

The Crystal Structure of LiVP_2O_7

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The structure of the vanadium(III) pyrophosphate LiVP_2O_7 was determined by single-crystal X-ray diffraction data. The title compound, which is isostructural with LiFeP_2O_7 , crystallizes in the monoclinic space group $P2_1$ (No. 4) with $a = 4.8048(6)$, $b = 8.113(1)$, $c = 6.9393(9)$ Å, $\beta = 109.01(1)^\circ$, $V = 255.75(7)$ Å³, $Z = 2$, and $R = 0.022$ for 607 unique reflections. The Li^+ cations, which are located in the tunnels which are formed by corner-sharing VO_6 octahedra and P_2O_7 groups, are each coordinated by four oxygen atoms in a geometry with the same general shape as that of SF_4 . The structure is discussed along with NaVP_2O_7 and CsVP_2O_7 . © 1990 Academic Press, Inc.

Introduction

There are a number of well-characterized compounds in the $M\text{-V-P-O}$ (M = metal cations) system containing vanadium in oxidation states less than +5. In the system $M\text{-V(IV)-P-O}$, LiVOPO_4 (1), $\text{M}_2\text{VOP}_2\text{O}_7$ (M = Cs, Rb, K) (2), $\text{M}_2\text{V}_3\text{P}_4\text{O}_{17}$ (M = Cs, Rb, K) (3), and $\text{PbV}_3\text{P}_4\text{O}_{17}$ (4) are known to exist. The phosphates of V(III) include $\text{Cs}_3\text{V}_3\text{P}_{12}\text{O}_{36}$ (5), $\text{CsV}_2\text{P}_5\text{O}_{16}$ (6), $\text{Na}_3\text{V}_2\text{P}_3\text{O}_{12}$ (7), and MVP_2O_7 (M = Cs, Rb, K, Na) (8). Recently, an interesting mixed-valence vanadium phosphate containing V(III) and V(II), $\text{NaV}_3\text{P}_3\text{O}_{12}$, was reported (9).

We have been interested in the alkali metal environment and the role it may play in affecting the crystal structures of these phosphates. The framework of MVP_2O_7 (M = Cs, Rb, K, Na) phases is built up from corner-sharing VO_6 octahedra and P_2O_7

groups. (Cs, Rb, K) VP_2O_7 and NaVP_2O_7 are isostructural with KFeP_2O_7 (10) and the high-temperature form of NaFeP_2O_7 (11), respectively. The two structure types are characterized by different configurations of the pyrophosphate groups to the octahedra. Interestingly, the same size effect of alkali metal on the structures of MMoP_2O_7 is also observed. Namely, MMoP_2O_7 (M = Cs, Rb, K) (12) is isostructural with KFeP_2O_7 ; NaMoP_2O_7 (13) and NaVP_2O_7 adopt a common structure; LiMoP_2O_7 (14) and LiFeP_2O_7 (15) are isostructural. Therefore, it would be interesting to know whether LiVP_2O_7 adopts the same structure as that of LiFeP_2O_7 . During attempts to prepare the lithium analogue of $\text{Cs}_2\text{V}_3\text{P}_4\text{O}_{17}$, we unexpectedly obtained single crystals of LiVP_2O_7 . Subsequently, a single-crystal X-ray diffraction study showed that the title compound was isostructural with LiFe

P₂O₇. In the present paper we report the crystallographic study of LiVP₂O₇. The structure is compared with those of NaVP₂O₇ and CsVP₂O₇.

Experimental

Preparation

The reaction of LiVO₃, VO₂, V, and P₂O₅ in a mole ratio of 4 : 1 : 1 : 4 in a sealed silica tube at 800°C for 12 hr followed by slow cooling to room temperature yields green crystals of LiVP₂O₇. On the basis of powder X-ray diffraction patterns it was possible to prepare LiVP₂O₇ as a pure, single-phase material by heating a pressed pellet containing stoichiometric amounts of Li₂O, V₂O₃, and P₂O₅ in a sealed silica tube at 900°C for 1 day with an intermediate grinding. The contents of Li, V, and P of a single-phase product were analyzed by using an ICP-AE spectrometer after dissolving the sample in aqua regia. Anal. Calcd for LiVP₂O₇: Li, 2.99%; V, 21.97%; P, 26.72%. Found: Li, 2.98%; V, 21.9%; P, 27.3%. The green, polycrystalline product appeared somewhat hygroscopic in laboratory atmosphere.

Single-Crystal X-Ray Diffraction Study

A green crystal having the dimensions of 0.25 × 0.15 × 0.10 mm was selected for indexing and intensity data collection on an Enraf-Nonius CAD4 diffractometer at room temperature. The crystal was protected from the atmosphere with a layer of epoxy cement. An absorption correction was based on ψ -scans of a few suitable reflections with χ values close to 90° (16). On the basis of the statistical analysis of the intensity data, the extinction condition $k = 2n + 1$ for $0k0$ reflections, and successful solution and refinement of the structure, the space group was determined to be $P2_1$. All calculations were performed on a DEC MicroVAX II computer system using the SHELXTL-Plus programs (17). Direct

methods were used to locate V, P, and a few O atoms, and the remainder of the atoms were found by using the Fourier synthesis section of the program. The multiplicity for Li was allowed to refine, but did not deviate significantly from full occupancy. Therefore, the Li site was considered fully occupied in the final cycles of least-squares refinement. Crystal data, intensity measurements, and structure refinement parameters are listed in Table I. Atomic coordinates and thermal parameters are listed in Table II. Selected bond distances and angles are given in Table III. Tables of observed and calculated structure factor amplitudes are available on request from the authors.

Description of the Structure and Discussion

The crystal structure of LiVP₂O₇, viewed along the a -axis, is shown in Fig. 1 and con-

TABLE I
SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENT, AND REFINEMENT PARAMETERS FOR LiVP₂O₇

Crystal data	
Crystal system	Monoclinic
Space group	$P2_1$ (No. 4)
Cell constants	$a = 4.8048(6)$, $b = 8.113(1)$, $c = 6.9393(9)$ Å, $\beta = 109.01(1)^\circ$, $V = 255.75(7)$ Å ³
Z	2
Density (calcd)	3.010 g/cm ³
Abs. coeff. (MoK α)	24.7 cm ⁻¹
Intensity measurement	
λ (MoK α)	0.70930 Å
Scan mode	$\theta/2\theta$
Scan rate	5.5°/min
Scan width	$0.65^\circ + 0.35^\circ \tan \theta$
Maximum 2θ	55°
Standard reflections	$140, 21\bar{5}, 124$ (measured every 1 hr, no decay)
Unique reflections measured	626
Structure solution and refinement	
Reflections included	607 ($I > 2.5 \sigma(I)$)
Parameters refined	100
Agreement factors ^a	$R = 0.022$, $R_w = 0.030$
GOF	0.913
$(\Delta\rho)_{\max}; (\Delta\rho)_{\min}$	0.98 e/Å ³ ; -0.96 e/Å ³

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2}$, where $w = 1.0 / (\sigma^2(F) + 0.00075 F^2)$.

TABLE II
POSITIONAL AND THERMAL PARAMETERS
FOR LiVP_2O_7

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} ($\text{\AA}^2 \times 100$) ^a
V	0.21539(14)	0.43900(0)	0.72831(10)	0.472(30)
P(1)	0.21012(22)	0.72275(15)	0.08485(16)	0.54(4)
P(2)	0.40041(22)	0.11997(14)	0.52131(15)	0.52(4)
O(1)	-0.1857(6)	0.4773(4)	0.5189(4)	0.80(13)
O(2)	0.3959(6)	0.6172(4)	0.6066(4)	0.78(14)
O(3)	0.0524(6)	0.2632(4)	0.8512(5)	1.10(14)
O(4)	0.2489(6)	0.2846(4)	0.5075(4)	0.73(13)
O(5)	0.1302(6)	0.6337(4)	0.8835(4)	0.94(14)
O(6)	0.6031(6)	0.3727(4)	0.9179(5)	1.04(14)
O(7)	0.4024(6)	0.5913(4)	0.2458(4)	0.85(14)
Li	0.1959(21)	0.8050(13)	0.6816(14)	2.4(4)

Anisotropic thermal parameters ($\text{\AA}^2 \times 100$) ^b						
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	0.59(3)	0.40(3)	0.50(3)	0.02(3)	0.28(2)	-0.03(3)
P(1)	0.59(4)	0.57(5)	0.45(4)	0.05(3)	0.17(3)	-0.06(3)
P(2)	0.68(5)	0.46(5)	0.46(4)	-0.01(4)	0.26(3)	-0.15(4)
O(1)	0.87(13)	0.85(16)	0.75(13)	0.12(11)	0.37(11)	-0.04(11)
O(2)	0.98(13)	0.81(14)	0.88(13)	0.03(11)	0.73(11)	-0.18(12)
O(3)	1.00(13)	0.98(15)	1.52(15)	0.13(12)	0.65(12)	0.62(12)
O(4)	0.65(12)	0.75(14)	0.89(13)	0.20(10)	0.39(10)	-0.23(12)
O(5)	1.33(14)	1.00(16)	0.53(13)	-0.05(12)	0.35(11)	-0.37(12)
O(6)	0.90(13)	0.82(14)	1.20(14)	0.15(11)	0.09(11)	-0.22(12)
O(7)	1.27(13)	0.69(14)	0.42(12)	0.08(12)	0.07(10)	0.19(11)
Li	2.8(4)	2.6(5)	2.0(4)	1.1(4)	1.1(4)	0.7(4)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

^b 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
BOND DISTANCES (\AA) AND BOND ANGLES ($^\circ$)
FOR LiVP_2O_7

Bond distances			
V-O(1)	2.024(3)	V-O(2)	2.008(3)
V-O(3)	1.952(3)	V-O(4)	2.026(3)
V-O(5)	2.027(3)	V-O(6)	1.973(3)
P(1)-O(3) <i>a</i>	1.503(3)	P(1)-O(5) <i>b</i>	1.507(3)
P(1)-O(6) <i>c</i>	1.516(3)	P(1)-O(7)	1.602(3)
P(2)-O(1) <i>d</i>	1.515(3)	P(2)-O(2) <i>e</i>	1.520(3)
P(2)-O(4)	1.509(3)	P(2)-O(7) <i>e</i>	1.602(3)
Li-O(1) <i>a</i>	1.961(10)	Li-O(2)	1.960(10)
Li-O(4) <i>a</i>	2.119(10)	Li-O(5)	2.069(10)

Bond angles			
O(1)-V-O(2)	91.62(12)	O(1)-V-O(3)	90.13(12)
O(1)-V-O(4)	81.00(11)	O(1)-V-O(5)	87.25(12)
O(1)-V-O(6)	172.62(12)	O(2)-V-O(3)	178.19(13)
O(2)-V-O(4)	88.59(12)	O(2)-V-O(5)	81.49(12)
O(2)-V-O(6)	91.90(12)	O(3)-V-O(4)	91.19(13)
O(3)-V-O(5)	99.10(13)	O(3)-V-O(6)	86.31(13)
O(4)-V-O(5)	164.41(12)	O(4)-V-O(6)	92.60(12)
O(5)-V-O(6)	99.69(12)	O(3) <i>a</i> -P(1)-O(5) <i>b</i>	113.15(18)
O(3) <i>a</i> -P(1)-O(6) <i>c</i>	112.69(18)	O(3) <i>a</i> -P(1)-O(7)	106.75(18)
O(5) <i>b</i> -P(1)-O(6) <i>c</i>	110.26(18)	O(5) <i>b</i> -P(1)-O(7)	104.02(17)
O(6) <i>c</i> -P(1)-O(7)	109.50(17)	O(1) <i>d</i> -P(2)-O(2) <i>e</i>	114.24(17)
O(1) <i>d</i> -P(2)-O(4)	112.28(16)	O(1) <i>d</i> -P(2)-O(7) <i>e</i>	102.62(17)
O(2) <i>e</i> -P(2)-O(4)	111.38(17)	O(2) <i>e</i> -P(2)-O(7) <i>e</i>	107.78(16)
O(4)-P(2)-O(7) <i>e</i>	107.88(16)	O(1) <i>a</i> -Li-O(2)	105.5(4)
O(1) <i>a</i> -Li-O(4) <i>a</i>	80.2(4)	O(1) <i>a</i> -Li-O(5)	170.0(5)
O(2)-Li-O(4) <i>a</i>	104.9(5)	O(2)-Li-O(5)	81.6(4)
O(4) <i>a</i> -Li-O(5)	91.2(4)	P(1)-O(7)-P(2) <i>c</i>	128.61(21)

Note. Symmetry codes: *a*: $-x, 0.5 + y, 1 - z$; *b*: $x, y, -1 + z$; *c*: $1 - x, 0.5 + y, 1 - z$; *d*: $-x, -0.5 + y, 1 - z$; *e*: $1 - x, -0.5 + y, 1 - z$.

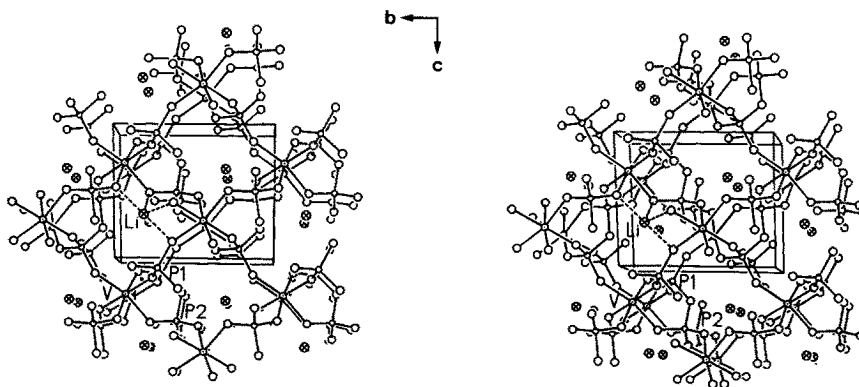


FIG. 1. A stereoscopic view of the LiVP_2O_7 structure along the *a*-axis. The Li, V, P, and O atoms are represented by cross-hatched, dotted, small, and large open circles, respectively. The bonds between a Li atom and the O atoms are denoted by dashed lines.

tains tunnels where the Li^+ cations are located. The framework of LiVP_2O_7 is built up from corner-sharing VO_6 octahedra and P_2O_7 groups. The tunnels result from stacking of rings formed by the edges of three octahedra and four tetrahedra. Similar rings were also found in CsVP_2O_7 , but the rings of adjacent layers have different orientations and are related by *c*-glide planes perpendicular to the *b*-axis. The framework of NaVP_2O_7 forms tunnels along the [101] di-

rection where the Na^+ cations reside. The window of each tunnel in NaVP_2O_7 appears rather different from those in the lithium and cesium compounds. Figures 2a–2c show how the VO_6 octahedra are connected to the P_2O_7 groups along the tunnel direction in each of the three structure types. In each case a VO_6 octahedron is linked to five different P_2O_7 groups. The two adjacent VO_6 octahedra in the Li, Na, and Cs compounds are related by the unit cell repeat

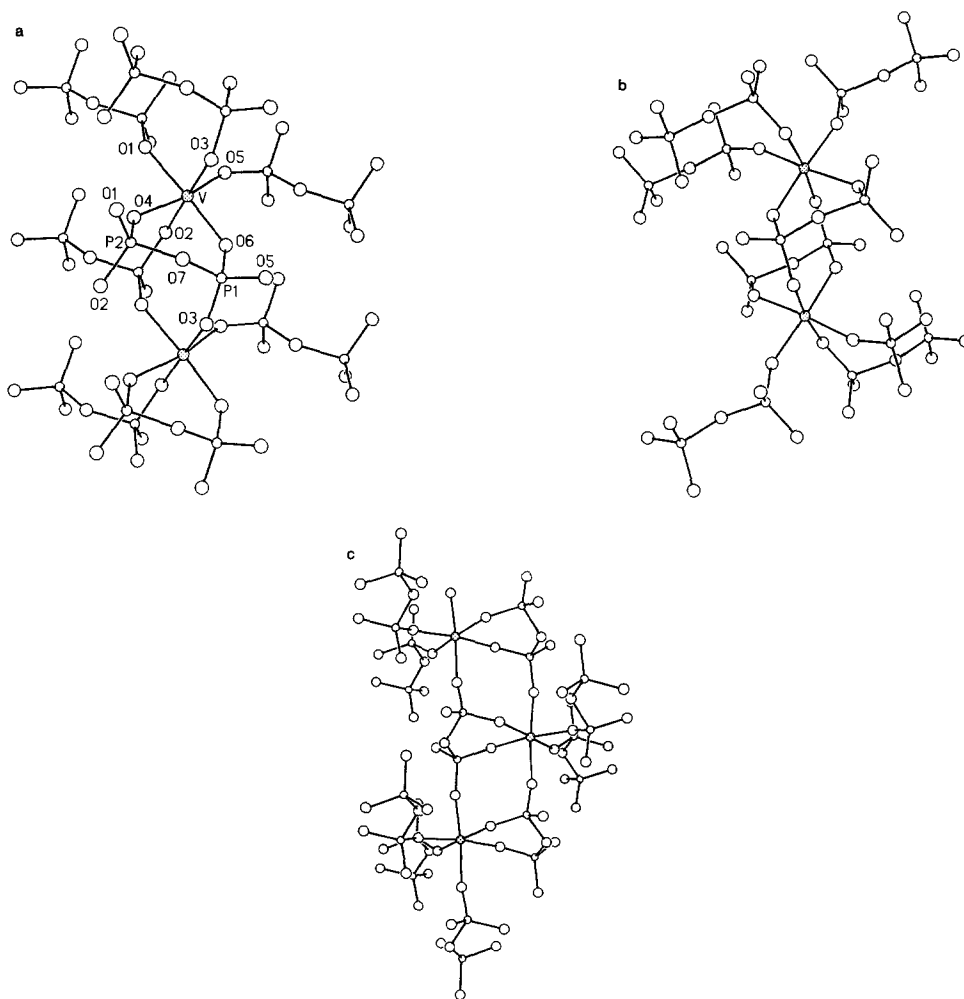


FIG. 2. The coordination of P_2O_7 ligands around VO_6 octahedra in (a) LiVP_2O_7 , (b) NaVP_2O_7 , and (c) CsVP_2O_7 . The V, P, and O atoms are represented by dotted, small open, and large open circles, respectively. Each is a view perpendicular to the tunnel direction.

along the a -axis, a center of symmetry, and a c -glide plane, respectively. In the cesium compound the connectivity of the P_2O_7 groups to the VO_6 octahedra is particularly interesting. The height of a P_2O_7 corresponds to that of an octahedron, and one P_2O_7 group alternates with an octahedron, thus forming a double chain along the tunnel direction. In all the three structure types, each P_2O_7 group shares its six corners with five different VO_6 octahedra and is bonded to one of the VO_6 octahedra through bidentate bonding. The PO_4 tetrahedra of a P_2O_7 group in the Li and the Na compounds point in the same direction and are in a semiclipped configuration. In contrast, the two PO_4 tetrahedra of a P_2O_7 group in CsVP_2O_7 point in opposite directions and are in a staggered configuration.

The VO_6 octahedron in LiVP_2O_7 is distorted as shown by the O–V–O bond angles in Table III. The V–O bond distances are similar to those found in CsVP_2O_7 and NaVP_2O_7 and the average value is 2.002 Å. The sum of bond strengths using the formula derived by Brown and Altermatt (18) leads to 2.99 for the V atom, which is in excellent agreement with the formal oxidation state +3 of V in this compound. In the PO_4 tetrahedra belonging to each pyrophosphate group the P atoms are displaced away from the bridging oxygen atom, O(7), so that one longer and three shorter P–O bonds are formed. Bond valence sums of the P–O bonds are 5.06 and 5.00 for P(1) and P(2), respectively. Both the PO_4 tetrahedra are slightly distorted as shown by the O–P–O bond angles in Table III. The P–O–P bond angle involving the bridging oxygen atom of the P_2O_7 group in LiVP_2O_7 (128.6°) is a little greater than that in the Cs compound (126.2°), but much smaller than that in the sodium compound (133.3°).

One of the major interests of the structure of LiVP_2O_7 involves the Li^+ environment in the tunnel. The coordination number of Li^+ can be determined by the

maximum bond distance for Li–O using the procedure by Donnay and Allmann (19) with the revised radii of Shannon (20) leading to 2.67 Å. Accordingly, the Li^+ ion is coordinated by four oxygen atoms at distances ranging from 2.12(1) to 1.97(1) Å. It should be noted that the fifth neighboring oxygen atom, O(6), is located at 2.68(1) Å. The very large gap between the fifth and the fourth bond suggests that one may, as an approximation, consider the coordination of Li as four instead of five. The bond strength sum (Σs) of four Li–O bonds is 0.89(2), which is close to the expected value 1.0. The esd for Σs is calculated by considering one esd for each Li–O bond distance. The four oxygen neighbors at about 2.0 Å define a geometry which is similar to SF_4 . The axial bonds of the LiO_4 unit bend toward the equatorial oxygen, O(4), and are approximately equal. The Li ion is located at the periphery of the tunnels because of its small ionic radius. The shortest diameter of the puckered heptagonal window of the tunnel is 4.01 Å, the distances between O(2) and O(7), which is greater than twice the sum of the Li^+ and O^{2-} radii. Thus the geometrical features of the skeleton satisfy the criterion for Li-ion transport.

This structural study also shows that the P_2O_7 group is very adaptive to the bonding requirements of the other groups in the structures by adjusting the P–O–P bond angle and the configurations of two PO_4 tetrahedra. The size of the alkali metal cation must play an important role in the crystal structures of MVP_2O_7 . To understand the crystal structures of MVP_2O_7 as a function of the size of alkali metal is part of our ongoing research.

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