

The Crystal Structure of $\text{KH}_5(\text{PO}_4)_2$

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$\text{KH}_5(\text{PO}_4)_2$ crystallizes in space group $P2_1/c$ with $a=7.849$, $b=10.688$, $c=9.557$ Å, $\beta=114.35^\circ$ and $Z=4$. The structure has been determined by means of three-dimensional Patterson and electron density summations. A final R value of 0.075 was obtained using 1246 independent reflections.

The structure is built up from phosphate tetrahedra connected by strong hydrogen bonds, the average $\text{O}-\text{O}$ distance being 2.562 Å, though one distance is as short as 2.405 Å. Approximate positions of the hydrogen atoms could be deduced from a difference electron density summation.

It was possible to distinguish different kinds of bonds within the PO_4 groups, viz., $\text{P}-\text{OH}$ bonds with lengths of 1.549, 1.550, 1.559, and 1.560 Å, and $\text{P}-\text{O}$ bonds of 1.490 and 1.502 Å. The two oxygen atoms which are involved in the short hydrogen bond have $\text{P}-\text{O}$ distances of 1.512 and 1.515 Å.

Recently, the chemistry of semi-metallic orthophosphates of the type $\text{M}^+\text{H}_5(\text{PO}_4)_2$, where $\text{M}^+=\text{NH}_4$, Na, K, Rb, and Cs, has been studied. Methods of preparation, stability conditions and reactivity have been reported¹ and cell dimensions have been determined,^{2,3} but, hitherto, no crystal structure investigation has been performed.

Since there is only one metal(I) ion per two phosphate groups in the structure, the question arises whether there is one H_3PO_4 molecule and one H_2PO_4^- ion, or whether the two phosphate groups are equivalent. Previous investigations of phosphoric acid^{4,5} and compounds containing H_2PO_4^- ions, like $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$,⁶ $\text{N}_2\text{H}_5\text{H}_2\text{PO}_4$,⁷ and $\text{N}_2\text{H}_6(\text{H}_2\text{PO}_4)_2$,⁸ have shown that it is possible to distinguish between $\text{P}-\text{OH}$ and $\text{P}-\text{O}$ bonds on the basis of the bond lengths. From this point of view it seemed interesting to study the crystal structure of a semi-metallic orthophosphate.

For the investigation, crystals of suitable size for an X-ray single crystal analysis were prepared of the potassium salt, $\text{KH}_5(\text{PO}_4)_2$. Crystals of this

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compound have been grown with dimensions as large as $5 \times 5 \times 5 \text{ cm}^3$, and a Raman spectroscopic study has been started⁹ which provides additional reasons for the choice of potassium as cation.

EXPERIMENTAL

The method of preparation of $\text{KH}_5(\text{PO}_4)_2$ has been described earlier.¹ The unit cell dimensions, the space group and the observed and calculated densities have also been reported in a previous paper.²

Crystals of $\text{KH}_5(\text{PO}_4)_2$ are not completely stable when mounted in air and irradiated for a long period of time. If, however, they are mounted in a glass capillary, the crystals appear to be unaffected, which may indicate that they are slightly hygroscopic. The crystal selected for the investigation did not have completely well-defined faces, but could, as a good approximation, be described as indicated in Table 1.

Table 1. Dimensions of the crystal used for the intensity measurements, given as indices of the boundary planes and the distances to these planes from an internal origin.

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (mm)
1	0	0	0.080
-1	0	0	0.080
0	1	0	0.150
0	-1	0	0.150
0	0	1	0.045
0	0	-1	0.045

Weissenberg equi-inclination films corresponding to the $h0l-h9l$ reflections were registered with $\text{CuK}\alpha$ radiation. A summary of the crystallographic data is given in Table 2.

Table 2. Crystallographic data for $\text{KH}_5(\text{PO}_4)_2$.

Unit cell ²	Monoclinic with
	$a = 7.849(2) \text{ \AA}$
	$b = 10.688(2) \text{ \AA}$
	$c = 9.557(2) \text{ \AA}$
	$\beta = 114.35(2)^\circ$
	$V = 730.30 \text{ \AA}^3$
Formula weight	$M = 936.16$
Density (20°C) ²	$D_m = 2.128(2) \text{ g.cm}^{-3}$
	$D_x = 2.128 \text{ g.cm}^{-3}$
Systematic absences	$h0l$ when $l = 2n + 1$
	$0k0$ when $k = 2n + 1$
Space group	$P2_1/c$
General point positions	$\pm(x, y, z); \pm(-x, \frac{1}{2} + y, \frac{1}{2} - z)$
Crystal habit	White plates
Linear absorption coefficient	$\mu = 105.8 \text{ cm}^{-1}$ ($\text{CuK}\alpha, \lambda = 1.5418 \text{ \AA}$)

The intensities were estimated visually by comparison with an intensity scale prepared from timed exposures of a suitable reflection from the crystal. The values from the six films, recorded for each layer line, were scaled together using the program SCALE, with weights according to the formula $w = [1.0 + [(I - 12.0)/6.0]]^{-1}$. The inter-layer scale factors were initially chosen in agreement with the corresponding exposure times.

A total of 1395 independent reflections were registered, 149 of which were too weak to be measured.

STRUCTURE ANALYSIS AND REFINEMENT

All independent reflections, corrected for Lorentz and polarization effects, were used to calculate a three-dimensional Patterson synthesis. The positions of the potassium and phosphorus atoms were deduced from the Patterson peaks, the atoms occupying three general positions (K, P₁, and P₂) in space group *P*2₁/*c*. The oxygen atoms were then located from subsequent electron density calculations. A preliminary isotropic refinement of the structure, including the refinement of separate scale factors between the layer lines, gave an *R* value of 0.133 ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$).

The reflections were then corrected for absorption and extinction, using the formula given by Zachariasen,¹⁰ applied as described by Åsbrink and Werner,¹¹ with *c* = 0.008. The isotropic refinement was then repeated, and, especially for the strong reflections, improved agreement between the calculated and observed structure factors was obtained (*R* = 0.108). Eight of the strongest reflections, however, still suffered from errors which had not been accounted for, and were therefore excluded from all further refinements.

In the final refinement, in which allowance was made for anisotropic temperature vibrations, the *R* value converged to 0.075 (0.092 including the eight strong reflections omitted and all unobserved reflections). The resulting positional and thermal parameters are given in Table 3, and the corresponding

Table 3. Final atomic parameters for KH₂(PO₄)₂. The anisotropic temperature factor is: $\exp[-2\pi^2(h^2a^{*2} U_{11} + k^2b^{*2} U_{22} + l^2c^{*2} U_{33} + hka^*b^* U_{12} + hla^*c^* U_{13} + klb^*c^* U_{23})]$. Standard deviations of the least significant figure in parentheses.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> Å ²		
K	0.7906 (2)	0.3769 (1)	0.3607 (1)	2.85	(5)	
P ₁	0.3529 (2)	0.2256 (1)	0.2121 (1)	2.04	(5)	
P ₂	0.8895 (2)	0.0703 (1)	0.2712 (1)	2.21	(5)	
O ₁	0.1463 (5)	0.2162 (4)	0.1101 (4)	2.96	(11)	
O ₂	0.4584 (5)	0.2883 (4)	0.1249 (4)	2.63	(10)	
O ₃	0.4242 (5)	0.0880 (4)	0.2478 (5)	2.90	(11)	
O ₄	0.4035 (6)	0.2994 (4)	0.3575 (4)	2.66	(10)	
O ₅	0.7749 (7)	-0.0032 (4)	0.1207 (5)	3.63	(13)	
O ₆	0.0808 (6)	0.0028 (4)	0.3455 (5)	3.42	(12)	
O ₇	0.9180 (5)	0.1985 (4)	0.2166 (4)	2.91	(11)	
O ₈	0.7924 (5)	0.0769 (4)	0.3762 (4)	2.46	(10)	
	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
K	0.041 (1)	0.033 (1)	0.032 (1)	-0.002 (1)	0.023 (1)	0.006 (1)
P ₁	0.027 (1)	0.032 (1)	0.023 (1)	0.003 (1)	0.023 (1)	-0.004 (1)
P ₂	0.031 (1)	0.026 (1)	0.027 (1)	-0.001 (1)	0.026 (1)	0.000 (1)
O ₁	0.030 (2)	0.062 (4)	0.029 (2)	0.003 (4)	0.023 (3)	0.002 (4)
O ₂	0.038 (2)	0.036 (3)	0.028 (2)	-0.012 (3)	0.031 (3)	-0.006 (3)
O ₃	0.036 (2)	0.023 (3)	0.049 (3)	0.001 (3)	0.035 (3)	-0.005 (4)
O ₄	0.045 (2)	0.033 (3)	0.023 (2)	0.010 (3)	0.027 (3)	-0.001 (3)
O ₅	0.075 (2)	0.040 (3)	0.029 (2)	0.034 (4)	0.041 (4)	0.005 (4)
O ₆	0.049 (3)	0.055 (3)	0.040 (2)	0.049 (4)	0.055 (4)	0.031 (4)
O ₇	0.034 (2)	0.022 (3)	0.057 (3)	0.000 (3)	0.042 (4)	0.004 (4)
O ₈	0.028 (2)	0.042 (3)	0.031 (3)	0.006 (3)	0.027 (3)	0.006 (3)

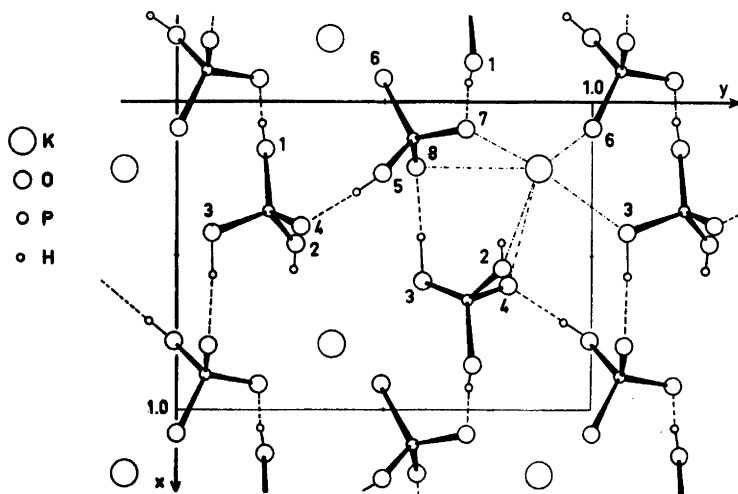


Fig. 1. A projection along the c axis showing all atoms with $0 \leq z \leq 0.5$. Hydrogen bonds are indicated as $\text{---} \circ \text{---}$, and the potassium co-ordination as $\text{---} \cdot \text{---}$.

containing $3/5$ of the hydrogen bonds and the major part of the K–O interactions run perpendicular to the c axis throughout the structure (*cf.* Fig. 1). Apart from van der Waals forces, these sheets are held together by hydrogen bonds and weak electrostatic forces (*cf.* Fig. 2).

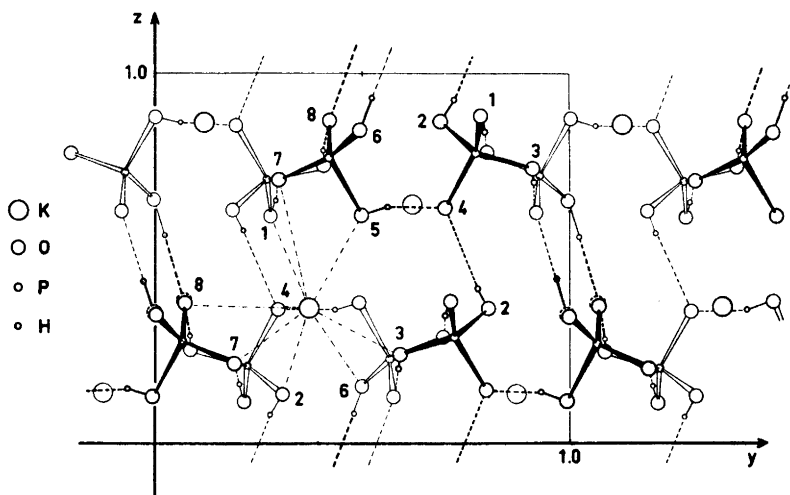


Fig. 2. A projection along the a axis. Phosphate groups having $0.5 < x < 1.0$ have been drawn with full lines. Hydrogen bonds and K–O interaction are indicated as in Fig. 1.

Within the two independent phosphate ions, the P–O distances range from 1.490 Å to 1.560 Å with a mean value of 1.530 Å. This value is slightly shorter than the mean value of 1.55 Å calculated for fourteen different monophosphates, reviewed by Liebau.¹⁴ This is, however, not unreasonable, since the influence of the hydrogen bonds on the P–O bonds is different in different phosphates, as already pointed out, for example by Jones and Cruickshank.⁶

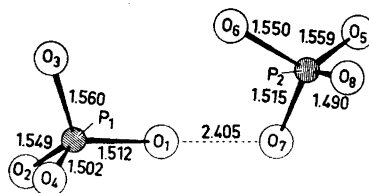
Since the expected bond length for a single P–O bond, as calculated from the normal covalent radii, is 1.71 Å,¹⁴ it is generally accepted that π bonds are formed between the $2p_{\text{O}}$ and the $3d_{\text{P}}$ orbitals. The conditions necessary for the formation of such $p_{\pi} - d_{\pi}$ bonds in phosphorus compounds have been extensively discussed by Hudson,¹⁵ and according to his study, a P–O bond distance of 1.53 Å should correspond to an approximate π bond order of 0.5 Å.

Four of the eight different P–O bond distances in $\text{KH}_5(\text{PO}_4)_2$ are significantly longer than the others (*cf.* Table 6 and Fig. 3). The corresponding

Table 6. Distances (Å) and angles ($^{\circ}$) in the phosphate ion, $\text{H}_5(\text{PO}_4)_2^-$ (standard deviations in parentheses).

$\text{P}_1 - \text{O}_1$	1.512 (4)	$\text{P}_2 - \text{O}_5$	1.559 (4)
$\text{P}_1 - \text{O}_2$	1.549 (4)	$\text{P}_2 - \text{O}_6$	1.550 (5)
$\text{P}_1 - \text{O}_3$	1.560 (4)	$\text{P}_2 - \text{O}_7$	1.515 (4)
$\text{P}_1 - \text{O}_4$	1.502 (4)	$\text{P}_2 - \text{O}_8$	1.490 (4)
$\text{O}_1 - \text{P}_1 - \text{O}_2$	110.6 (2)	$\text{O}_5 - \text{P}_2 - \text{O}_6$	105.6 (3)
$\text{O}_1 - \text{P}_1 - \text{O}_3$	105.7 (2)	$\text{O}_5 - \text{P}_2 - \text{O}_7$	104.4 (2)
$\text{O}_1 - \text{P}_1 - \text{O}_4$	115.7 (2)	$\text{O}_5 - \text{P}_2 - \text{O}_8$	112.6 (3)
$\text{O}_2 - \text{P}_1 - \text{O}_3$	107.6 (2)	$\text{O}_6 - \text{P}_2 - \text{O}_7$	109.0 (2)
$\text{O}_2 - \text{P}_1 - \text{O}_4$	105.9 (2)	$\text{O}_6 - \text{P}_2 - \text{O}_8$	112.4 (2)
$\text{O}_3 - \text{P}_1 - \text{O}_4$	111.0 (2)	$\text{O}_7 - \text{P}_2 - \text{O}_8$	112.3 (2)
$\text{O}_1 - \text{O}_2$	2.517 (5)	$\text{O}_5 - \text{O}_6$	2.476 (6)
$\text{O}_1 - \text{O}_3$	2.449 (6)	$\text{O}_5 - \text{O}_7$	2.429 (6)
$\text{O}_1 - \text{O}_4$	2.553 (5)	$\text{O}_5 - \text{O}_8$	2.537 (6)
$\text{O}_2 - \text{O}_3$	2.509 (5)	$\text{O}_6 - \text{O}_7$	2.496 (6)
$\text{O}_2 - \text{O}_4$	2.585 (5)	$\text{O}_6 - \text{O}_8$	2.527 (6)
$\text{O}_3 - \text{O}_4$	2.524 (6)	$\text{O}_7 - \text{O}_8$	2.495 (6)

Fig. 3. The two independent PO_4 tetrahedra in $\text{KH}_5(\text{PO}_4)_2$.



oxygen atoms, O_2 , O_3 , O_5 , and O_6 , can therefore be considered to belong to hydroxyl groups. The P–OH bond distances in $\text{KH}_5(\text{PO}_4)_2$ of 1.549–1.560 Å (mean value 1.555 Å) are in close agreement with the results found in

$\text{H}_3\text{PO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ⁵ with six independent P—OH distances of 1.542–1.561 Å and in $\text{N}_2\text{H}_5\text{H}_2\text{PO}_4$ ⁷ and $\text{N}_2\text{H}_6(\text{H}_2\text{PO}_4)_2$ ⁸ with corresponding distances of 1.550–1.573 Å. The P—OH bonds reported in H_3PO_4 ⁴ (1.56₈–1.57 Å), and in CaHPO_4 and $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ⁶ (1.57₆–1.62₃ Å) are not significantly longer than these in $\text{KH}_5(\text{PO}_4)_2$, since the accuracy of these distances is approximately ± 0.02 Å.

Further support that O_2 , O_3 , and O_5 represent hydroxyl groups is provided by the positions indicated for the adjacent hydrogen atoms, since these yield probable O—H distances (*cf.* Table 5). In the neighbourhood of O_6 , no definite hydrogen peak could be detected in the final difference electron density maps, but since only four of the five hydrogen atoms in the structure have been identified, it is reasonable to assume that the missing one is situated close to O_6 .

Among the four shorter P—O bond distances it can only be stated, that P_2-O_8 is significantly shorter than P_1-O_1 and P_2-O_7 (*cf.* Table 6), and, hence, O_8 should correspond to a “keto” oxygen. It is not possible to decide on which of the remaining three oxygen atoms the fifth hydrogen atom is situated in terms of the P—O bond distances alone. However, there were indications in the final ($F_o - F_c$) maps that it might be attached to O_1 . The mean “keto” P—O bond distance in $\text{KH}_5(\text{PO}_4)_2$ would then be 1.502 Å (calculated for O_4 , O_7 , and O_8) which is in good agreement with the corresponding values found in other monophosphates, for example in $\text{N}_2\text{H}_5\text{H}_2\text{PO}_4$ (1.505 Å), in $\text{N}_2\text{H}_6(\text{H}_2\text{PO}_4)_2$ (1.509 Å), and in $\text{H}_3\text{PO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (1.490 Å).

The localisation of the hydrogen atoms based on the P—O bond distances and indications in the difference electron density maps, is in good agreement with the hydrogen bond net which can be deduced from the short intermolecular O—O distances. The existence of five such distances below 2.65 Å indicates where each hydrogen bond ought to be situated, since the next shortest intermolecular O—O distance is as long as 3.307 Å. The most probable arrangement of the hydrogen bonds is given in Table 7 (*cf.* also Figs. 1 and 2). How-

Table 7. Distances (Å) and angles (°) describing the hydrogen bonds in $\text{KH}_5(\text{PO}_4)_2$ (standard deviations in parentheses).

	O—H	O...H	O—O	$\angle \text{P—O—H}$	$\angle \text{O—H...O}$
$\text{P}_1-\text{O}_1-\text{H}_1 \cdots \text{O}_7$	0.90	1.51	2.405 (5)	118.4	174
$\text{P}_1-\text{O}_2-\text{H}_2 \cdots \text{O}_4$	0.99	2.09	2.585 (5)	149.8	108
$\text{P}_1-\text{O}_3-\text{H}_3 \cdots \text{O}_8$	0.97	1.68	2.636 (5)	108.6	170
$\text{P}_2-\text{O}_5-\text{H}_5 \cdots \text{O}_4$	0.88	1.72	2.587 (6)	111.0	170
$\text{P}_2-\text{O}_6-\text{H}_6 \cdots \text{O}_8$			2.596 (5)		

ever, although H_1 is found to be close to O_1 , it is tempting to suggest that the extremely short O_1-O_7 distance of 2.405(5) Å corresponds to a symmetrical hydrogen bond. In view of the fact that the determination of the hydrogen atom positions is rather uncertain, the location of H_1 alone ought not to exclude the possibility of a symmetrical hydrogen bond between O_1 and O_7 . The existence of such a bond is also supported by the distances P_1-O_1 and

P_2-O_7 , which are approximately the same, and both significantly shorter than pure $\text{P}-\text{OH}$ bonds. They are also slightly longer than the pure "keto" bonds, although both O_4 and O_8 serve as acceptors in two hydrogen bonds (*cf.* Table 7).

However, in spite of the fact that the O_1-O_7 hydrogen bond is one of the shortest ever found (*cf. e.g., Structural Inorganic Chemistry* by Wells¹⁶ or review articles by Blinc and Hadzi¹⁷ and Hamilton¹⁸), this fact alone cannot provide proof for a symmetrical hydrogen bond, since no simple relationship between the hydrogen bond type and the corresponding $\text{O}-\text{O}$ distance has been found.¹⁷ Further information could probably be obtained from a neutron diffraction investigation, which will be commenced in the near future.

On the average, the hydrogen bonds are strong in $\text{KH}_5(\text{PO}_4)_2$, which is in accordance with the results reported for many other similar phosphorus compounds (*cf.* Table 8).

Table 8. Hydrogen bond distances in some phosphorus compounds.

Compound	Ref.	O—H...O	Average
H_3PO_3	19	2.525, 2.545, 2.592, 2.599	2.565
LiH_2PO_3	20	2.567	2.567
KH_2PO_4	21	2.487	2.487
Tetr., room temp.			
KH_2PO_4	22	2.486	2.486
Orth., at 77°K			
KH_2PO_4	23	2.51	2.51
Orth., at 116°K			
$\text{NH}_4\text{H}_2\text{PO}_4$	24	2.48	2.48
CaHPO_4	6	2.44, 2.65, 2.58	2.56
$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	6	2.48, 2.58, 2.60, 2.67, 2.72, 2.74	2.63
$\text{N}_2\text{H}_5\text{H}_2\text{PO}_4$	7	2.555, 2.515	2.535
$\text{N}_2\text{H}_6(\text{H}_2\text{PO}_4)_2$	8	2.642, 2.612	2.627
$\text{KH}_5(\text{PO}_4)_2$	Present work	2.405, 2.585, 2.587, 2.636	2.553
$\text{H}_3\text{PO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	5	2.55, 2.58, 2.62	2.58
H_3PO_4	4	2.53, 2.53	2.53

Table 9. Distances (\AA) less than 3.5 \AA in the $\text{K}-\text{O}$ polyhedron. The notation is in accordance with Figs. 1 and 2 (standard deviations in parentheses).

$\text{K}-\text{O}_1$	2.996 (4)	$\text{K}-\text{O}_6$	2.890 (4)
$\text{K}-\text{O}_2$	2.816 (4)	$\text{K}-\text{O}_7$	2.770 (4)
$\text{K}-\text{O}_3$	2.750 (4)	$\text{K}-\text{O}_7$	3.226 (4)
$\text{K}-\text{O}_4$	3.138 (4)	$\text{K}-\text{O}_8$	3.210 (5)
$\text{K}-\text{O}_5$	2.874 (4)		

The coordination of the potassium ion is ninefold (*cf.* Table 9) and irregular. The average $\text{K}-\text{O}$ interaction distance is 2.963 \AA which seems reasonable in comparison with the values reported in the *International Tables* (2.96 \AA).²⁵

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