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Short Note

Pentapotassium Bis(hydrogenphospate) Dihydrogenphospate Monohydrate

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Abstract: The structure of $K_5(HPO_4)_2(H_2PO_4)\cdot H_2O$ was determined via single crystal diffraction. The crystal structures of phosphate salts of potassium have been known since the early days of crystallography. Here, we present a new monohydrate adduct between K_2HPO_4 and KH_2PO_4.

Keywords: crystal structure; monopotassium phosphate; dipotassium phosphate; adduct

1. Introduction

Potassium phosphate finds its use as a food additive and fertilizer. The latter mostly contains monopotassium phosphate (MKP) (also known as potassium dihydrogenphosphate, KDP, or monobasic potassium phosphate) and dipotassium phosphate (also known as dipotassium hydrogen phosphate or potassium phosphate dibasic). The same combination is often used as a buffer for enzyme studies, where it is referred to as the Gomori buffer [1].

Structures of potassium phosphate have been known since the early days of crystallography, with the structure of KH_2PO_4 by Hassel in 1925 [2]. It is a known ferroelectric material showing a phase transition below 122 K [3]. For K_2HPO_4, orthorhombic crystal structures of the trihydrate [4] and anhydrate are known [5], as well as a monoclinic form [6] of the latter. Here, we report the structure of a monohydrate adduct of K_2HPO_4 and KH_2PO_4 in a 2:1 ratio. It can be seen as a double salt with two different anions and can be named pentapotassium bis(hydrogenphospate) dihydrogenphospate monohydrate. Given the common nature of the starting compounds and their general use, it is quite surprising that new phases can still be found. The moiety formula of the structure can be written as $K_5(HPO_4)_2(H_2PO_4)\cdot H_2O$ (Figure 1).

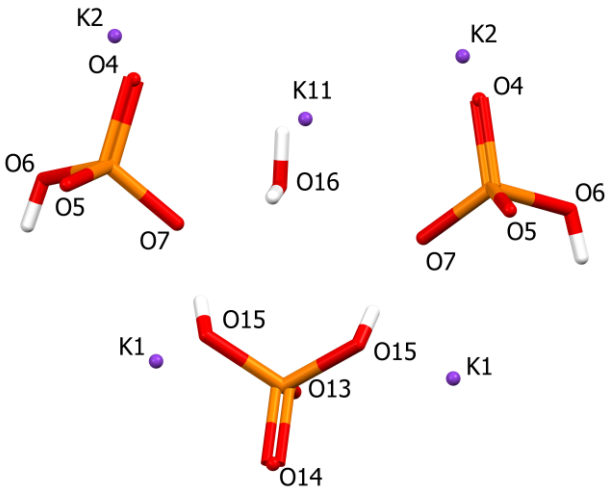

Figure 1. Moiety formula of $K_5(HPO_4)_2(H_2PO_4)\cdot H_2O$.

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2. Results and Discussion

The title compound was obtained from a cocrystallization experiment between (R)-(+)-1-(4-bromophenyl)ethylamine and L-Lactic acid in a potassium phosphate buffer (0.5 M, pH 7) in an attempt to crystallize L-Lactic acid in an environment suitable for enzymatic activity.

Rather than cocrystals with L-Lactic acid, the obtained crystals proved to be the 2:1 adduct of K_2HPO_4 and KH_2PO_4.

The obtained structure resolved from single crystal data showed the structure crystallizing in the monoclinic system with the space group $P2_1/m$.

The unit cell is filled with 6 PO_4 tetrahedra surrounded by 10 potassium cations. The PO_4 tetrahedra belonging to H_2PO_4 anions and 1 K^+ are found on a mirror plane, giving a total of 2 formula units per unit cell ($Z' = 0.5$). Every phosphate oxygen not carrying a hydrogen is coordinated to at least 3 potassium cations, and for those with a hydrogen atom to 2 potassium cations, the hydrogens are involved in hydrogen bonds with neighbouring phosphate oxygens. Potassium is known for its high coordination number (CN), with reported coordination numbers up to 12 [7]. A CN of 8 is found for K1 and K11, involving phosphate oxygens and the water molecule. K2 is coordinated to 9 oxygen atoms all from PO_4 units. The water molecule, also completely located on the mirror plane, interacts with 3 potassium atoms and its hydrogens bridge 2 H_2PO_4 anions.

K2 sits in a distorted capped square antiprismatic geometry (Figure 2B) made from four edge- and face-coordinating PO_4 units, while K1 only interacts with the vertices of seven PO_4 units and the water molecule, giving a bicapped trigonal prismatic geometry (Figure 2A). K11, on the other hand, is more regularly surrounded in a trigonal dodecahedron from three edge-coordinating PO4 tetrahedra, a vertex of another, and the water molecule (Figure 2C).

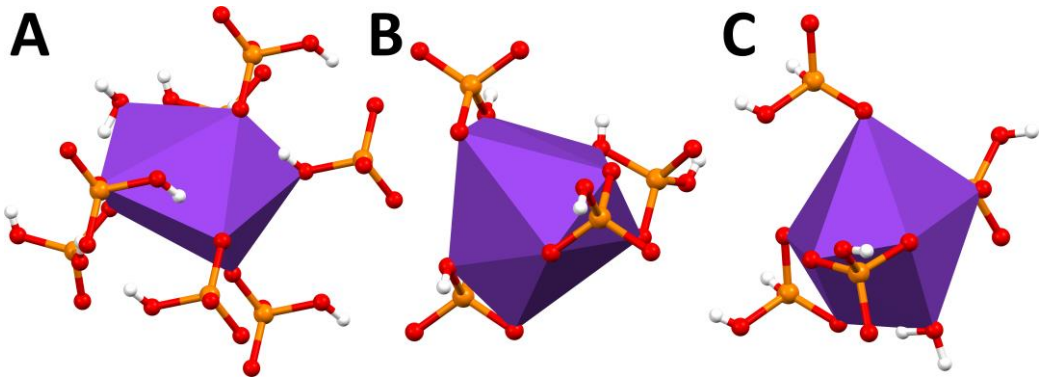

Figure 2. Coordination polyhedral for K1 ((**A**), bicapped trigonal prismatic geometry); for K2 ((**B**), capped square antiprismatic geometry), and K3 ((**C**), trigonal dodecahedron).

3. Materials and Methods

(R)-(+)-1-(4-bromophenyl)ethylamine (CAS: 45791-36-4; 98%) was obtained from Fluorochem Ltd. (Hadfield, UK), and L-lactic acid (CAS: 79-33-4; >85.0%(T)) was bought from TCI Europe N.V. (Zwijndrecht, Belgium). Potassium phosphate monobasic (cas: 7778-77-0; powder, suitable for cell culture, suitable for insect cell culture, suitable for plant cell culture ≥99.0%) and potassium phosphate dibasic (cas: 7758-11-4; anhydrous for analysis EMSURE®), used to prepare the potassium phosphate buffer, were acquired from MERCK (Overijse, Belgium). All the materials were used as received, without any further purification.

Single crystals were obtained from an undersaturated solution of an equimolar amount (0.3 mmol) of (R)-(+)-1-(4-bromophenyl)ethylamine and L-Lactic acid in 3 mL of potassium phosphate buffer (0.5 M, pH 7), or more explicitly a buffer containing 38.5% de KH_2PO_4 (monobasic) et 61.5% of K_2HPO_4 (dibasic). The solution was left to evaporate slowly

(10 days) at room temperature, and suitable single crystals of 2(HPO_4), H_2PO_4, H_2O, and 5(K) were retrieved.

The diffraction data were collected on a MAR345 image plate detector using monochromated MoKα radiation (Incoatec IμS microfocus, montel mirrors). CrysAlis^{PRO} was used for integration and data reduction, and the implemented absorption correction was used [8]. The structure was solved via SHELXT [9] and refined against $|F^2|$ using SHELXL-2018/3 [10]. No restraints were applied, apart from a similarity restraint on the O-H bond lengths of the crystal water. All hydrogen atoms were located in the difference maps and refined freely.

Table 1 gives the crystallographic and refinement details of $K_5(HPO_4)_2(H_2PO_4)\cdot H_2O$. CCDC 2262315 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table 1. Crystallographic and refinement details of $K_5(HPO_4)_2(H_2PO_4)\cdot H_2O$.

Empirical formula	$H_6\ K_5\ O_{13}\ P_3$
Formula weight	502.46
Temperature (K)	297(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions (Å,°)	a = 5.7719(14)
	b = 17.711(2)
	c = 7.3317(18)
	B = 113.28(3)
Volume (Å^3)	688.5(3)
Z	2
Density (calculated) (g/cm^3)	2.424
Absorption coefficient (mm^{-1})	2.006
F(000)	500
Crystal size (mm^3)	0.40 × 0.25 × 0.20
Theta range for data collection (°)	3.025 to 26.274
Reflections collected	5780
Independent reflections	1408 [R(int) = 0.0625]
Completeness to θ = 25.242° (%)	98.4
Max. and min. transmission	1.00000 and 0.62462
Data/restraints/parameters	1408/1/113
Goodness-of-fit on F^2	1.102
Final R indices [I > 2s(I)]	R_1 = 0.0438, wR_2 = 0.1208
R indices (all data)	R_1 = 0.0505, wR_2 = 0.1241
(Max, min)(e.Å^{-3})	0.638, −0.653

Supplementary Materials: The following supporting information can be downloaded online. Crystallographic information file: UCL2464_ccg_LAL22_h2o.cif.

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editing, T.L. and C.C.G.; supervision, T.L.; funding acquisition, T.L. and K.R. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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