

Crystal structure of the deuterated heptahydrate of potassium phosphate, $K_3PO_4 \cdot 7D_2O$

Matthias Weil^{a*} and Berthold Stöger^b^aInstitute for Chemical Technologies and Analytics, Division of Structural Chemistry, Vienna University of Technology, Getreidemarkt 9/164-SC, A-1060 Vienna, Austria, and ^bX-Ray Centre, Getreidemarkt 9, A-1060 Vienna, Austria.

*Correspondence e-mail: matthias.weil@tuwien.ac.at

Received 16 December 2019

Accepted 8 January 2020

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; potassium phosphate; hydrogen bonding; absolute structure; hydrate.**CCDC reference:** 1976170**Supporting information:** this article has supporting information at journals.iucr.org/e

Deuterated potassium orthophosphate heptahydrate, $K_3PO_4 \cdot 7D_2O$, crystallizes in the Sohnke space group $P2_1$, and its absolute structure was determined from 2017 Friedel pairs [Flack parameter 0.004 (16)]. Each of the three crystallographically unique K^+ cations is surrounded by six water molecules and one oxygen atom from the orthophosphate group, using a threshold for $K-O$ bonds of 3.10 Å. The highly irregular coordination polyhedra are linked by corner- and edge-sharing into a three-dimensional network that is consolidated by an intricate network of $O-D \cdots O$ hydrogen bonds of medium strength.

1. Chemical context

Following projects devoted to studying the formation and crystal chemistry of hydrous arsenate and phosphate phases of monovalent metals, *viz.* NaH_2AsO_4 (Ring *et al.*, 2017), $K_2HAsO_4(H_2O)_{2.5}$ and $K_2HAsO_4(H_2O)_6$ (Stöger *et al.*, 2012), $M_2HXO_4 \cdot 2H_2O$ ($M = Rb, Cs$; $X = P, As$; Stöger & Weil, 2014), and several acidic thallium(I) arsenate phases (Schroffenegger *et al.*, 2019), we became interested in the system K_3PO_4/H_2O . Although hydrate phases of potassium orthophosphate have been known for a very long time to exist for the 3-hydrate and the 7-hydrate (Gmelin, 1938), crystal-structure determinations of these two phases or of any other hydrate of K_3PO_4 have not been reported so far. Previous investigations on the trihydrate revealed that the crystal structure of $K_3PO_4 \cdot 3H_2O$ is incommensurately modulated below 300 K (Stöger, 2020). To better elucidate the role of hydrogen bonding in this structure with the aid of single-crystal neutron diffraction, we started crystal-growth experiments to obtain the deuterium analogue $K_3PO_4 \cdot 3D_2O$. The title compound, $K_3PO_4 \cdot 7D_2O$, was the unexpected product of such a crystallization attempt at temperatures below the freezing point of pure water, and its crystal structure is reported here.

2. Structural commentary

Taking 3.1 Å as the upper limit of $K-O$ bond lengths in the first coordination sphere, each of the three crystallographically independent potassium cations is surrounded by six water molecules and one oxygen atom of the phosphate group (Fig. 1). The highly irregular coordination polyhedra show $K-O$ bond lengths ranging between 2.6665 (9) and 3.0151 Å (Table 1). The overall mean of 2.821 Å for the 21 bonds is in good agreement with the value of 2.861 Å calculated from 469 individual $K-O$ bonds in crystal structures with coordination

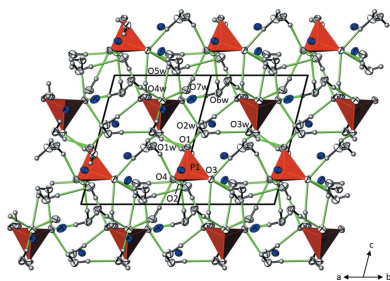


Table 1
Selected bond lengths (Å).

K1—O5w	2.7153 (10)	K2—O6w ⁱ	3.0151 (10)
K1—O1w	2.7183 (11)	K3—O2w	2.6665 (9)
K1—O7w	2.7381 (10)	K3—O4 ^{iv}	2.7867 (9)
K1—O6w	2.7532 (9)	K3—O4w ^v	2.7983 (10)
K1—O3w	2.8479 (9)	K3—O5w ^{vi}	2.8344 (10)
K1—O2w	2.8486 (9)	K3—O1w ^{iv}	2.8394 (10)
K1—O1	2.9757 (9)	K3—O7w ^{vi}	2.9094 (9)
K2—O1	2.7317 (10)	K3—O5w	2.9246 (10)
K2—O4w	2.7391 (10)	P1—O1	1.5414 (8)
K2—O7w	2.7659 (9)	P1—O2	1.5440 (8)
K2—O1w ⁱ	2.7836 (9)	P1—O4	1.5472 (10)
K2—O2w ⁱⁱ	2.8269 (9)	P1—O3	1.5523 (8)
K2—O3w ⁱⁱⁱ	3.0144 (9)		

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x, y - \frac{1}{2}, -z + 1$; (iii) $-x, y + \frac{1}{2}, -z + 1$; (iv) $-x + 1, y + \frac{1}{2}, -z + 1$; (v) $x + 1, y, z$; (vi) $-x + 1, y + \frac{1}{2}, -z + 2$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1w—D11...O3w ^{iv}	0.86 (2)	1.91 (2)	2.7255 (13)	158 (2)
O1w—D12...O4	0.78 (2)	1.98 (2)	2.7391 (11)	164 (2)
O2w—D21...O2 ⁱⁱⁱ	0.87 (2)	1.85 (2)	2.7149 (13)	177 (2)
O2w—D22...O1	0.73 (2)	1.99 (2)	2.7029 (11)	167 (3)
O3w—D31...O1	0.80 (2)	1.97 (2)	2.7242 (11)	159 (2)
O3w—D32...O3 ⁱⁱ	0.98 (3)	1.77 (3)	2.7395 (14)	171 (2)
O4w—D41...O3 ^{vii}	0.80 (2)	2.10 (2)	2.8870 (14)	169 (2)
O4w—D42...O2 ⁱⁱⁱ	0.79 (2)	1.97 (2)	2.7679 (13)	177 (2)
O5w—D51...O6w ^{vi}	0.80 (2)	2.11 (2)	2.9025 (13)	168 (2)
O5w—D52...O3 ^{viii}	0.80 (2)	1.92 (2)	2.6944 (12)	166 (2)
O6w—D61...O2 ^{viii}	0.75 (2)	1.96 (2)	2.7087 (12)	176 (2)
O6w—D62...O4 ^{ix}	0.85 (2)	1.86 (2)	2.6931 (12)	165 (2)
O7w—D71...O3 ⁱⁱ	0.78 (2)	2.02 (2)	2.7498 (12)	155 (2)
O7w—D72...O4 ^{vii}	0.82 (2)	1.97 (2)	2.7859 (13)	171 (2)

Symmetry codes: (ii) $-x, y - \frac{1}{2}, -z + 1$; (iii) $-x, y + \frac{1}{2}, -z + 1$; (iv) $-x + 1, y + \frac{1}{2}, -z + 1$; (vi) $-x + 1, y + \frac{1}{2}, -z + 2$; (vii) $x, y, z + 1$; (viii) $x + 1, y, z + 1$; (ix) $-x + 1, y - \frac{1}{2}, -z + 1$.

numbers of 7 for the potassium cation (Gagné & Hawthorne, 2016). The $[\text{K}(\text{D}_2\text{O})_6\text{O}]$ polyhedra share corners and edges to build up a three-dimensional network (Fig. 2). Each water molecule is a donor group of two slightly bent $\text{O}-\text{D}\cdots\text{O}$ hydrogen bonds, but only two of the water molecules (O3w,

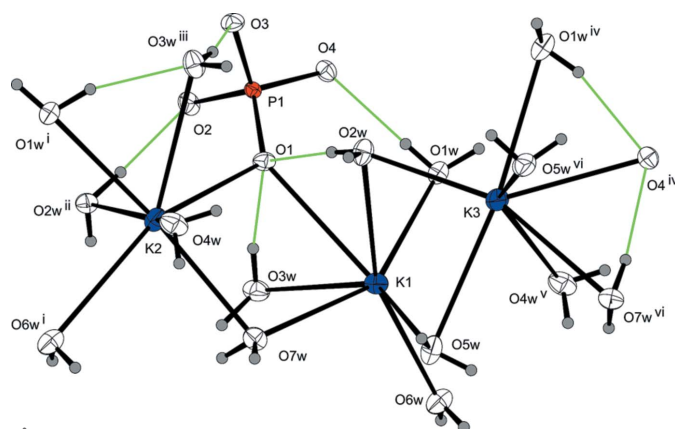


Figure 1
The expanded asymmetric unit of $\text{K}_3\text{PO}_4 \cdot 7\text{D}_2\text{O}$ showing the complete potassium coordination polyhedra. Displacement ellipsoids are displayed at the 74% probability level; $\text{O}-\text{D}\cdots\text{O}$ hydrogen bonds are indicated by green lines; symmetry codes refer to Table 1.

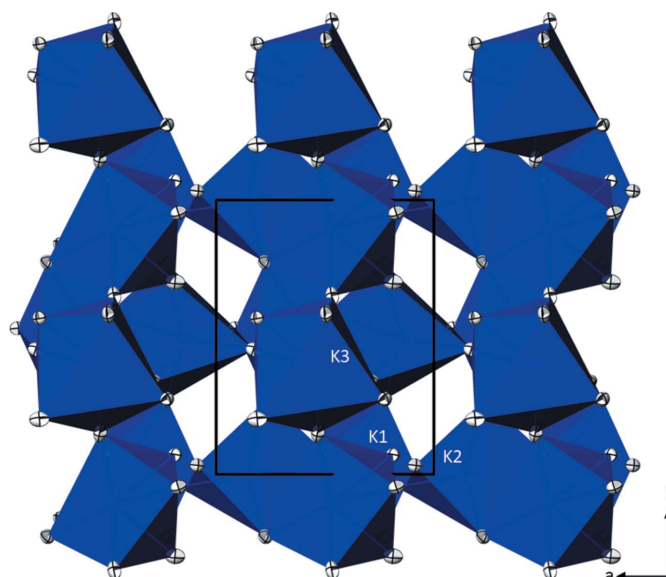


Figure 2
Network of corner- and edge-sharing $[\text{KO}_7]$ polyhedra in the crystal structure of $\text{K}_3\text{PO}_4 \cdot 7\text{D}_2\text{O}$, viewed along $[001]$. Displacement ellipsoids are displayed at the 90% probability level. For clarity, D atoms are not shown.

O6w) also serve as acceptor groups for one hydrogen bond. All other hydrogen bonds are directed towards the O atoms of the phosphate group, with O1 being twofold, O2 threefold, O3 fourfold and O4 threefold acceptor atoms, respectively (Fig. 3). Judging from the $\text{O}\cdots\text{O}$ distances [range 2.6931 (12)–2.9025 (13) Å; Table 2], hydrogen bonds of medium strength are formed in the crystal structure. The PO_4 tetrahedron shows almost equal P—O bond lengths typical of a fully deprotonated orthophosphate group (mean 1.546 Å), with marginal angular distortions.

A bond-valence analysis (Brown, 2002), using the parameters of Brese & O’Keeffe (1991), reveals bond-valence sums (BVS, in valence units) of $\text{K1} = 1.18$, $\text{K2} = 1.08$, $\text{K3} =$

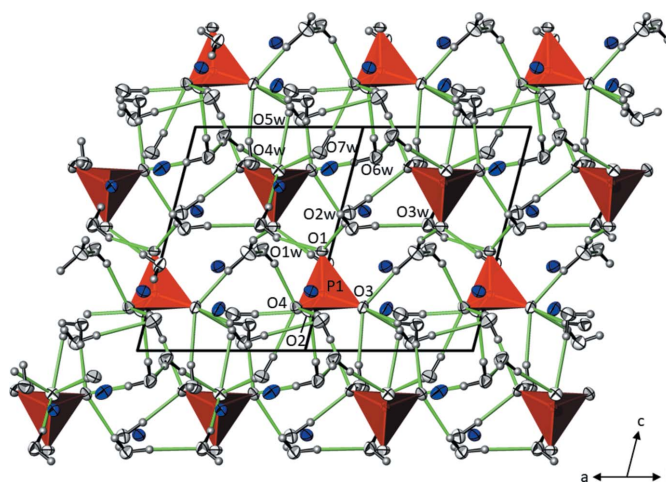


Figure 3
 $\text{O}-\text{D}\cdots\text{O}$ hydrogen-bonding network (green lines) in the crystal structure of $\text{K}_3\text{PO}_4 \cdot 7\text{D}_2\text{O}$, viewed along $[101]$. Displacement ellipsoids are displayed at the 90% probability level.

1.11, and $P1 = 4.85$, in good agreement with the expected values of +1 and +5, respectively. The four oxygen atoms of the orthophosphate tetrahedron are considerably underbonded and show BVS values of 1.53 (O1), 1.22 (O2), 1.10 (O3) and 1.38 (O4). O1 with the highest BVS of the four phosphate O atoms has two K^+ cations as additional bonding partners, O4 with the second highest BVS has one additional K^+ as bonding partner whereas O2 and O3 with the lowest BVS values are solely bonded to the P atom. The four O atoms compensate for underbonding by means of their role as acceptor atoms in hydrogen bonding (see above).

3. Database survey

In the Inorganic Structure Database (ICSD; Zagorac *et al.*, 2019), the crystal structures of not less than 14 different phases in the system $K_2O/P_2O_5/H_2O$ are listed, including partly protonated PO_4 or other condensed phosphate groups, and/or phases with water molecules. The only other phosphates of an alkali metal, thallium or ammonium with a fully deprotonated orthophosphate group are $Na_3PO_4(H_2O)_8$ (Larbot & Durand, 1983), $Na_3PO_4(H_2O)_{0.5}$ (Averbuch-Pouchot & Durif, 1983) and $(NH_4)_3(PO_4) \cdot 3H_2O$ (Mootz & Wunderlich, 1970). As a result of the different size of the Na^+ cation compared to K^+ , the role of NH_4^+ as an active species in hydrogen bonding, and the different amounts of water molecules in these three crystal structures, there is no evident structural relation to $K_3PO_4 \cdot 7D_2O$.

4. Synthesis and crystallization

Commercial anhydrous K_3PO_4 (Sigma–Aldrich) was dissolved in a small amount of warm D_2O . Cooling to 255 K afforded rod-like crystals of the title heptahydrate that grew over night, with maximum edge lengths in the millimetre range.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Positions of the D atoms were located in a difference-Fourier map and were refined freely under consideration of scattering factors for hydrogen atoms.

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Table 3
Experimental details.

Crystal data	
Chemical formula	$K_3PO_4 \cdot 7D_2O$
M_r	352.5
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
a, b, c (Å)	7.8325 (7), 9.3406 (8), 8.4471 (7)
β (°)	108.727 (2)
V (Å ³)	585.28 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	1.34
Crystal size (mm)	0.46 × 0.09 × 0.01
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2016)
T_{min} , T_{max}	0.54, 0.99
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	9464, 4273, 4127
R_{int}	0.021
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.759
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.016, 0.020, 1.02
No. of reflections	4273
No. of parameters	193
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.16, -0.13
Absolute structure	2017 Friedel pairs used in the refinement (Flack, 1983)
Absolute structure parameter	0.004 (16)

Computer programs: *APEX2* and *SAINTE-Plus* (Bruker, 2016), *SHELXT* (Sheldrick, 2015), *JANA2006* (Petříček *et al.*, 2014), *ATOMS* (Dowty, 2006) and *PUBLICIF* (Westrip, 2010).

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supporting information

Acta Cryst. (2020). E76, 177-179 [https://doi.org/10.1107/S2056989020000201]

Crystal structure of the deuterated heptahydrate of potassium phosphate, $K_3PO_4 \cdot 7D_2O$

Matthias Weil and Berthold Stöger

Computing details

Data collection: *APEX2* (Bruker, 2016); cell refinement: *SAINTE-Plus* (Bruker, 2016); data reduction: *SAINTE-Plus* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015); program(s) used to refine structure: *Jana2006* (Petříček *et al.*, 2014); molecular graphics: *ATOMS* (Dowty, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Potassium phosphate heptahydrate

Crystal data

$K_3PO_4 \cdot 7D_2O$

$M_r = 352.5$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 7.8325$ (7) Å

$b = 9.3406$ (8) Å

$c = 8.4471$ (7) Å

$\beta = 108.727$ (2)°

$V = 585.28$ (9) Å³

$Z = 2$

$F(000) = 348$

$D_x = 2.000$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7382 reflections

$\theta = 2.6$ – 32.6 °

$\mu = 1.34$ mm⁻¹

$T = 100$ K

Rod, colourless

$0.46 \times 0.09 \times 0.01$ mm

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: X-ray tube

Graphite monochromator

ω - and ϕ -scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2016)

$T_{\min} = 0.54$, $T_{\max} = 0.99$

9464 measured reflections

4273 independent reflections

4127 reflections with $I > 3\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 32.6$ °, $\theta_{\min} = 2.6$ °

$h = -10 \rightarrow 11$

$k = -14 \rightarrow 14$

$l = -12 \rightarrow 10$

Refinement

Refinement on F

$R[F^2 > 2\sigma(F^2)] = 0.016$

$wR(F^2) = 0.020$

$S = 1.02$

4273 reflections

193 parameters

0 restraints

1 constraint

Weighting scheme based on measured s.u.'s $w =$

$1/(\sigma^2(F) + 0.0001F^2)$

$(\Delta/\sigma)_{\max} = 0.019$

$\Delta\rho_{\max} = 0.16$ e Å⁻³

$\Delta\rho_{\min} = -0.13$ e Å⁻³

Absolute structure: 2017 Friedel pairs used in
the refinement (Flack, 1983)

Absolute structure parameter: 0.004 (16)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
K1	0.42550 (3)	0.01804 (2)	0.73444 (3)	0.00950 (6)
K2	-0.14458 (3)	-0.00537 (2)	0.62341 (3)	0.00990 (6)
K3	0.52865 (3)	0.39152 (2)	0.81480 (3)	0.01224 (6)
P1	0.02505 (3)	0.04285 (3)	0.25261 (3)	0.00571 (7)
O1	0.08740 (10)	0.03291 (8)	0.44490 (9)	0.00823 (19)
O2	-0.06671 (10)	-0.09902 (8)	0.17723 (10)	0.0101 (2)
O3	-0.10938 (10)	0.16905 (8)	0.19358 (10)	0.0092 (2)
O4	0.18924 (10)	0.07033 (8)	0.19270 (10)	0.0086 (2)
O1w	0.50577 (11)	0.08478 (8)	0.45314 (11)	0.0119 (2)
O2w	0.22528 (11)	0.27301 (8)	0.61723 (11)	0.0106 (2)
O3w	0.23569 (11)	-0.22553 (8)	0.56243 (11)	0.0116 (2)
O4w	-0.18873 (12)	0.20109 (9)	0.83725 (11)	0.0129 (2)
O5w	0.53272 (11)	0.15028 (9)	1.03669 (11)	0.0126 (2)
O6w	0.71314 (11)	-0.16355 (8)	0.86601 (11)	0.0119 (2)
O7w	0.17243 (11)	-0.04581 (9)	0.88427 (10)	0.0103 (2)
D11	0.564 (2)	0.161 (2)	0.442 (2)	0.027 (5)*
D12	0.409 (3)	0.091 (2)	0.390 (3)	0.033 (5)*
D21	0.172 (3)	0.315 (2)	0.680 (2)	0.034 (5)*
D22	0.173 (3)	0.213 (2)	0.570 (3)	0.037 (6)*
D31	0.182 (2)	-0.162 (2)	0.506 (3)	0.031 (5)*
D32	0.179 (3)	-0.261 (3)	0.642 (3)	0.052 (7)*
D41	-0.153 (2)	0.1885 (19)	0.936 (3)	0.022 (4)*
D42	-0.113 (3)	0.258 (3)	0.837 (3)	0.049 (7)*
D51	0.477 (2)	0.2098 (19)	1.068 (2)	0.021 (4)*
D52	0.634 (2)	0.1654 (19)	1.093 (2)	0.023 (4)*
D61	0.776 (3)	-0.143 (2)	0.950 (3)	0.031 (5)*
D62	0.759 (2)	-0.240 (2)	0.842 (2)	0.023 (4)*
D71	0.132 (2)	-0.123 (2)	0.877 (2)	0.023 (4)*
D72	0.166 (2)	-0.0150 (19)	0.973 (2)	0.019 (4)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.01055 (8)	0.00951 (9)	0.00895 (9)	0.00141 (6)	0.00384 (7)	0.00041 (7)
K2	0.00815 (8)	0.01323 (9)	0.00836 (9)	0.00028 (7)	0.00272 (7)	-0.00109 (7)
K3	0.01205 (9)	0.00943 (9)	0.01200 (11)	-0.00261 (7)	-0.00067 (8)	0.00104 (7)
P1	0.00639 (10)	0.00552 (10)	0.00530 (11)	-0.00037 (8)	0.00201 (8)	0.00003 (8)
O1	0.0102 (3)	0.0084 (3)	0.0056 (3)	0.0002 (2)	0.0020 (2)	-0.0001 (2)
O2	0.0131 (3)	0.0080 (3)	0.0086 (3)	-0.0040 (3)	0.0027 (3)	-0.0020 (3)
O3	0.0086 (3)	0.0090 (3)	0.0099 (4)	0.0029 (2)	0.0028 (3)	0.0022 (3)
O4	0.0089 (3)	0.0088 (3)	0.0092 (4)	-0.0002 (2)	0.0046 (3)	0.0004 (2)
O1w	0.0078 (3)	0.0150 (4)	0.0114 (4)	-0.0011 (3)	0.0010 (3)	0.0026 (3)
O2w	0.0091 (3)	0.0103 (3)	0.0120 (4)	-0.0011 (3)	0.0026 (3)	-0.0033 (3)
O3w	0.0127 (3)	0.0109 (3)	0.0123 (4)	0.0032 (3)	0.0056 (3)	0.0032 (3)
O4w	0.0182 (4)	0.0112 (3)	0.0102 (4)	-0.0007 (3)	0.0059 (3)	0.0003 (3)

O5w	0.0084 (3)	0.0168 (4)	0.0122 (4)	-0.0016 (3)	0.0030 (3)	-0.0033 (3)
O6w	0.0111 (3)	0.0099 (3)	0.0122 (4)	0.0020 (3)	0.0003 (3)	-0.0024 (3)
O7w	0.0126 (3)	0.0098 (3)	0.0091 (4)	-0.0010 (3)	0.0041 (3)	-0.0008 (3)

Geometric parameters (Å, °)

K1—O5w	2.7153 (10)	K3—O5w	2.9246 (10)
K1—O1w	2.7183 (11)	P1—O1	1.5414 (8)
K1—O7w	2.7381 (10)	P1—O2	1.5440 (8)
K1—O6w	2.7532 (9)	P1—O4	1.5472 (10)
K1—O3w	2.8479 (9)	P1—O3	1.5523 (8)
K1—O2w	2.8486 (9)	O1w—D11	0.86 (2)
K1—O1	2.9757 (9)	O1w—D12	0.778 (18)
K2—O1	2.7317 (10)	O2w—D21	0.87 (2)
K2—O4w	2.7391 (10)	O2w—D22	0.73 (2)
K2—O7w	2.7659 (9)	O3w—D31	0.796 (19)
K2—O1w ⁱ	2.7836 (9)	O3w—D32	0.98 (3)
K2—O2w ⁱⁱ	2.8269 (9)	O4w—D41	0.80 (2)
K2—O3w ⁱⁱⁱ	3.0144 (9)	O4w—D42	0.79 (2)
K2—O6w ⁱ	3.0151 (10)	O5w—D51	0.80 (2)
K3—O2w	2.6665 (9)	O5w—D52	0.795 (17)
K3—O4 ^{iv}	2.7867 (9)	O6w—D61	0.748 (19)
K3—O4w ^v	2.7983 (10)	O6w—D62	0.85 (2)
K3—O5w ^{vi}	2.8344 (10)	O7w—D71	0.783 (19)
K3—O1w ^{iv}	2.8394 (10)	O7w—D72	0.823 (19)
K3—O7w ^{vi}	2.9094 (9)		
O1—K1—O1w	70.45 (2)	O1w ^{iv} —K3—O5w ^{vi}	79.89 (3)
O1—K1—O2w	55.25 (2)	O1w ^{iv} —K3—O7w ^{vi}	114.35 (2)
O1—K1—O3w	55.73 (2)	O2w—K3—O4w ^v	107.76 (3)
O1—K1—O5w	132.58 (3)	O2w—K3—O5w	84.57 (2)
O1—K1—O6w	139.24 (2)	O2w—K3—O5w ^{vi}	112.79 (3)
O1—K1—O7w	78.74 (2)	O2w—K3—O7w ^{vi}	159.36 (3)
O1w—K1—O2w	76.14 (3)	O4w ^v —K3—O5w	67.74 (3)
O1w—K1—O3w	88.09 (3)	O4w ^v —K3—O5w ^{vi}	139.02 (2)
O1w—K1—O5w	128.98 (3)	O4w ^v —K3—O7w ^{vi}	70.82 (3)
O1w—K1—O6w	96.04 (3)	O5w—K3—O5w ^{vi}	109.99 (3)
O1w—K1—O7w	149.19 (2)	O5w—K3—O7w ^{vi}	75.81 (2)
O2w—K1—O3w	110.59 (2)	O5w ^{vi} —K3—O7w ^{vi}	69.21 (2)
O2w—K1—O5w	85.18 (3)	O1—P1—O2	109.32 (4)
O2w—K1—O6w	160.60 (2)	O1—P1—O3	109.69 (5)
O2w—K1—O7w	86.75 (3)	O1—P1—O4	109.83 (4)
O3w—K1—O5w	142.78 (3)	O2—P1—O3	109.96 (4)
O3w—K1—O6w	86.52 (2)	O2—P1—O4	109.46 (5)
O3w—K1—O7w	74.04 (3)	O3—P1—O4	108.56 (4)
O5w—K1—O6w	86.26 (3)	K2—O1—P1	123.21 (4)
O5w—K1—O7w	73.48 (3)	K3 ^{vii} —O4—P1	131.03 (4)
O6w—K1—O7w	107.41 (3)	K1—O1w—K2 ^v	86.80 (2)

O1—K2—O1w ⁱ	113.18 (3)	K1—O1w—K3 ^{vii}	124.16 (3)
O1—K2—O2w ⁱⁱ	74.56 (3)	K2 ^v —O1w—K3 ^{vii}	92.60 (3)
O1—K2—O3w ⁱⁱⁱ	71.77 (3)	K1—O2w—K2 ⁱⁱⁱ	146.43 (4)
O1—K2—O4w	121.27 (3)	K1—O2w—K3	81.32 (2)
O1—K2—O6w ⁱ	153.61 (2)	K2 ⁱⁱⁱ —O2w—K3	95.43 (3)
O1—K2—O7w	82.62 (3)	D21—O2w—D22	113 (3)
O1w ⁱ —K2—O2w ⁱⁱ	83.93 (2)	K1—O3w—D31	78.3 (13)
O1w ⁱ —K2—O3w ⁱⁱⁱ	55.91 (2)	K1—O3w—D32	101.6 (14)
O1w ⁱ —K2—O4w	79.41 (3)	D31—O3w—D32	114 (2)
O1w ⁱ —K2—O6w ⁱ	88.99 (3)	K2—O4w—K3 ⁱ	131.87 (3)
O1w ⁱ —K2—O7w	159.32 (3)	K2—O4w—D41	120.6 (14)
O2w ⁱⁱ —K2—O3w ⁱⁱⁱ	107.43 (3)	K2—O4w—D42	102.2 (19)
O2w ⁱⁱ —K2—O4w	160.62 (3)	K3 ⁱ —O4w—D41	99.7 (15)
O2w ⁱⁱ —K2—O6w ⁱ	94.81 (3)	K3 ⁱ —O4w—D42	98.8 (17)
O2w ⁱⁱ —K2—O7w	114.15 (3)	D41—O4w—D42	95 (2)
O3w ⁱⁱⁱ —K2—O4w	70.97 (3)	K1—O5w—K3 ^{viii}	89.03 (2)
O3w ⁱⁱⁱ —K2—O6w ⁱ	134.55 (3)	K1—O5w—D51	126.3 (11)
O3w ⁱⁱⁱ —K2—O7w	122.36 (2)	K1—O5w—D52	126.4 (16)
O4w—K2—O6w ⁱ	75.19 (3)	K3 ^{viii} —O5w—D51	104.9 (14)
O4w—K2—O7w	80.90 (3)	K3 ^{viii} —O5w—D52	99.4 (13)
O6w ⁱ —K2—O7w	79.91 (3)	D51—O5w—D52	102.5 (18)
O4 ^{iv} —K3—O1w ^{iv}	58.26 (2)	K1—O6w—D61	115.4 (16)
O4 ^{iv} —K3—O2w	142.03 (3)	K1—O6w—D62	140.5 (11)
O4 ^{iv} —K3—O4w ^v	76.51 (3)	D61—O6w—D62	104 (2)
O4 ^{iv} —K3—O5w	129.11 (2)	K1—O7w—K2	101.53 (3)
O4 ^{iv} —K3—O5w ^{vi}	75.37 (3)	K1—O7w—D71	120.0 (16)
O4 ^{iv} —K3—O7w ^{vi}	58.52 (2)	K1—O7w—D72	127.9 (12)
O1w ^{iv} —K3—O2w	85.85 (3)	K2—O7w—D71	80.0 (11)
O1w ^{iv} —K3—O4w ^v	109.19 (3)	K2—O7w—D72	112.2 (11)
O1w ^{iv} —K3—O5w	168.35 (2)	D71—O7w—D72	105 (2)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x, y-1/2, -z+1$; (iii) $-x, y+1/2, -z+1$; (iv) $-x+1, y+1/2, -z+1$; (v) $x+1, y, z$; (vi) $-x+1, y+1/2, -z+2$; (vii) $-x+1, y-1/2, -z+1$; (viii) $-x+1, y-1/2, -z+2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1w—D11 \cdots O3w ^{iv}	0.86 (2)	1.91 (2)	2.7255 (13)	158 (2)
O1w—D12 \cdots O4	0.78 (2)	1.98 (2)	2.7391 (11)	164 (2)
O2w—D21 \cdots O2 ⁱⁱⁱ	0.87 (2)	1.85 (2)	2.7149 (13)	177 (2)
O2w—D22 \cdots O1	0.73 (2)	1.99 (2)	2.7029 (11)	167 (3)
O3w—D31 \cdots O1	0.80 (2)	1.97 (2)	2.7242 (11)	159 (2)
O3w—D32 \cdots O3 ⁱⁱ	0.98 (3)	1.77 (3)	2.7395 (14)	171 (2)
O4w—D41 \cdots O3 ^{ix}	0.80 (2)	2.10 (2)	2.8870 (14)	169 (2)
O4w—D42 \cdots O2 ⁱⁱⁱ	0.79 (2)	1.97 (2)	2.7679 (13)	177 (2)
O5w—D51 \cdots O6w ^{vi}	0.80 (2)	2.11 (2)	2.9025 (13)	168 (2)
O5w—D52 \cdots O3 ^x	0.80 (2)	1.92 (2)	2.6944 (12)	166 (2)
O6w—D61 \cdots O2 ^x	0.75 (2)	1.96 (2)	2.7087 (12)	176 (2)
O6w—D62 \cdots O4 ^{vii}	0.85 (2)	1.86 (2)	2.6931 (12)	165 (2)

$O7_w-D71\cdots O3^{ii}$	0.78 (2)	2.02 (2)	2.7498 (12)	155 (2)
$O7_w-D72\cdots O4^{ix}$	0.82 (2)	1.97 (2)	2.7859 (13)	171 (2)

Symmetry codes: (ii) $-x, y-1/2, -z+1$; (iii) $-x, y+1/2, -z+1$; (iv) $-x+1, y+1/2, -z+1$; (vi) $-x+1, y+1/2, -z+2$; (vii) $-x+1, y-1/2, -z+1$; (ix) $x, y, z+1$; (x) $x+1, y, z+1$.