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## Structure Reports

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**K<sub>2</sub>Ho(PO<sub>4</sub>)(WO<sub>4</sub>)**

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 Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{W}-\text{O}) = 0.004$  Å;  $R$  factor = 0.029;  $wR$  factor = 0.071; data-to-parameter ratio = 25.2.

A new compound, dipotassium holmium(III) phosphate(V) tungstate(VI), K<sub>2</sub>Ho(PO<sub>4</sub>)(WO<sub>4</sub>), has been obtained during investigation of the K<sub>2</sub>O–P<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>–HoF<sub>3</sub> phase system using the flux technique. The compound is isotypic with K<sub>2</sub>Bi(PO<sub>4</sub>)(WO<sub>4</sub>). Its framework structure consists of flat  $\infty^2[\text{HoPO}_4]$  layers parallel to (100) that are made up of  $\infty^1[\text{HoO}_8]$  zigzag chains interlinked *via* slightly distorted PO<sub>4</sub> tetrahedra. WO<sub>4</sub> tetrahedra are attached above and below these layers, leaving space for the K<sup>+</sup> counter-cations. The HoO<sub>8</sub>, PO<sub>4</sub> and WO<sub>4</sub> units exhibit 2 symmetry.

## Related literature

For related structures, see: Ben Amara &amp; Dabbabi (1987); Marsh (1987); Zatovsky, Terebilenko, Slobodyanik &amp; Baumer (2006); Zatovsky, Terebilenko, Slobodyanik, Baumer &amp; Shishkin (2006).

## Experimental

## Crystal data

K <sub>2</sub> Ho(PO <sub>4</sub> )(WO <sub>4</sub> )	$V = 1646.6$ (4) Å <sup>3</sup>
$M_r = 585.95$	$Z = 8$
Orthorhombic, <i>Ibca</i>	Mo $K\alpha$ radiation
$a = 6.8820$ (10) Å	$\mu = 24.72$ mm <sup>-1</sup>
$b = 12.1485$ (18) Å	$T = 293$ (2) K
$c = 19.695$ (3) Å	$0.10 \times 0.09 \times 0.07$ mm

## Data collection

Oxford Diffraction Xcalibur-3 CCD diffractometer	8608 measured reflections
Absorption correction: multi-scan based on the method by Blessing (1995)	1561 independent reflections
$T_{\min} = 0.102$ , $T_{\max} = 0.177$	1257 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.055$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	62 parameters
$wR(F^2) = 0.071$	$\Delta\rho_{\text{max}} = 1.90$ e Å <sup>-3</sup>
$S = 1.15$	$\Delta\rho_{\text{min}} = -1.73$ e Å <sup>-3</sup>
1561 reflections	

Table 1

Selected bond lengths (Å).

W1—O2	1.749 (4)	Ho1—O3 <sup>ii</sup>	2.401 (3)
W1—O1	1.788 (3)	Ho1—O4	2.428 (3)
Ho1—O4 <sup>i</sup>	2.274 (3)	P1—O3	1.525 (3)
Ho1—O1	2.342 (3)	P1—O4	1.552 (3)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2196).

## References

- Ben Amara, M. & Dabbabi, M. (1987). *Acta Cryst.* **C43**, 616–618.  
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.  
 Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.  
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.  
 Marsh, R. E. (1987). *Acta Cryst.* **C43**, 2470.  
 Oxford Diffraction (2005). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Zatovsky, I. V., Terebilenko, K. V., Slobodyanik, N. S. & Baumer, V. N. (2006). *J. Solid State Chem.* **179**, 3550–3555.  
 Zatovsky, I. V., Terebilenko, K. V., Slobodyanik, N. S., Baumer, V. N. & Shishkin, O. V. (2006). *Acta Cryst.* **E62**, i193–i195.

## supporting information

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**K<sub>2</sub>Ho(PO<sub>4</sub>)(WO<sub>4</sub>)**

**Katherina V. Terebilenko, Igor V. Zatonvsky, Vyacheslav N. Baumer, Nikolay S. Slobodyanik and Oleg V. Shishkin**

**S1. Comment**

The co-existence of different anionic units in crystal structures represents an interesting field of investigation. One of the first structural examples of a combination of PO<sub>4</sub> with MoO<sub>4</sub>/WO<sub>4</sub> tetrahedra, *viz.* Na<sub>2</sub>Y(MoO<sub>4</sub>)(PO<sub>4</sub>), was reported to be monoclinic with space group *C2/c* (Ben Amara & Dabbabi, 1987). Later this structure was reinvestigated and described as orthorhombic, space group *Ibca* (Marsh, 1987). Recently, the compounds K<sub>2</sub>Bi(PO<sub>4</sub>)(MO<sub>4</sub>) (*M*=Mo, W) with isotypic structures were obtained by application of the flux method (Zatonvsky, Terebilenko, Slobodyanik & Baumer, 2006; Zatonvsky, Terebilenko, Slobodyanik, Baumer & Shishkin, 2006). Herein, we report the flux synthesis and crystal structure of a new member of the *A<sub>2</sub>B(PO<sub>4</sub>)(AO<sub>4</sub>)* (*A* = Na, K; *B* = lanthanide, Y, Bi; *M* = Mo, W) family.

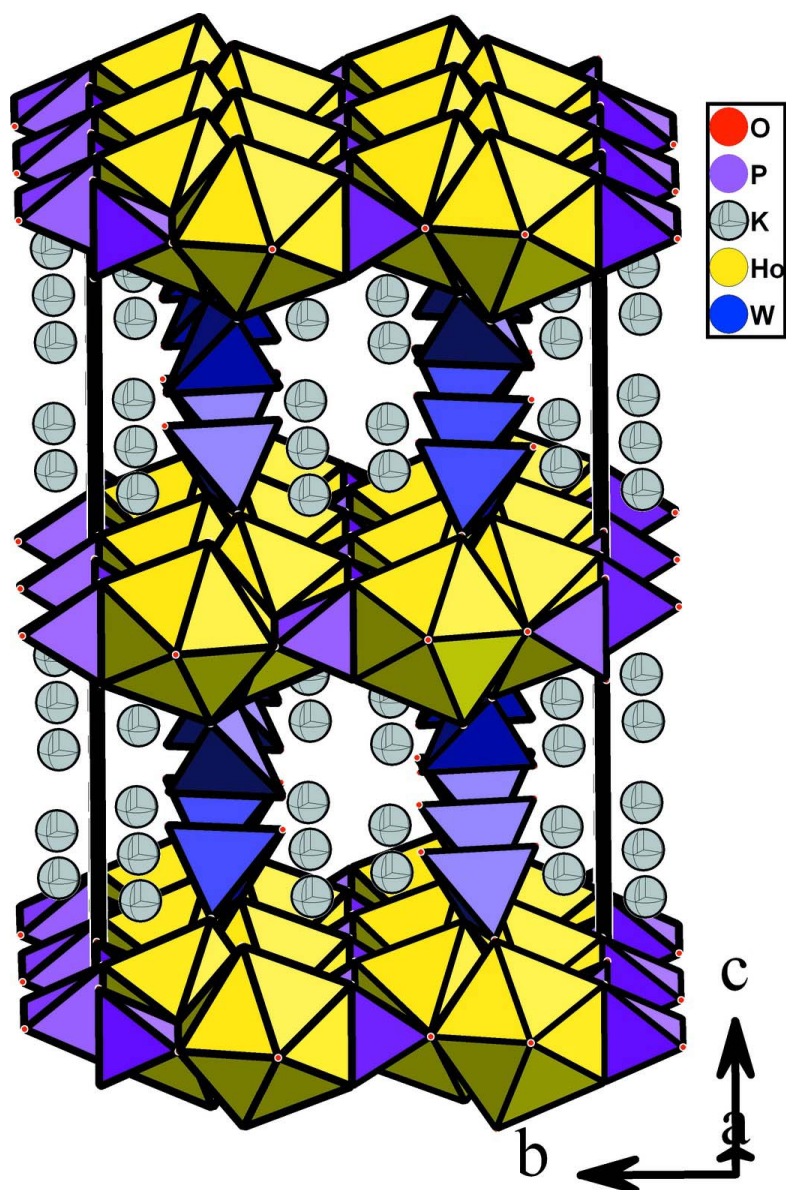
One of the characteristic features of this structure type is the "segregation" of slightly distorted PO<sub>4</sub> and WO<sub>4</sub> tetrahedra into adjacent layers (Fig. 1). The first layer with composition <sup>2</sup><sub>∞</sub>[HoPO<sub>4</sub>] contains <sup>1</sup><sub>∞</sub>[HoO<sub>8</sub>] zigzag chains (Fig. 2). The connection between neighboring chains is achieved *via* PO<sub>4</sub> tetrahedra. On the top and on the bottom of the <sup>2</sup><sub>∞</sub>[HoPO<sub>4</sub>] layer, WO<sub>4</sub> tetrahedra are attached. All [HoO<sub>8</sub>], PO<sub>4</sub> and WO<sub>4</sub> units exhibit 2 symmetry with bond lengths in the typical ranges (Table 1). The K<sup>+</sup> cations are situated in the resulting interlayer space and are surrounded by 8 oxygen atoms with K—O bond lengths ranging from 2.683 (4) Å to 3.133 (4) Å.

**S2. Experimental**

Single crystals of the title compound were grown from a multicomponent high-temperature solution. A mixture of 4.645 g K<sub>2</sub>W<sub>2</sub>O<sub>7</sub>, 0.865 g KPO<sub>3</sub>, and 1.150 g K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> was heated in a platinum crucible up to 1173 K which is above the melting temperature. Then 0.200 g of HoF<sub>3</sub> were added to this melt under stirring. The final mixture was held at this temperature for 1 h and cooled down to room temperature with a rate of 30 K h<sup>-1</sup>. The solidified melt was leached out with warm water to dissolve the superfluous flux. The final product consisted of beige needle-like crystals with a maximum length of up to 5 mm.

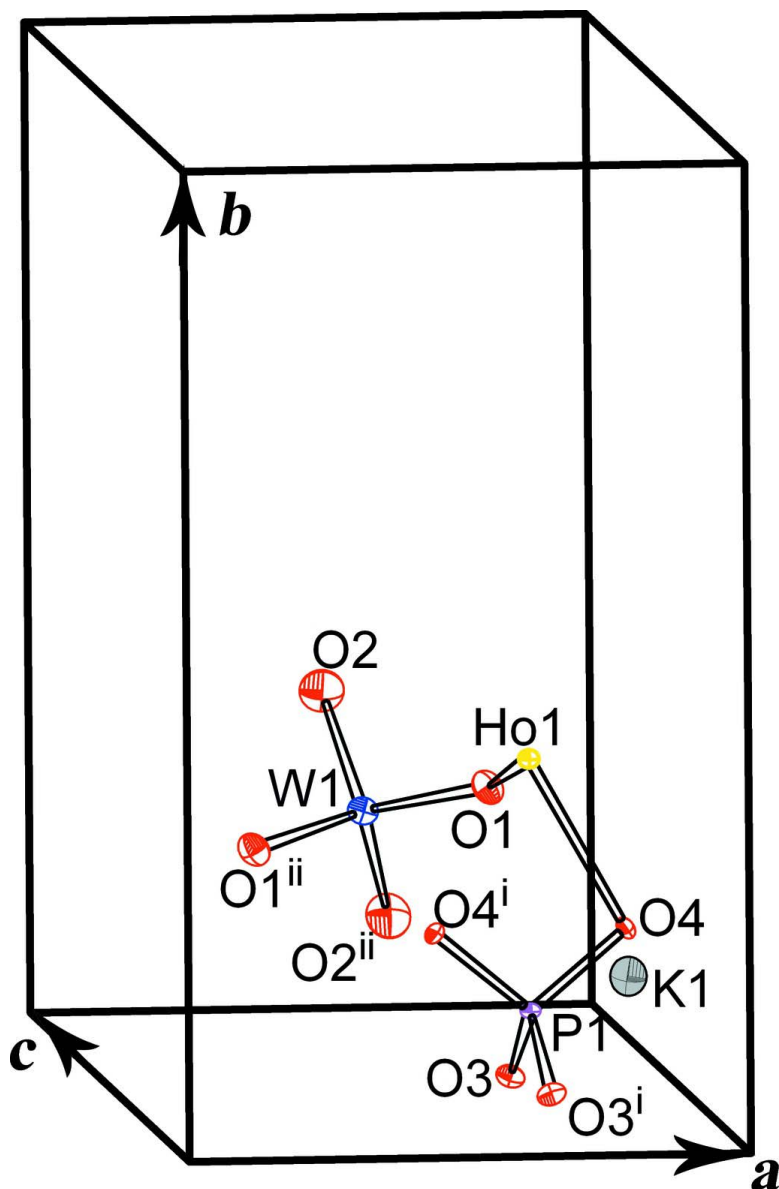
**S3. Refinement**

The highest peak and the deepest hole of the final Fourier map are located 0.58 Å from atom W1 and 1.11 Å from the same atom, respectively.



**Figure 1**

The layered structure of  $K_2Ho(PO_4)(WO_4)$ , leaving space where the  $K^+$  ions are located.



**Figure 2**

View of  $\text{K}_2\text{Ho}(\text{PO}_4)(\text{WO}_4)$  with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) 1,5- $x$ ;  $y$ ; 1- $z$ ; (ii) 1- $x$ ; 0.5- $y$ ;  $z$ ].

### Dipotassium holmium(III) phosphate(V) tungstate(VI)

#### Crystal data

$\text{K}_2\text{Ho}(\text{PO}_4)(\text{WO}_4)$   
 $M_r = 585.95$   
 Orthorhombic, *Ibca*  
 Hall symbol: -I 2b 2c  
 $a = 6.882$  (1) Å  
 $b = 12.1485$  (18) Å  
 $c = 19.695$  (3) Å  
 $V = 1646.6$  (4) Å<sup>3</sup>  
 $Z = 8$

$F(000) = 2064$   
 $D_x = 4.727$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 8608 reflections  
 $\theta = 3.4\text{--}33.0^\circ$   
 $\mu = 24.72$  mm<sup>-1</sup>  
 $T = 293$  K  
 Prism, pale beige  
 $0.10 \times 0.09 \times 0.07$  mm

Data collection

Oxford Diffraction XCalibur-3 CCD diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan based on the method by Blessing (1995)  
 $T_{\min} = 0.102$ ,  $T_{\max} = 0.177$

8608 measured reflections  
 1561 independent reflections  
 1257 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.055$   
 $\theta_{\max} = 33.0^\circ$ ,  $\theta_{\min} = 3.4^\circ$   
 $h = -10 \rightarrow 10$   
 $k = -18 \rightarrow 18$   
 $l = -30 \rightarrow 29$

Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.071$   
 $S = 1.15$   
 1561 reflections  
 62 parameters  
 0 restraints

$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 3.2575P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 1.90 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -1.73 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: *SHELXL97* (Sheldrick, 2008),  $F_c^* = kFc[1 + 0.001x \text{Fc}^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.00010 (2)

Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
W1	0.5	0.25	0.334530 (12)	0.01088 (5)
Ho1	0.75	0.325113 (17)	0.5	0.00662 (5)
K1	0.96872 (15)	0.07992 (10)	0.34389 (5)	0.0196 (2)
P1	0.75	0.07042 (10)	0.5	0.0065 (2)
O1	0.7088 (4)	0.2796 (3)	0.38536 (17)	0.0146 (7)
O2	0.4420 (6)	0.3643 (4)	0.2845 (2)	0.0269 (8)
O3	0.7308 (4)	-0.0047 (2)	0.43834 (16)	0.0102 (6)
O4	0.9229 (4)	0.1514 (2)	0.49215 (17)	0.0105 (6)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
W1	0.01432 (9)	0.01167 (9)	0.00666 (9)	-0.00095 (8)	0	0
Ho1	0.00652 (9)	0.00523 (9)	0.00811 (10)	0	-0.00005 (9)	0
K1	0.0204 (4)	0.0248 (5)	0.0137 (4)	-0.0002 (4)	0.0021 (3)	0.0039 (4)
P1	0.0064 (5)	0.0034 (5)	0.0098 (6)	0	0.0000 (5)	0
O1	0.0154 (14)	0.0171 (14)	0.0113 (14)	-0.0035 (11)	-0.0012 (11)	-0.0031 (11)
O2	0.0308 (17)	0.0296 (19)	0.0203 (17)	-0.0008 (17)	0.0013 (15)	0.0126 (16)
O3	0.0126 (13)	0.0079 (11)	0.0101 (13)	-0.0018 (10)	-0.0002 (11)	-0.0010 (9)
O4	0.0052 (10)	0.0066 (11)	0.0198 (16)	-0.0017 (9)	0.0011 (10)	-0.0016 (11)

*Geometric parameters (Å, °)*

W1—O2 <sup>i</sup>	1.749 (4)	Ho1—K1 <sup>vii</sup>	3.8119 (11)
W1—O2	1.749 (4)	Ho1—K1 <sup>vi</sup>	3.8119 (12)
W1—O1	1.788 (3)	K1—O3	2.683 (3)
W1—O1 <sup>i</sup>	1.788 (3)	K1—O2 <sup>v</sup>	2.689 (4)
W1—K1	3.8352 (12)	K1—O3 <sup>x</sup>	2.747 (3)
W1—K1 <sup>i</sup>	3.8352 (12)	K1—O1 <sup>vi</sup>	2.916 (3)
W1—K1 <sup>ii</sup>	4.0181 (13)	K1—O2 <sup>xi</sup>	2.934 (5)
W1—K1 <sup>iii</sup>	4.0181 (13)	K1—O4	3.063 (3)
W1—K1 <sup>iv</sup>	4.0821 (12)	K1—O1	3.122 (4)
W1—K1 <sup>v</sup>	4.0821 (12)	K1—O2 <sup>i</sup>	3.133 (4)
Ho1—O4 <sup>vi</sup>	2.274 (3)	K1—P1	3.4251 (11)
Ho1—O4 <sup>vii</sup>	2.274 (3)	K1—Ho1 <sup>vi</sup>	3.8119 (11)
Ho1—O1	2.342 (3)	K1—K1 <sup>iii</sup>	3.9511 (13)
Ho1—O1 <sup>viii</sup>	2.342 (3)	P1—O3	1.525 (3)
Ho1—O3 <sup>ix</sup>	2.401 (3)	P1—O3 <sup>viii</sup>	1.525 (3)
Ho1—O3 <sup>ii</sup>	2.401 (3)	P1—O4	1.552 (3)
Ho1—O4 <sup>viii</sup>	2.428 (3)	P1—O4 <sup>viii</sup>	1.552 (3)
Ho1—O4	2.428 (3)	P1—Ho1 <sup>xii</sup>	2.9802 (13)
Ho1—P1 <sup>ix</sup>	2.9802 (13)	P1—K1 <sup>viii</sup>	3.4251 (11)
Ho1—P1	3.0941 (13)		
O2 <sup>i</sup> —W1—O2	111.4 (3)	O3 <sup>x</sup> —K1—O4	61.07 (8)
O2 <sup>i</sup> —W1—O1	106.94 (17)	O1 <sup>vi</sup> —K1—O4	69.23 (9)
O2—W1—O1	109.83 (19)	O2 <sup>xi</sup> —K1—O4	130.90 (10)
O2 <sup>i</sup> —W1—O1 <sup>i</sup>	109.83 (19)	O3—K1—O1	76.52 (9)
O2—W1—O1 <sup>i</sup>	106.94 (17)	O2 <sup>v</sup> —K1—O1	100.44 (12)
O1—W1—O1 <sup>i</sup>	111.9 (2)	O3 <sup>x</sup> —K1—O1	117.21 (9)
O4 <sup>vi</sup> —Ho1—O4 <sup>vii</sup>	165.59 (15)	O1 <sup>vi</sup> —K1—O1	84.72 (10)
O4 <sup>vi</sup> —Ho1—O1	94.81 (11)	O2 <sup>xi</sup> —K1—O1	156.62 (10)
O4 <sup>vii</sup> —Ho1—O1	88.59 (11)	O4—K1—O1	58.09 (8)
O4 <sup>vi</sup> —Ho1—O1 <sup>viii</sup>	88.59 (11)	O3—K1—O2 <sup>i</sup>	77.94 (10)
O4 <sup>vii</sup> —Ho1—O1 <sup>viii</sup>	94.81 (11)	O2 <sup>v</sup> —K1—O2 <sup>i</sup>	78.50 (9)
O1—Ho1—O1 <sup>viii</sup>	152.68 (18)	O3 <sup>x</sup> —K1—O2 <sup>i</sup>	156.48 (11)
O4 <sup>vi</sup> —Ho1—O3 <sup>ix</sup>	88.91 (10)	O1 <sup>vi</sup> —K1—O2 <sup>i</sup>	131.64 (12)
O4 <sup>vii</sup> —Ho1—O3 <sup>ix</sup>	78.65 (10)	O2 <sup>xi</sup> —K1—O2 <sup>i</sup>	103.49 (13)
O1—Ho1—O3 <sup>ix</sup>	133.18 (11)	O4—K1—O2 <sup>i</sup>	101.64 (9)
O1 <sup>viii</sup> —Ho1—O3 <sup>ix</sup>	73.88 (12)	O1—K1—O2 <sup>i</sup>	54.04 (10)
O4 <sup>vi</sup> —Ho1—O3 <sup>ii</sup>	78.65 (10)	O3—P1—O3 <sup>viii</sup>	106.4 (2)
O4 <sup>vii</sup> —Ho1—O3 <sup>ii</sup>	88.91 (10)	O3—P1—O4	111.52 (16)
O1—Ho1—O3 <sup>ii</sup>	73.88 (12)	O3 <sup>viii</sup> —P1—O4	113.10 (16)
O1 <sup>viii</sup> —Ho1—O3 <sup>ii</sup>	133.18 (12)	O3—P1—O4 <sup>viii</sup>	113.10 (16)
O3 <sup>ix</sup> —Ho1—O3 <sup>ii</sup>	61.17 (15)	O3 <sup>viii</sup> —P1—O4 <sup>viii</sup>	111.52 (16)
O4 <sup>vi</sup> —Ho1—O4 <sup>viii</sup>	126.77 (7)	O4—P1—O4 <sup>viii</sup>	101.3 (2)
O4 <sup>vii</sup> —Ho1—O4 <sup>viii</sup>	67.63 (12)	W1—O1—Ho1	133.20 (16)
O1—Ho1—O4 <sup>viii</sup>	78.27 (12)	W1—O1—K1 <sup>vi</sup>	124.93 (16)
O1 <sup>viii</sup> —Ho1—O4 <sup>viii</sup>	78.03 (12)	Ho1—O1—K1 <sup>vi</sup>	92.27 (11)

O3 <sup>ix</sup> —Ho1—O4 <sup>viii</sup>	133.56 (10)	W1—O1—K1	99.08 (14)
O3 <sup>ii</sup> —Ho1—O4 <sup>viii</sup>	143.86 (10)	Ho1—O1—K1	111.49 (12)
O4 <sup>vi</sup> —Ho1—O4	67.63 (12)	K1 <sup>vi</sup> —O1—K1	86.88 (9)
O4 <sup>vii</sup> —Ho1—O4	126.77 (8)	W1—O2—K1 <sup>v</sup>	132.6 (2)
O1—Ho1—O4	78.03 (12)	W1—O2—K1 <sup>ii</sup>	115.89 (19)
O1 <sup>viii</sup> —Ho1—O4	78.27 (12)	K1 <sup>v</sup> —O2—K1 <sup>ii</sup>	95.86 (13)
O3 <sup>ix</sup> —Ho1—O4	143.86 (10)	W1—O2—K1 <sup>i</sup>	99.64 (16)
O3 <sup>ii</sup> —Ho1—O4	133.56 (10)	K1 <sup>v</sup> —O2—K1 <sup>i</sup>	120.18 (15)
O4 <sup>viii</sup> —Ho1—O4	59.26 (13)	K1 <sup>ii</sup> —O2—K1 <sup>i</sup>	81.21 (11)
O3—K1—O2 <sup>v</sup>	152.62 (12)	P1—O3—Ho1 <sup>xii</sup>	96.20 (15)
O3—K1—O3 <sup>x</sup>	78.69 (8)	P1—O3—K1	105.64 (14)
O2 <sup>v</sup> —K1—O3 <sup>x</sup>	124.78 (11)	Ho1 <sup>xii</sup> —O3—K1	130.32 (12)
O3—K1—O1 <sup>vi</sup>	119.65 (10)	P1—O3—K1 <sup>iii</sup>	142.66 (16)
O2 <sup>v</sup> —K1—O1 <sup>vi</sup>	86.67 (12)	Ho1 <sup>xii</sup> —O3—K1 <sup>iii</sup>	95.30 (9)
O3 <sup>x</sup> —K1—O1 <sup>vi</sup>	60.35 (9)	K1—O3—K1 <sup>iii</sup>	93.37 (11)
O3—K1—O2 <sup>xi</sup>	93.55 (11)	P1—O4—Ho1 <sup>vi</sup>	146.28 (18)
O2 <sup>v</sup> —K1—O2 <sup>xi</sup>	78.59 (14)	P1—O4—Ho1	99.72 (13)
O3 <sup>x</sup> —K1—O2 <sup>xi</sup>	80.53 (10)	Ho1 <sup>vi</sup> —O4—Ho1	111.83 (11)
O1 <sup>vi</sup> —K1—O2 <sup>xi</sup>	118.34 (11)	P1—O4—K1	89.66 (13)
O3—K1—O4	52.05 (8)	Ho1 <sup>vi</sup> —O4—K1	89.92 (10)
O2 <sup>v</sup> —K1—O4	148.06 (12)	Ho1—O4—K1	110.96 (11)

Symmetry codes: (i)  $-x+1, -y+1/2, z$ ; (ii)  $-x+3/2, y+1/2, z$ ; (iii)  $x-1/2, -y, z$ ; (iv)  $x-1/2, y, -z+1/2$ ; (v)  $-x+3/2, -y+1/2, -z+1/2$ ; (vi)  $-x+2, -y+1/2, z$ ; (vii)  $x-1/2, -y+1/2, -z+1$ ; (viii)  $-x+3/2, y, -z+1$ ; (ix)  $x, y+1/2, -z+1$ ; (x)  $x+1/2, -y, z$ ; (xi)  $-x+3/2, y-1/2, z$ ; (xii)  $x, y-1/2, -z+1$ .