

12-Membered borophosphate rings in  
 $\text{KNi}_5[\text{P}_6\text{B}_6\text{O}_{23}(\text{OH})_{13}]$ Olga V. Yakubovich,<sup>a\*</sup> Ian M. Steele,<sup>b</sup> Werner Massa<sup>c</sup> and  
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The title compound, potassium pentanickel hexaborophosphate tridecahydroxide, was synthesized under hydrothermal conditions from the  $\text{NiCl}_2\text{-K}_3\text{PO}_4\text{-B}_2\text{O}_3\text{-K}_2\text{CO}_3\text{-H}_2\text{O}$  system. The crystal structure was determined using single-crystal X-ray diffraction at 100 K. The  $\text{KNi}_5[\text{P}_6\text{B}_6\text{O}_{23}(\text{OH})_{13}]$  phase is cubic. For the three crystallographically distinct Ni centers, two occupy sites with 3 symmetry, while the third Ni and the K atom are located on  $\bar{3}$  sites. The structure is built from alternating borate and phosphate tetrahedra forming 12-membered puckered rings with  $\text{K}^+$  ions at the centers. These rings are arranged as in cubic dense sphere packing. A novel feature of the new crystal structure is the presence of linear trimers of face-sharing  $[\text{NiO}_6]$  octahedra occupying the octahedral interstices of this sphere packing, and of single  $[\text{NiO}_6]$  octahedra in the tetrahedral interstices. All oxygen corners of the Ni octahedra are linked to phosphate or borate tetrahedra of the 12-membered rings to form a mixed anionic framework.

## Comment

Since the first report on the synthesis and characterization of a borophosphate in 1994 (Kniep *et al.*, 1994), the borophosphate family has grown quickly. Presently, it incorporates a large number of compounds having various structures ranging from densely packed to microporous (Ewald *et al.*, 2007). There are many borophosphate complexes with diverse transition metal ions. These occupy a niche within this group because of their promising properties, in particular as good candidates for generating novel magnetic materials (Maspoeh *et al.*, 2007). Compared with the tetrahedral or tetrahedral/triangular oxo-complexes in borophosphates, transition metal ions show higher flexibility in coordination geometry and a stronger tendency for forming edge-sharing (or even face-sharing) linkages of metal–oxygen polyhedra, providing different

modes of magnetic exchange. For example, antiferromagnetic properties were found for  $(\text{NH}_4)_4[\text{Mn}_9\text{B}_2(\text{OH})_2(\text{HPO}_4)_4(\text{PO}_4)_6]$ , which has a mixed anionic framework built from  $\text{PO}_4$  and  $\text{BO}_4$  tetrahedra, and Mn five-vertex polyhedra and octahedra (Yang *et al.*, 2006). The compound  $\text{NH}_4[\text{FeBP}_2\text{O}_8(\text{OH})]$  exhibits one-dimensional channels and antiferromagnetic ordering at 17 K (Huang *et al.*, 2001).

So-called mixed anionic frameworks constructed from polyhedra that differ both in chemistry and geometry are often present in natural minerals and in many synthetic compounds. Some of them combine the usual properties of microporous materials with the novel ones of, for example, magnetic, optical and ion-conductive solids, and may be promising candidates for applications in various technologies (Cheetham *et al.*, 1999; Davis, 2002; Yakubovich, 2008). Only two natural phases built from borate and phosphate oxo-complexes are known: these are the minerals seamanite,  $\text{Mn}_3(\text{OH})_2[\text{B}(\text{OH})_4][\text{PO}_4]$ , and lüneburgite,  $\text{Mg}_3(\text{H}_2\text{O})_6[\text{B-PO}_4(\text{OH})_3]_2$ . Both structures contain B atoms in a tetrahedral coordination. The first one should not formally be considered as a borophosphate because there are no shared oxygen vertices between  $[\text{B}(\text{OH})_4]$  and  $[\text{PO}_4]$  tetrahedra in its crystal structure; thus, it is classified as a borate–phosphate (Yakubovich, Steele, Mochenova *et al.*, 2009; Ewald *et al.*, 2007). Dimers of B and P tetrahedra sharing a common vertex constitute the anionic part of the lüneburgite crystal structure. Our research is aimed at the synthesis and structural characterization of novel anionic borophosphate/transition metal systems containing alkali-metal counter-cations. We describe here a new compound based on a mixed anionic framework formed from  $[\text{PO}_4]$ ,  $[\text{BO}_4]$  and  $[\text{NiO}_6]$ .

The asymmetric unit of the cubic structure, space group  $P\bar{a}3$  (Fig. 1), consists of one unique tetrahedral P site, one unique tetrahedral B site (both on the general position  $24d$ ), three

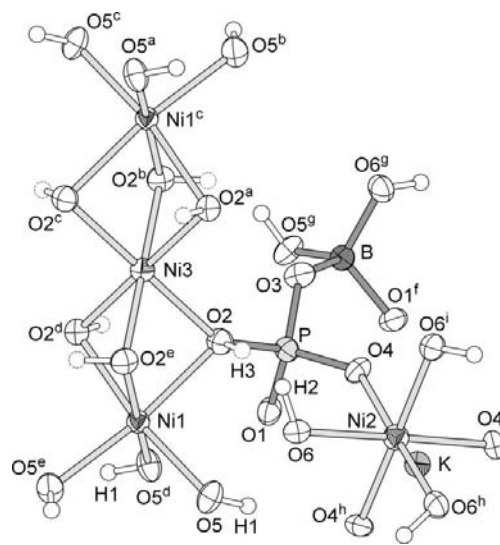
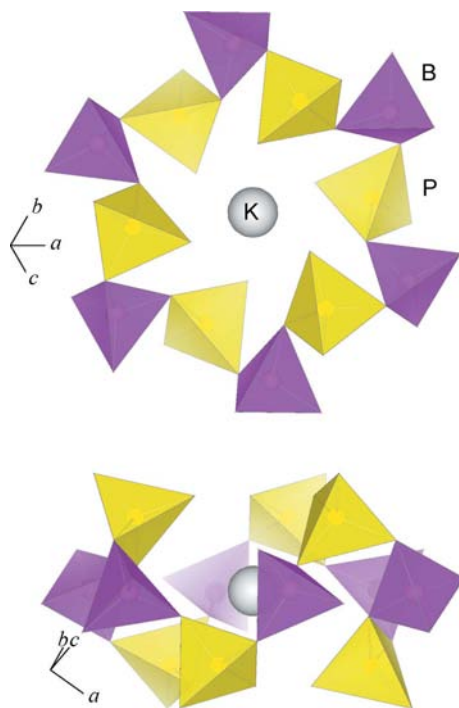


Figure 1

The main structural elements of the title compound. Displacement ellipsoids are drawn at the 90% probability level. Dashed spheres are H3 disordered with  $\frac{1}{6}$  occupation. [Symmetry codes: (a)  $-y, -z, -x$ ; (b)  $-z, -x, -y$ ; (c)  $-x, -y, -z$ ; (d)  $y, z, x$ ; (e)  $z, x, y$ ; (f)  $-\frac{1}{2} + z, x, \frac{1}{2} - y$ ; (g)  $-\frac{1}{2} + x, y, \frac{1}{2} - z$ ; (h)  $\frac{1}{2} - z, -x, \frac{1}{2} + y$ ; (i)  $-y, -\frac{1}{2} + z, \frac{1}{2} - x$ .]

octahedral Ni sites (Ni1 and Ni2 on  $8c$  with site symmetry  $3$ , Ni3 on  $4a, \bar{3}$ ), one K site ( $4b, \bar{3}$ ) and six O atoms on general positions. The phosphate polyhedron is strongly distorted: the P—O distances vary from 1.510 (2) to 1.565 (2) Å. As expected, the longer bonds are to O1 and O3 which are further linked to B; the short bonds are to O2 and O4 linked to Ni. The borate tetrahedron  $[\text{BO}_2(\text{OH})_2]$  is more regular, with two B—OH bond lengths of 1.457 (4) and 1.471 (4) Å, and two equal B—O distances of 1.479 (4) Å. Similarly, the similarity of B—O bond distances to  $\text{O}^{2-}$  and  $\text{OH}^-$  may be explained by the further bridging to P and Ni, respectively.

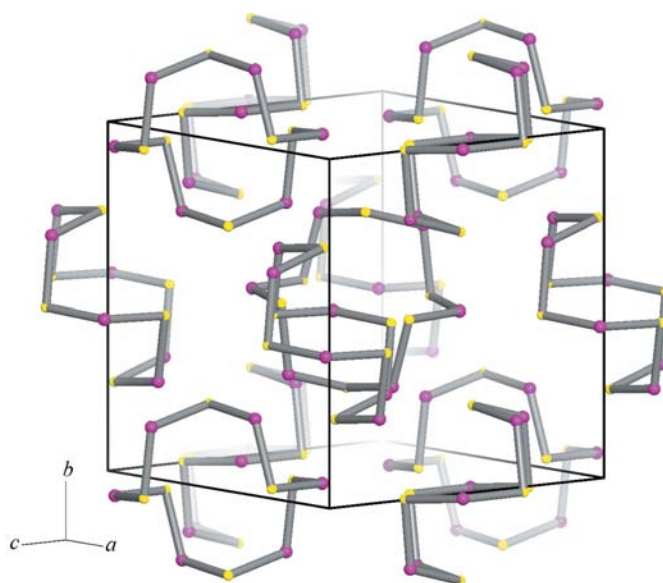
While Ni2 has nearly regular octahedral coordination (Table 1), Ni1 and Ni3 show strong angular distortions due to the formation of a linear  $\text{Ni1}\cdots\text{Ni3}\cdots\text{Ni1}(-x, -y, -z)$  trimer composed of face-sharing octahedra with  $\bar{3}$  symmetry (Fig. 1). The angles  $\text{O2}(-y, -z, -x)-\text{Ni3}-\text{O2}(-x, -y, -z)$ , including O2 atoms of the shared face, are only  $79.6(1)^\circ$ , while those between O2 atoms of the opposite faces are  $100.4(1)^\circ$ . Even the outer Ni1 octahedra are rather deformed, with narrower angles toward the common face and angles greater than  $90^\circ$  for the outer  $\text{O5}-\text{Ni1}-\text{O5}(z, x, y)$  angles. The  $\text{K}^+$  ion in the  $\bar{3}$  position has six O atoms at distances of 2.792 (2) Å and six at 2.841 (2) Å (Table 1). All O atoms except O1 are involved in a system of  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds, providing additional crosslinking in the structure. With  $\text{O}\cdots\text{O}$  distances between 2.846 (3) and 3.193 (3) Å, they are classed as medium to weak. The O5 and O6 hydrogen-bond donors participate in the formation of a coordination sphere around the B atoms typical for borate and borophosphate structures.



**Figure 2**

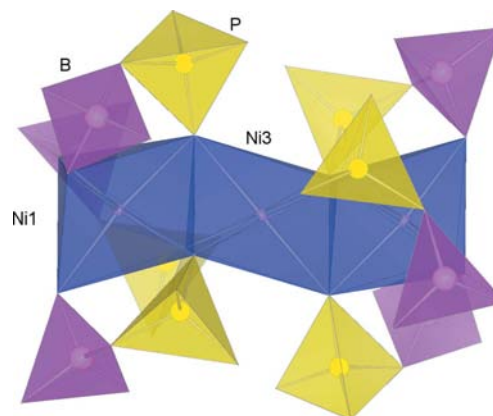
The 12-membered puckered ring of alternating  $[\text{PO}_4]$  and  $[\text{BO}_4]$  tetrahedra centered on K shown (a) along the threefold axis along  $[\bar{1}11]$  and (b) approximately from  $[011]$ .

An essential building unit of the crystal structure is a 12-membered ring of alternating  $[\text{BO}_2(\text{OH})_2]$  and  $[\text{PO}_4]$  tetrahedra sharing oxygen vertices. These rings with 3 ( $C_3$ ) symmetry (Fig. 2) are aligned with their threefold axes along the four diagonals of the cubic unit cell. Their centers are occupied by the  $\text{K}^+$  ions and form a face-centered cubic (f.c.c.) arrangement (Fig. 3). The octahedral interstices of this f.c.c. packing are occupied by the face-sharing linear trimers of  $[\text{NiO}_6]$  octahedra ( $\text{Ni1}\cdots\text{Ni3}\cdots\text{Ni1}$ ) inclined in varying directions about the diagonals (Figs. 1 and 4) and connected over a borate and a phosphate tetrahedron to each of its six neighboring rings. The Ni2 centers, also in octahedral coordination, occupy all tetrahedral interstices of this f.c.c. sphere packing but avoid contact with the inclined trimers, in varying off-center positions. All oxygen corners of the Ni octahedra are linked to phosphate or borate tetrahedra of the 12-membered rings. Two Ni2 octahedra close the 12-membered



**Figure 3**

Face-centered cubic (f.c.c.) arrangement of the borophosphate rings in four orientations. Only the B and P atoms and their direct connections are shown.

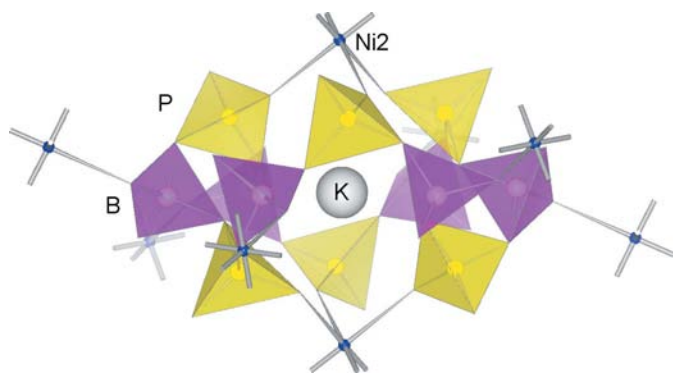


**Figure 4**

Linear trimer of the  $[\text{NiO}_6]$  octahedra with  $\bar{3}$  symmetry and its connection to the fragments of six neighboring borophosphate rings.

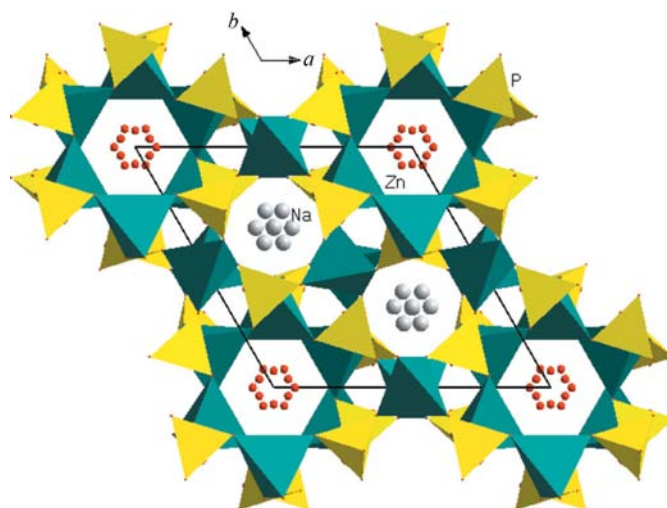
ring to form a cage by bridging the three  $[\text{PO}_4]$  tetrahedra on the top and bottom (with regard to the threefold axis) over octahedral faces (O4) (Fig. 5). The free opposite faces of these Ni2 octahedra (O6) make the connection to three equatorial  $[\text{BO}_4]$  groups of three neighboring rings. Correspondingly, the six  $[\text{BO}_4]$  tetrahedra in the equatorial plane of the 12-membered ring are linked to Ni2 octahedra of six neighboring rings by sharing common vertices. The linear trimeric  $[\text{Ni}_3\text{O}_{12}]$  unit built from octahedra sharing faces (Fig. 4) shows very short Ni···Ni distances of 2.800 (1) Å. Thus, interesting magnetic properties may be expected. Possible magnetic superexchange through Ni—O—Ni pathways with an angle close to  $90^\circ$  may lead to ferromagnetic interactions within the trimer. Analogous trimeric units with even shorter Ni···Ni distances of 2.727 (1) Å were observed in  $\text{Cs}_4\text{Ni}_3\text{F}_{10}$  for which spontaneous magnetization was observed between 9.5 and 21 K (Schmidt *et al.*, 1992). It is worth mentioning that anti-ferromagnetic behavior has been found for several Ni phosphates with microporous crystal structures (Sanz *et al.*, 1999; Daidouh *et al.*, 1999; Liu *et al.*, 2004; Guillou *et al.*, 1999, 2001).

The title compound presents the second example of a borophosphate with a zwölf single ring according to the nomenclature introduced by Ewald *et al.* (2007). We obtained the first compound with a similar structure also under hydrothermal conditions:  $\text{Na}_{0.45}\text{K}(\text{Mg}_{0.6}\text{Ni}_{0.2}\text{Al}_{0.2})\text{Ni}_2\{(\text{Ni}_{0.5}\text{Al}_{0.3}\text{Mg}_{0.2})_2[\text{B}_6\text{P}_6\text{O}_{24}(\text{OH})_{12}]\}$ , (II) (Yakubovich, Steele, Mochenova *et al.*, 2009). The same anionic sublattice formed from O atoms characterizes both crystal structures. Both have K ions encapsulated in borophosphate rings built from 12 tetrahedra. In (II), two of the three symmetrically independent Ni<sup>2+</sup> octahedra are ‘diluted’ by Mg<sup>2+</sup> and Al<sup>3+</sup> cations and differ slightly in size from the ‘pure’ polyhedra discussed here. The main difference between the crystal structures of (I) and (II) is the distribution of other cations in their micropores. In (II) (Yakubovich, Steele, Mochenova *et al.*, 2009), Na cations are statistically distributed in the centers of octahedra with  $C_3$  symmetry [Na—O distances = 2.203 (9) and 2.261 (9) Å] which are empty in the present structure, (I). In contrast, in the crystal structure of the pure Ni–borophosphate additional H atoms occupy  $\frac{1}{6}$  of a general position near O2, forming disordered hydroxyl groups.

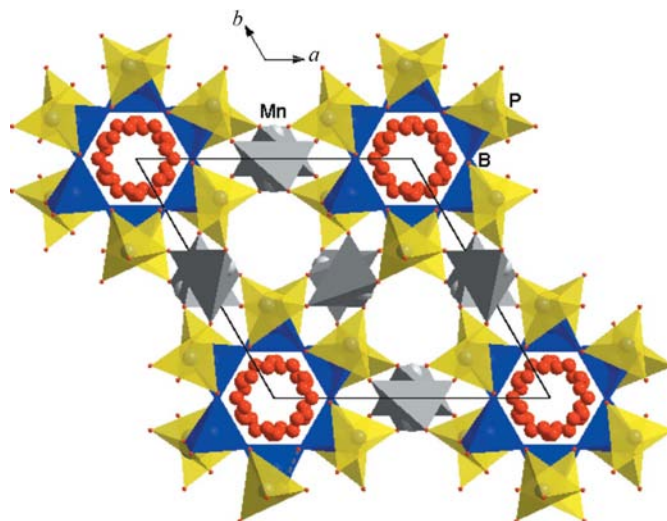


**Figure 5**  
Linkage of the Ni2 octahedra to the borophosphate rings. For clarity, the O ligands at Ni are cut off.

The new compound  $\text{KNi}_5[\text{P}_6\text{B}_6\text{O}_{23}(\text{OH})_{13}]$ , (I), is topologically related to the cyclophosphates  $\text{Cs}_3\text{V}_3(\text{PO}_3)_{12}$  (Lavrov *et al.*, 1981), (III), and  $\text{NaM}(\text{PO}_3)_3$  ( $M = \text{Zn}$  or  $\text{Mg}$ ) (Abrahams *et al.*, 2000), (IV), as parent structures. The anionic sublattices of all three structures are based on six symmetrically independent O atoms and are very similar. In the case of (I), the 12-membered cyclophosphate ring with two independent P sites transforms to the borophosphate architecture by ordered occupation by B and P. The rings are all filled by 12-coordinate alkali-metal cations (site 4b). The single octahedral site of Ni2 in (I) corresponds to that of V2 in (III) and Zn2 in (IV). The peculiar trimeric octahedral face-sharing  $[\text{Ni}_3\text{O}_{12}]$  unit in (I) is replaced in (III) by a Cs–V–Cs unit, and in (IV) by a Zn–Na–Zn group. Of course, the geometric and bonding properties of these groups are rather different in all three cases and, therefore, despite having the same space-group type and the close topological relationship, the structures are not isotopic.



**Figure 6**  
The  $\text{Na}[\text{Zn}(\text{PO}_4)](\text{H}_2\text{O})$  (CZP) crystal structure in an [001] projection.



**Figure 7**  
The  $A^+M^{2+}(\text{H}_2\text{O})_2(\text{BP}_2\text{O}_8)(\text{H}_2\text{O})$  crystal structure transformed to the CZP type shown for the Na/Mn variety.

This is especially true for Zn compound (IV), as here an additional octahedral site is occupied by Na3.

It is interesting that another sodium zincophosphate Na[Zn(PO<sub>4</sub>)](H<sub>2</sub>O), a zeolite-type material 'CZP' (Harrison *et al.*, 1996) is considered as an archetype for some borophosphates, namely for  $A^+M^{2+}(H_2O)_2(BP_2O_8)(H_2O)$ ,  $A_{0.5}^{2+}M^{2+}(H_2O)_2(BP_2O_8)(H_2O)$  and  $M^{3+}(H_2O)_2(BP_2O_8)(H_2O)$  ( $A = Na, K, Ca$ , and  $M = Zn, Co, Ni, Fe, Mn, Cd, Sc, In$ ; Boy *et al.*, 2001*a,b*; Boy, Stowasser *et al.*, 2001; Shi, Shan, Dai *et al.*, 2003; Shi, Shan, He *et al.*, 2003; Menezes *et al.*, 2007; Yakubovich, Steele & Dimitrova, 2009; Yilmaz *et al.*, 2000; Ge *et al.*, 2003; Ewald *et al.*, 2004, 2006). The 'CZP' crystal structure is based on an anionic framework formed from [ZnO<sub>4</sub>] and [PO<sub>4</sub>] tetrahedra sharing vertices. In borophosphates, the [BO<sub>4</sub>] tetrahedron plays the role of one independent [ZnO<sub>4</sub>] polyhedron, while the second [ZnO<sub>4</sub>] tetrahedron transforms in an [M(H<sub>2</sub>O)<sub>2</sub>O<sub>4</sub>] octahedron. According to Boy, Stowasser *et al.* (2001), at 453 K water molecules that coordinate Zn centers in NaZn(H<sub>2</sub>O)<sub>2</sub>(BP<sub>2</sub>O<sub>8</sub>)(H<sub>2</sub>O) are lost from the crystal structure. This leads to a transformation of Zn octahedra into tetrahedra, and the mixed anionic framework {ZnBP<sub>2</sub>O<sub>8</sub>} in the borophosphate becomes topologically identical to that of {Zn<sub>2</sub>P<sub>2</sub>O<sub>8</sub>} in Na[Zn(PO<sub>4</sub>)](H<sub>2</sub>O) (Figs. 6 and 7). The above examples demonstrate the relevance of phosphate archetypes to borophosphate compounds. To our knowledge, no cases of opposite processes have been cited in the literature up to now.

## Experimental

The title compound was synthesized under mild hydrothermal conditions. The starting materials, *viz.* fine chemicals of NiCl<sub>2</sub>, K<sub>3</sub>PO<sub>4</sub>, B<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>, were mixed in distilled water (weight ratio 4:2:8:1:45) and placed in a PTFE-lined stainless steel autoclave. The pH of the initial solution was 5–6. The experiment was performed at a temperature of 553 K and a pressure of  $7 \times 10^3$  kPa over a period of 20 d. Light-green crystals of an octahedral shape up to 0.3 mm in size were filtered off, washed with water and dried in air. The presence of Ni, K, P, O and B in the samples was confirmed by qualitative X-ray spectral analysis (Jeol JSM-6480LV, EDSINCA-Wave 500).

### Crystal data

KNi <sub>5</sub> [P <sub>6</sub> B <sub>6</sub> O <sub>23</sub> (OH) <sub>13</sub> ]	$Z = 2$
$M_r = 2344.67$	Mo $K\alpha$ radiation
Cubic, $Pa\bar{3}$	$\mu = 4.52 \text{ mm}^{-1}$
$a = 13.467(2) \text{ \AA}$	$T = 100 \text{ K}$
$V = 2442.3(6) \text{ \AA}^3$	$0.1 \times 0.1 \times 0.1 \text{ mm}$

### Data collection

Bruker SMART CCD area-detector diffractometer	27118 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1012 independent reflections
$T_{\min} = 0.637$ , $T_{\max} = 0.643$	821 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.093$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.061$	
$S = 1.03$	$\Delta\rho_{\max} = 0.45 \text{ e \AA}^{-3}$
1012 reflections	$\Delta\rho_{\min} = -0.58 \text{ e \AA}^{-3}$
89 parameters	
2 restraints	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

K1—O4	2.792 (2)	Ni2—O4	2.064 (2)
B1—O6 <sup>i</sup>	1.457 (4)	Ni2—O6	2.071 (2)
B1—O5 <sup>i</sup>	1.471 (4)	Ni3—O2	2.055 (2)
B1—O3	1.479 (4)	P1—O2	1.510 (2)
B1—O1 <sup>ii</sup>	1.480 (4)	P1—O4	1.512 (2)
Ni1—O5	2.032 (2)	P1—O3	1.543 (2)
Ni1—O2	2.077 (2)	P1—O1	1.565 (2)
Ni1...Ni3	2.8000 (9)		
O6 <sup>i</sup> —B1—O5 <sup>i</sup>	111.3 (3)	O4—P1—O3	107.89 (13)
O6 <sup>i</sup> —B1—O3	106.8 (3)	O2—P1—O1	107.96 (13)
O5 <sup>i</sup> —B1—O3	107.0 (3)	O4—P1—O1	107.96 (13)
O6 <sup>i</sup> —B1—O1 <sup>ii</sup>	112.9 (3)	O3—P1—O1	109.38 (13)
O5 <sup>i</sup> —B1—O1 <sup>ii</sup>	109.0 (3)	B1—O3—P1	130.6 (2)
O3—B1—O1 <sup>ii</sup>	109.6 (3)	Ni3—O2—Ni1	85.30 (9)
O2—P1—O4	115.12 (14)	B1 <sup>iii</sup> —O1—P1	128.9 (2)
O2—P1—O3	108.44 (13)		

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

The positions of two independent H atoms at O5 and O6 were obtained by difference Fourier techniques and they were refined with isotropic displacement parameters. The O—H bond lengths were constrained to 0.85 Å. As in this stage the formula remained unbalanced, namely {KNi<sub>5</sub>P<sub>6</sub>B<sub>6</sub>O<sub>24</sub>(OH)<sub>12</sub>}<sup>−</sup> ( $Z = 4$ ), the coordinates of one more H atom per formula had to be localized. The only reasonable position for an additional H atom was found at O2 which had a low bond valence sum and enough space for OH<sup>−</sup>. Thus, it could bear  $\frac{1}{6}$  disordered H in a 24*d* position. A structure model including a calculated position for this H3 atom gave a small lowering of *R* values and reasonable geometric parameters for a hydrogen bond toward O6.

Data collection: SMART (Bruker, 2001); cell refinement: SMART; data reduction: SAINT (Bruker, 2001); 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: publCIF (Westrip, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3039). Services for accessing these data are described at the back of the journal.

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