–O(4)	1.979(6)
V–O(5)	1.961(7)		
Σs(V–O) = 4.04			
P–O(1)	1.545(6)	P–O(3)d	1.501(7)
P–O(4)	1.554(7)	P–O(5)f	1.537(7)
Σs(P–O) = 5.01			
		$CsVOPO_4$	
Cs–O(1)	3.324(8)	Cs–O(1)a	3.072(7)
Cs–O(2)	3.151(8)	Cs–O(2)a	3.065(7)
Cs–O(2)c	3.410(8)	Cs–O(3)d	3.240(7)
Cs–O(4)e	3.072(7)	Cs–O(4)b	3.265(7)
Cs–O(5)a	3.288(7)		
Σs(Cs–O) = 1.11			
V–O(1)	1.988(7)	V–O(2)	1.587(7)
V–O(3)	1.969(7)	V–O(4)	2.012(7)
V–O(5)	1.952(7)		
Σs(V–O) = 4.06			
P–O(1)	1.559(7)	P–O(3)f	1.522(7)
P–O(4)	1.545(7)	P–O(5)d	1.529(7)
Σs(P–O) = 4.95			

Note. Symmetry codes for $RbVOPO_4$: (a) $0.5 + x, 0.5 - y, -z$; (b) $-0.5 + x, 0.5 - y, -z$; (c) $1 - x, -0.5 + y, -0.5 - z$; (d) $-0.5 + x, 1.5 - y, -z$; (e) $x, -1 + y, z$; (f) $1.5 - x, 1 - y, 0.5 + z$. $CsVOPO_4$: (a) $0.5 + x, 0.5 - y, -z$; (b) $2 - x, -0.5 + y, 0.5 - z$; (c) $1 - x, -0.5 + y, 0.5 - z$; (d) $1.5 - x, 1 - y, 0.5 + z$; (e) $x, -1 + y, z$; (f) $-0.5 + x, 1.5 - y, -z$.

teratomic distances and bond order sums (*13*) are given in Table III. Lists of structure factors and anisotropic thermal parameters have been deposited as supplementary materials. The coordination numbers of the alkali metals are determined on the basis of maximum gap in the alkali metal–oxygen distances ranked in increasing order. The maximum cation–anion distance, L_{max}, according to Donnay and Allmann (*14*) is also considered. Therefore, both the Rb^+ and Cs^+ cations are 9-coordinated, and the 10th Rb–O and Cs–O bond lengths are 3.598 and 3.650 Å, respectively. Bond valence sums for V and P are in good accordance with their formal oxidation states. The values for Rb and Cs are somewhat higher.

The most noticeable structural feature of the title compounds is the discrete VO_5 square pyramids in contrast to the infinite chains of corner-sharing MO_6 octahedra in the other compounds with the stoichiometry $AMOPO_4$ (A = alkali metals; M = V, Ti). The V atoms in vanadyl(IV) phosphates are frequently pseudo-octahedral, i.e., "5 + 1"-coordinate. In the title compounds, the next closest oxyen is at 3.46 and 3.57 Å, making the V atoms truly 5-coordinate, not 5 + 1. As indicated by Benhamada *et al.* (*15*), few phosphates involving only VO_5 pyramids have been reported. $A_2VOP_2O_7$ (A = K, Rb, Cs) (*16, 17*) and $Na_5V_2P_3O_{14} \cdot H_2O$ (*15*) have layered structures and seem to be the only examples of structure built up from pure VO_5 pyramids and PO_4 tetrahedra. The bidimensional character of the structures appears to favor the pure pyramidal coordination. In contrast, the frameworks of $RbVOPO_4$ and $CsVOPO_4$ show windows formed by the edges of four VO_5

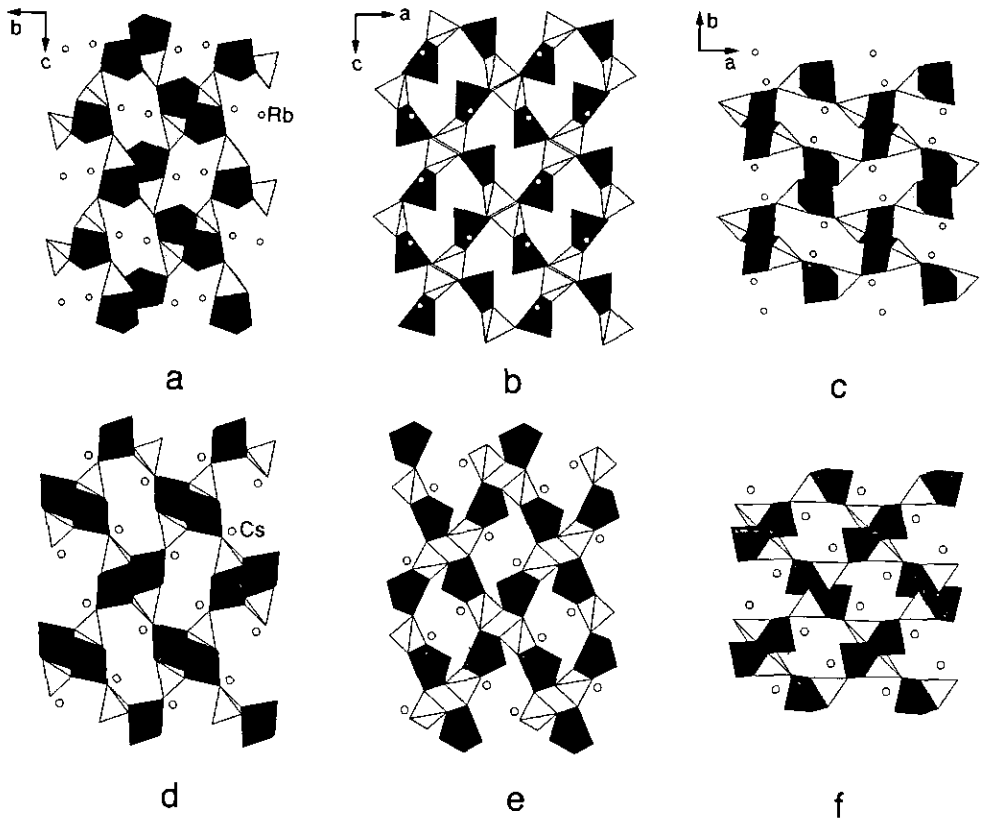

FIG. 1. Projection of the $RbVOPO_4$ and $CsVOPO_4$ structures along [100] (a,d), [010] (b,e), and [001] (c,f), showing the alkali metal positions (open circles), VO_5 pyramids (darker), and PO_4 tetrahedra (lighter).

pyramids and four PO_4 tetrahedra. These windows are stacked in such a way that they delimit tunnels running along the *a*, *b*, and *c* axes (Fig. 1). At the intersection of these tunnels, the alkali metal cations are located.

The four basal O atom vertices of each VO_5 pyramid are shared with three different PO_4 tetrahedra. One of the PO_4 tetrahedra is coordinated to the V atom as a bidentate ligand, i.e., the PO_4 tetrahedron shares one edge with a VO_5 pyramid. The resulting $[VPO_7]$ units are characterized by very short V–P distances of 2.614 Å in $RbVOPO_4$ and 2.602 Å in $CsVOPO_4$. These $[VPO_7]$ units are connected along [100] through O(3) forming $[VPO_6]_\infty$ helices. The helices sit on the 2_1 screw axes along [100] and are linked through O(5) to form a three-dimensional architecture. The ability of a PO_4 tetrahedron to share one edge with a VO_6 octahedron has been observed in $NaV_3P_3O_{12}$ (*18*), $Na_{1+x}V_4P_4O_{17}(OH)$ (*19*), and $K_6V_2P_4O_{16}$ (*20*). In $Zn_2VO(PO_4)_2$ each PO_4 tetrahedron shares one edge with a ZnO_5 pyramid (*21*). The V–O bond distances range from 1.581 to 2.018 Å and from 1.587 to 2.012 Å for $RbVOPO_4$ and $CsVOPO_4$, respectively. The shortest V–O distance involves the apical oxygen, O(2), which is also bonded to alkali metal cations. The VO_5 pyramids are strongly distorted as shown by the O · · · O distances of 2.361–3.005 Å in $RbVOPO_4$ and

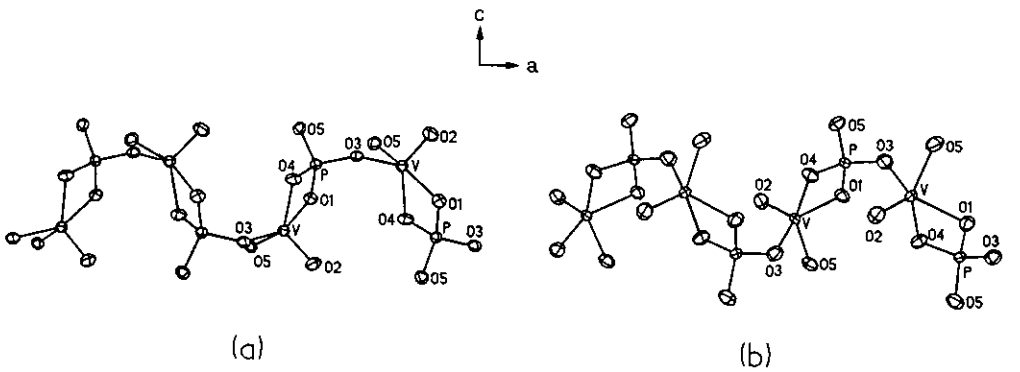

FIG. 2. Section of the $RbVOPO_4$ (a) and $CsVOPO_4$ (b) structures viewed along [010]. Thermal ellipsoids are shown at 60% probability.

2.377–2.920 Å in $CsVOPO_4$. The two O anions forming the common edge of the VO_5 pyramid and the PO_4 tetrahedron draw closer together so that the separation of the positive ions is somewhat increased and the two anions better shield the positive charges on the cations. The shortening of the shared edge provides evidence of a predominantly ionic bond. Each PO_4 tetrahedron shares four apices with three different VO_5 pyramids, leading to two longer P–O distances and two shorter ones. The longer P–O bonds involve the O atoms which form the common edges. The PO_4 tetrahedra are also strongly distorted as shown by the O · · · O distances of 2.361–2.573 Å in $RbVOPO_4$ and 2.377–2.572 Å in $CsVOPO_4$.

Although $RbVOPO_4$ and $CsVOPO_4$ have similar unit-cell parameters and crystallize in the same space group, their structures should be referred to as related structures rather than isomorphous structures because the atomic coordinates of O(2) are markedly different. To better illustrate the structural differences, sections of the views in Fig. 1(b) and 1(e) are shown in Fig. 2 in ball-and-stick representation. It is clear that the vanadyl groups (V–O(2)) in the two structures are directed toward opposite directions. Vanadyl orientation is not the only structural difference. For example, O(3) and O(4) have different coordination numbers in the two structures.

The lithium and sodium compounds $LiTiOPO_4$, α, β-$LiVOPO_4$, α-$NaTiOPO_4$, and $NaVOPO_4$ consist of infinite chains formed from trans-corner-sharing MO_6 octahedra. In β-$NaTiOPO_4$, $KVOPO_4$, $ATiOPO_4$ (A = K, Rb, Cs), the MO_6 octahedra in the infinite chains are alternately *cis* and *trans* vertex sharing. In contrast, $RbVOPO_4$ and $CsVOPO_4$ consist of discrete VO_5 pyramids and do not show close structural relationships with other members in the family. These results confirm the great adaptibility of vanadium oxide polyhedra and phosphate groups to forming numerous frameworks. However, it is not obvious to us why $AMOPO_4$ (A = Rb, Cs; M = Ti, V) adopt two rather different structure types. Further study on the rubidium and cesium compounds using different synthetic approaches is in progress.

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