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## Structure Reports

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# Rietveld refinement of the langbeinite-type mixed-metal phosphate $K_2Ni_{0.5}Zr_{1.5}(PO_4)_3$

Igor V. Zatovsky

Department of Inorganic Chemistry, Taras Shevchenko National University, 64/13, Volodymyrska St, 01601 Kyiv, Ukraine

Correspondence e-mail: zvigov@yandex.ru

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Key indicators: powder X-ray study;  $T = 293$  K; mean  $\sigma(P-O) = 0.016$  Å; disorder in main residue;  $R$  factor = 0.100;  $wR$  factor = 0.134; data-to-parameter ratio = 43.9.

Dipotassium [nickel(II) zirconium(IV)] tris(orthophosphate) was prepared from a self-flux in the system  $K_2O-P_2O_5-NiO-K_2ZrF_6$ . The title compound belongs to the langbeinite family and is built up from two  $[MO_6]$  octahedra [ $M = Ni:Zr$  with mixed occupancy in ratios of 0.21 (4):0.79 (4) and 0.29 (4):0.71 (4), respectively] and  $[PO_4]$  tetrahedra inter-linked *via* vertices into a  $\infty^3[M_2(PO_4)_3]$  framework. Two independent  $K^+$  cations are located in large cavities of the framework, with coordination numbers to  $O^{2-}$  anions of nine and twelve. The K, Ni, and Zr sites are located on threefold rotation axes.

## Related literature

For the structure of the mineral langbeinite, see: Zemmann & Zemmann (1957). For langbeinite-related phosphates based on different pairs of polyvalent metals, see: Wulff *et al.* (1992) for  $K_2REZr(PO_4)_3$  ( $RE = Y, Gd$ ); Orlova *et al.* (2003) for  $K_2FeZr(PO_4)_3$ ; Ogorodnyk *et al.* (2007a) for  $K_{1.96}Mn_{0.57}Zr_{1.43}(PO_4)_3$  and  $K_{1.93}Mn_{0.53}Hf_{1.47}(PO_4)_3$ ; Ogorodnyk *et al.* (2007b) for  $K_2Ni_{0.5}Ti_{1.5}(PO_4)_3$ . For the profile function used in the Rietveld refinement, see: Thompson *et al.* (1987).

## Experimental

### Crystal data

$K_2Ni_{0.5}Zr_{1.5}(PO_4)_3$   
 $M_r = 529.29$   
 Cubic,  $P2_13$   
 $a = 10.15724$  (13) Å  
 $V = 1047.92$  (2) Å<sup>3</sup>

$Z = 4$   
 Cu  $K\alpha$  radiation,  $\lambda = 1.540598$  Å  
 $T = 293$  K  
 Flat sheet,  $25 \times 25$  mm

### Data collection

Shimadzu LabX XRD-6000 diffractometer  
 Specimen mounting: glass container  
 Data collection mode: reflection

Scan method: step  
 $2\theta_{\min} = 10.910^\circ$ ,  $2\theta_{\max} = 104.911^\circ$ ,  
 $2\theta_{\text{step}} = 0.020^\circ$

### Refinement

$R_p = 0.100$   
 $R_{wp} = 0.134$   
 $R_{\text{exp}} = 0.034$   
 $R_{\text{Bragg}} = 0.041$   
 $R(F) = 0.035$   
 $\chi^2 = 15.761$   
 4701 data points  
 107 parameters  
 2 restraints

Table 1

Selected bond lengths (Å).

K1—O1 <sup>i</sup>	2.956 (16)	Zr1—O2 <sup>iv</sup>	2.098 (14)
K1—O2 <sup>ii</sup>	3.165 (14)	Zr2—O4	2.036 (12)
K1—O4 <sup>ii</sup>	3.325 (14)	Zr2—O3 <sup>i</sup>	2.041 (16)
K2—O3 <sup>ii</sup>	2.973 (15)	P1—O3	1.530 (18)
K2—O2 <sup>iii</sup>	3.026 (16)	P1—O4	1.523 (13)
K2—O4 <sup>ii</sup>	3.127 (15)	P1—O2	1.515 (15)
K2—O4 <sup>iii</sup>	3.332 (15)	P1—O1	1.493 (16)
Zr1—O1	2.070 (14)		

Symmetry codes: (i)  $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$ ; (iii)  $-z + 1, x + \frac{1}{2}, -y + \frac{3}{2}$ ; (iv)  $x - \frac{1}{2}, -y + \frac{1}{2}, -z$ .

Data collection: *PCXRD* (Shimadzu, 2006); cell refinement: *DICVOL-2004* (Boultif & Louër, 2004); data reduction: *FULLPROF* (Rodriguez-Carvajal, 2006); program(s) used to solve structure: *FULLPROF*; program(s) used to refine structure: *FULLPROF*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *PLATON* (Spek, 2009) and *enCIFer* (Allen *et al.*, 2004).

Supporting information for this paper is available from the IUCr electronic archives (Reference: WM5021).

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## supporting information

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## Rietveld refinement of the langbeinite-type mixed-metal phosphate



Igor V. Zatovsky

## S1. Comment

Phosphates of the langbeinite structure type are considered as favorable for environmentally safe crystalline forms of radioactive waste solidification (Orlova *et al.*, 2003). Langbeinite-type frameworks  ${}^3_{\infty}[\text{M}_2(\text{PO}_4)_3]$  can be composed of various polyvalent metal pairs, for example,  $\text{K}_2\text{Ni}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$  (Ogorodnyk *et al.*, 2007*b*),  $\text{K}_{1.96}\text{Mn}_{0.57}\text{Zr}_{1.43}(\text{PO}_4)_3$  and  $\text{K}_{1.93}\text{Mn}_{0.53}\text{Hf}_{1.47}(\text{PO}_4)_3$  (Ogorodnyk *et al.*, 2007*b*),  $\text{K}_2\text{FeZr}(\text{PO}_4)_3$  (Orlova *et al.*, 2003),  $\text{K}_2\text{REZr}(\text{PO}_4)_3$ ,  $\text{RE} = \text{Y}, \text{Gd}$  (Wulff *et al.*, 1992). Herein the powder X-ray refinement of a phosphate, structurally isotypic with the mineral langbenite,  $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$  (Zemann & Zemann, 1957),  $\text{K}_2\text{Ni}_{0.5}\text{Zr}_{1.5}(\text{PO}_4)_3$ , (I), is presented (Fig. 1).

The K, Ni, and Zr sites lie on threefold rotation axes in positions  $4a$  with the sequence  $\{(\text{Zr},\text{Ni})1-(\text{Zr},\text{Ni})2-\text{K}1-\text{K}2\}$  where  $(\text{Zr},\text{Ni})1$  and  $(\text{Zr},\text{Ni})2$  are metal sites with a mixed occupancy (Fig. 2). P and O atoms are located in  $12b$  positions.

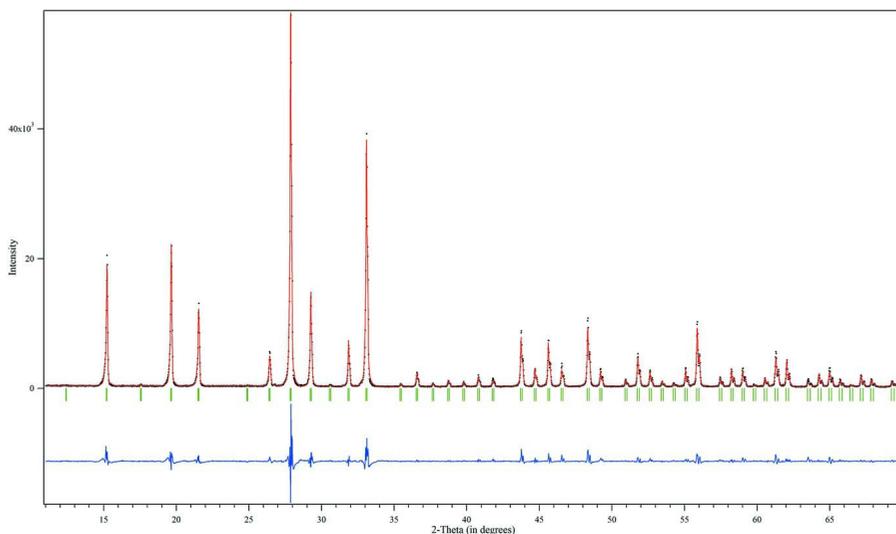
The structure of (I) contains two independent  $[(\text{Zr},\text{Ni})\text{O}_6]$  octahedra and one  $[\text{PO}_4]$  tetrahedron which are linked together *via* common vertices, forming a three-dimensional framework (Fig. 3). The  $(\text{Zr},\text{Ni})-\text{O}$  bond lengths are 2.070 (14) Å, 2.098 (14) Å and 2.036 (12) Å, 2.041 (16) Å for  $[(\text{Zr},\text{Ni})\text{O}_6]$  and  $[(\text{Zr},\text{Ni})2\text{O}_6]$ , respectively. It should be noted that the occupancy of the metal sites by  $\text{Ni}^{2+}$  is slightly different (0.21 (4) for the  $M1$  site and 0.29 (4) for the  $M2$  site) whereas in case of  $\text{K}_2\text{Ni}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$  (Ogorodnyk *et al.*, 2007*b*)  $\text{Ni}^{2+}$  ions are almost equally distributed (occupancy of 0.25 for both positions), with  $(\text{Ti},\text{Ni})-\text{O}$  bonds ranging from 1.938 (5) to 1.962 (5) Å. The three-dimensional framework  ${}^3_{\infty}[(\text{Zr},\text{Ni})_2(\text{PO}_4)_3]$  has large closed cavities where the two independent  $\text{K}^+$  cations are located. K1 is coordinated by nine O atoms, while K2 is surrounded by twelve O atoms (Fig. 4), with  $\text{K}-\text{O}$  bond lengths ranging from 2.956 (16) to 3.332 (15) Å (Table 1).

## S2. Experimental

A well-ground mixture of 11.8 g  $\text{KPO}_3$  and 1.12 g  $\text{NiO}$  was placed in a platinum crucible and then was heated up to 1273 K. The temperature was kept constant during one hour and after that it was decreased to 1173 K. 4.25 g of  $\text{K}_2\text{ZrF}_6$  were added to the flux under stirring with a platinum stirrer (initial K:P, Zr:P and Zr:Ni ratio equal to 1.3, 0.15, and 1.0, respectively). The crystallization of the melt was performed in the temperature range from 1173 to 913 K at an rate of 25 K/h. Finally, the crucible was cooled down to room temperature. The obtained material of (I) was recovered by washing with hot deionized water. The small crystals of (I) had the form of regular tetrahedra and were of light-yellow colour. The atomic ratio of the elements in (I) was found to be 4:1:3:6 for K/Ni/Zr/P, respectively: The sample was dissolved in 80% sulfuric acid under heating. The amount of the elements was then determined by atomic emission spectroscopy with inductive coupled plasma, AES-ICP, Spectroflame Modula ICP "Spectro".

### S3. Refinement

The powder pattern of (I) was indexed in the cubic system using *DICVOL-2004* (Boultif & Louër, 2004). The pattern indexing showed that the sample was a single phase. Atomic coordinates of  $\text{K}_{1.96}\text{Mn}_{0.57}\text{Zr}_{1.43}(\text{PO}_4)_3$  (Ogorodnyk *et al.*, 2007a) were used during Rietveld refinement as a starting model. For profile refinement a pseudo-Voigt function with axial divergence asymmetry (Thompson *et al.*, 1987) was used. First, the scaling factor, background, cell parameters *etc.* were refined during profile matching. Atomic coordinates were then refined during the next step. Atomic coordinates and displacement parameters of corresponding Zr and Ni sites were constrained to be the same. Isotropic displacement parameters of all atoms were appended to the refinement. The occupancies of K, Ni and Zr were refined taking into account that the occupancies of the hexacoordinated metal site should be equal to unity which was done using occupancy constraints. As the occupancy of the K sites was found to be 1, the occupancy factors of K1 and K2 were fixed at 1. The displacement factors of the O atoms were spread over a large range which is meaningless in this case due to the quality of the powder diffraction data. Thus  $U_{\text{iso}}$  values for all O atoms were constrained to be equal. As a result, the values of  $U_{\text{iso}}$  and their e.s.d.'s have close values. At the final refinement cycles two geometric restraints were applied to the lengths of P—O bonds because their values were unsatisfactory for the model (without restraints, one was  $\approx 1.44 \text{ \AA}$  while another was close to  $1.57 \text{ \AA}$ ). Experimental, calculated and difference patterns are shown in Fig. 1.



**Figure 1**

Results of the Rietveld refinement of  $\text{K}_2\text{Ni}_{0.5}\text{Zr}_{1.5}(\text{PO}_4)_3$ . Experimental (dots), calculated (red curve) and difference (blue curve) data.

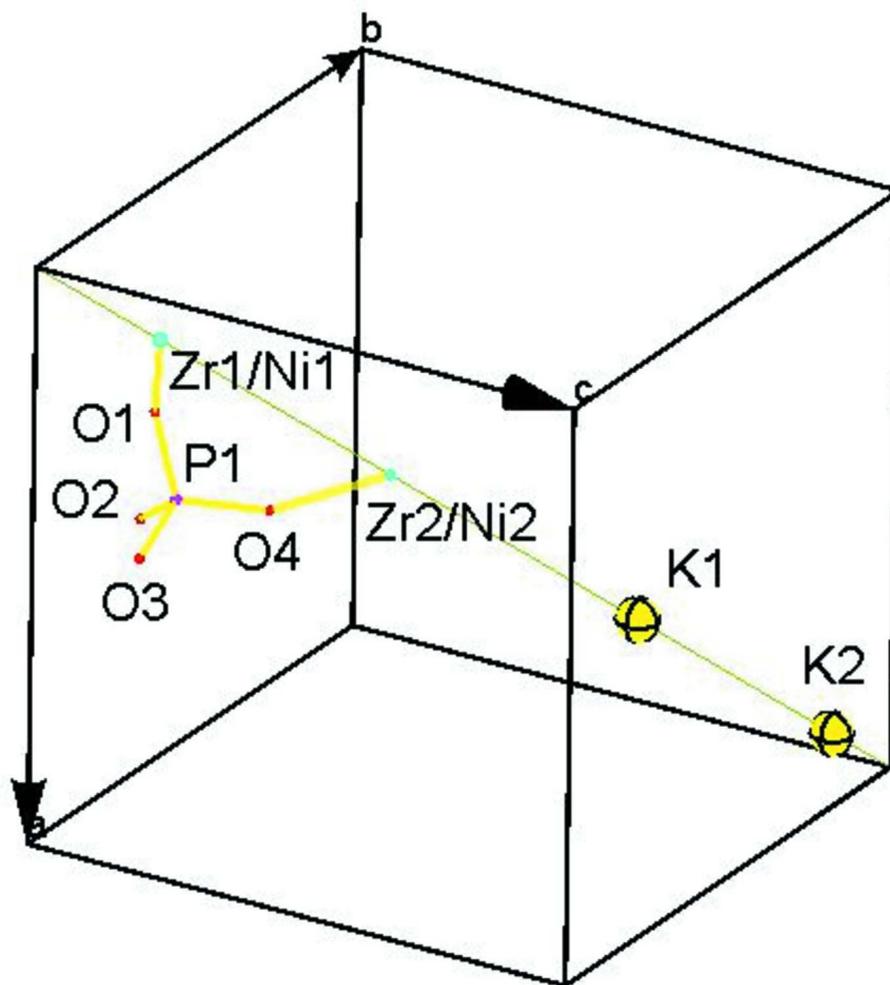


Figure 2

A view of the asymmetric unit of  $K_2Ni_{0.5}Zr_{1.5}(PO_4)_3$ . Displacement ellipsoid are drawn at the 50% probability level.

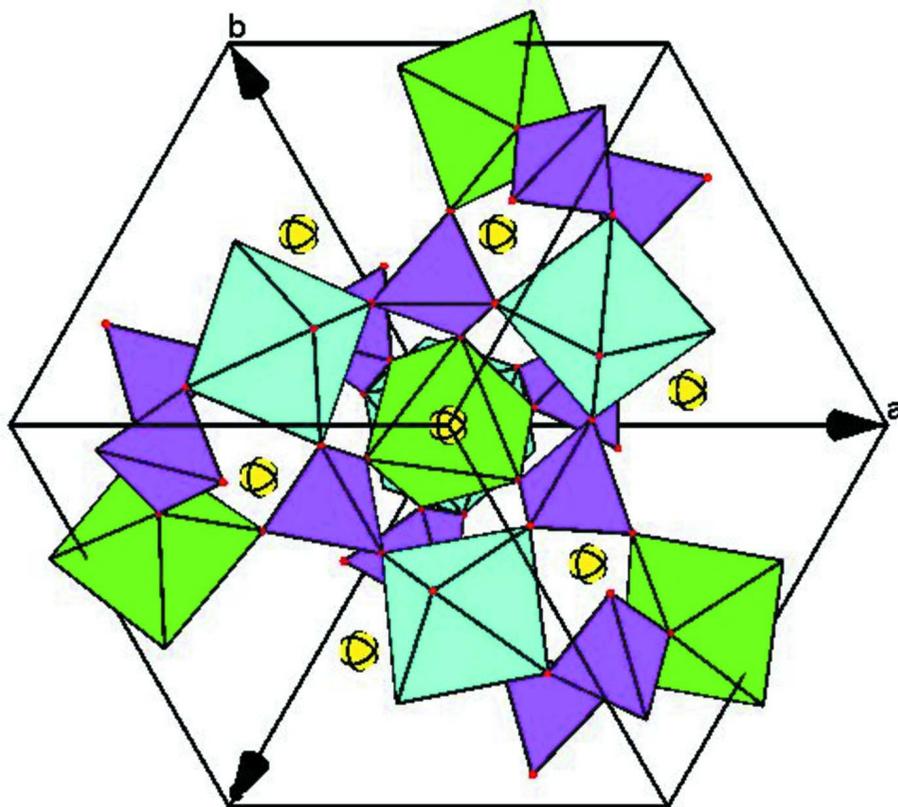


Figure 3

A projection of the structure of (I) along  $[111]$ .  $\text{PO}_4$  tetrahedra are pink,  $(\text{Zr,Ni})\text{IO}_6$  octahedra are turquoise,  $(\text{Zr,Ni})_2\text{O}_6$  octahedra are green,  $\text{K}^+$  cations are shown as yellow spheres.

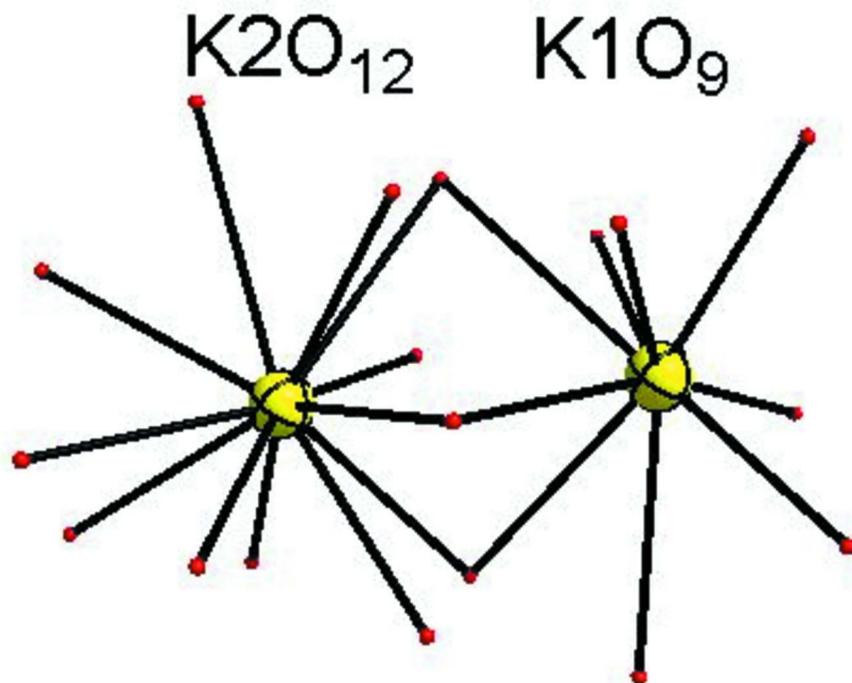


Figure 4

The O environment of  $K1^+$  and  $K2^+$  cations for (I). Displacement ellipsoid are drawn at the 50% probability level.

#### Dipotassium [nickel(II) zirconium(IV)] tris(orthophosphate)

##### Crystal data

$K_2Ni_{0.5}Zr_{1.5}(PO_4)_3$

$M_r = 529.29$

Cubic,  $P2_13$

Hall symbol: P 2ac 2ab 3

$a = 10.15724 (13) \text{ \AA}$

$V = 1047.92 (2) \text{ \AA}^3$

$Z = 4$

$D_x = 3.355 \text{ Mg m}^{-3}$

Cu  $K\alpha$  radiation,  $\lambda = 1.540598 \text{ \AA}$

$T = 293 \text{ K}$

Particle morphology: isometric  
yellow

flat sheet,  $25 \times 25 \text{ mm}$

Specimen preparation: Prepared at 293 K and  
101.3 kPa

##### Data collection

Shimadzu LabX XRD-6000  
diffractometer

Radiation source: X-ray tube, X-ray  
Graphite monochromator

Specimen mounting: glass container

Data collection mode: reflection

Scan method: step

$2\theta_{\min} = 10.910^\circ$ ,  $2\theta_{\max} = 104.911^\circ$ ,  $2\theta_{\text{step}} = 0.020^\circ$

##### Refinement

$R_p = 0.100$

$R_{wp} = 0.134$

$R_{\text{exp}} = 0.034$

$R_{\text{Bragg}} = 0.041$

$R(F) = 0.035$

4701 data points

Profile function: Thompson-Cox-Hastings  
pseudo-Voigt \* Axial divergence asymmetry

107 parameters

2 restraints

9 constraints

Standard least squares refinement

$(\Delta/\sigma)_{\max} = 0.001$

Background function: Linear Interpolation  
between a set background points with refinable  
heights

Preferred orientation correction: March-Dollase

Numeric Multiaxial Function

*Special details*

**Geometry.** Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
K1	0.7043 (6)	0.7043 (6)	0.7043 (6)	0.054 (5)*	
K2	0.9317 (7)	0.9317 (7)	0.9317 (7)	0.052 (4)*	
Zr1	0.1448 (2)	0.1448 (2)	0.1448 (2)	0.007 (2)*	0.79 (4)
Zr2	0.4146 (3)	0.4146 (3)	0.4146 (3)	0.004 (2)*	0.71 (4)
Ni1	0.1448 (2)	0.1448 (2)	0.1448 (2)	0.007 (2)*	0.21 (4)
Ni2	0.4146 (3)	0.4146 (3)	0.4146 (3)	0.004 (2)*	0.29 (4)
P1	0.4581 (6)	0.2296 (8)	0.1286 (7)	0.004 (2)*	
O1	0.3180 (14)	0.2335 (14)	0.0844 (15)	0.003 (2)*	
O2	0.5417 (12)	0.2950 (14)	0.0238 (14)	0.003 (2)*	
O3	0.5025 (12)	0.0869 (16)	0.1471 (13)	0.003 (2)*	
O4	0.4729 (14)	0.3039 (12)	0.2580 (10)	0.003 (2)*	

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
?	?	?	?	?	?	?

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

K1—O1 <sup>i</sup>	2.956 (16)	Zr1—O1 <sup>xiii</sup>	2.070 (14)
K1—O2 <sup>ii</sup>	3.165 (14)	Zr1—O2 <sup>xiv</sup>	2.098 (14)
K1—O4 <sup>ii</sup>	3.325 (14)	Zr2—O4	2.036 (12)
K1—O1 <sup>iii</sup>	2.956 (16)	Zr2—O3 <sup>i</sup>	2.041 (16)
K1—O2 <sup>iv</sup>	3.165 (14)	Zr2—O4 <sup>xi</sup>	2.036 (12)
K1—O4 <sup>iv</sup>	3.325 (14)	Zr2—O3 <sup>iii</sup>	2.041 (16)
K1—O1 <sup>v</sup>	2.956 (16)	Zr2—O4 <sup>xiii</sup>	2.036 (12)
K1—O2 <sup>vi</sup>	3.165 (14)	Zr2—O3 <sup>v</sup>	2.041 (16)
K1—O4 <sup>vi</sup>	3.325 (14)	Ni1—O2 <sup>xii</sup>	2.098 (14)
K2—O3 <sup>ii</sup>	2.973 (15)	Ni1—O1 <sup>xiii</sup>	2.070 (14)
K2—O2 <sup>vii</sup>	3.026 (16)	Ni1—O2 <sup>xiv</sup>	2.098 (14)
K2—O4 <sup>ii</sup>	3.127 (15)	Ni1—O1 <sup>xi</sup>	2.070 (14)
K2—O4 <sup>vii</sup>	3.332 (15)	Ni1—O1	2.070 (14)
K2—O3 <sup>iv</sup>	2.973 (15)	Ni1—O2 <sup>x</sup>	2.098 (14)
K2—O2 <sup>viii</sup>	3.026 (16)	Ni2—O4	2.036 (12)
K2—O4 <sup>iv</sup>	3.127 (15)	Ni2—O3 <sup>v</sup>	2.041 (16)
K2—O4 <sup>viii</sup>	3.332 (15)	Ni2—O3 <sup>i</sup>	2.041 (16)
K2—O3 <sup>vi</sup>	2.973 (15)	Ni2—O4 <sup>xi</sup>	2.036 (12)
K2—O2 <sup>ix</sup>	3.026 (16)	Ni2—O3 <sup>iii</sup>	2.041 (16)
K2—O4 <sup>vi</sup>	3.127 (15)	Ni2—O4 <sup>xiii</sup>	2.036 (12)
K2—O4 <sup>ix</sup>	3.332 (15)	P1—O3	1.530 (18)

Zr1—O1	2.070 (14)	P1—O4	1.523 (13)
Zr1—O2 <sup>x</sup>	2.098 (14)	P1—O2	1.515 (15)
Zr1—O1 <sup>xi</sup>	2.070 (14)	P1—O1	1.493 (16)
Zr1—O2 <sup>xii</sup>	2.098 (14)		
O1—Zr1—O2 <sup>x</sup>	93.2 (5)	O1—Ni1—O2 <sup>x</sup>	93.2 (5)
O1—Zr1—O1 <sup>xi</sup>	90.6 (6)	O1—Ni1—O1 <sup>xi</sup>	90.6 (6)
O1—Zr1—O2 <sup>xii</sup>	175.9 (5)	O1—Ni1—O2 <sup>xii</sup>	175.9 (5)
O1—Zr1—O1 <sup>xiii</sup>	90.6 (6)	O1—Ni1—O1 <sup>xiii</sup>	90.6 (6)
O1—Zr1—O2 <sup>xiv</sup>	87.7 (6)	O1—Ni1—O2 <sup>xiv</sup>	87.7 (6)
O1 <sup>xi</sup> —Zr1—O2 <sup>x</sup>	87.7 (6)	O1 <sup>xi</sup> —Ni1—O2 <sup>x</sup>	87.7 (6)
O2 <sup>x</sup> —Zr1—O2 <sup>xii</sup>	88.6 (5)	O2 <sup>x</sup> —Ni1—O2 <sup>xii</sup>	88.6 (5)
O1 <sup>xiii</sup> —Zr1—O2 <sup>x</sup>	175.9 (5)	O1 <sup>xiii</sup> —Ni1—O2 <sup>x</sup>	175.9 (5)
O2 <sup>x</sup> —Zr1—O2 <sup>xiv</sup>	88.6 (5)	O2 <sup>x</sup> —Ni1—O2 <sup>xiv</sup>	88.6 (5)
O1 <sup>xi</sup> —Zr1—O2 <sup>xii</sup>	93.2 (5)	O4 <sup>xi</sup> —Ni2—O4 <sup>xiii</sup>	87.5 (5)
O1 <sup>xi</sup> —Zr1—O1 <sup>xiii</sup>	90.6 (6)	O3 <sup>v</sup> —Ni2—O4 <sup>xi</sup>	170.8 (5)
O1 <sup>xi</sup> —Zr1—O2 <sup>xiv</sup>	175.9 (5)	O3 <sup>iii</sup> —Ni2—O4 <sup>xiii</sup>	84.5 (5)
O1 <sup>xiii</sup> —Zr1—O2 <sup>xii</sup>	87.7 (6)	O3 <sup>iii</sup> —Ni2—O3 <sup>v</sup>	92.1 (5)
O2 <sup>xii</sup> —Zr1—O2 <sup>xiv</sup>	88.6 (5)	O3 <sup>v</sup> —Ni2—O4 <sup>xiii</sup>	96.5 (5)
O1 <sup>xiii</sup> —Zr1—O2 <sup>xiv</sup>	93.2 (5)	O3 <sup>i</sup> —Ni2—O3 <sup>iii</sup>	92.1 (5)
O3 <sup>i</sup> —Zr2—O4	96.5 (5)	O3 <sup>i</sup> —Ni2—O4	96.5 (5)
O4—Zr2—O4 <sup>xi</sup>	87.5 (5)	O4—Ni2—O4 <sup>xi</sup>	87.5 (5)
O3 <sup>iii</sup> —Zr2—O4	170.8 (5)	O3 <sup>iii</sup> —Ni2—O4	170.8 (5)
O4—Zr2—O4 <sup>xiii</sup>	87.5 (5)	O4—Ni2—O4 <sup>xiii</sup>	87.5 (5)
O3 <sup>v</sup> —Zr2—O4	84.5 (5)	O3 <sup>v</sup> —Ni2—O4	84.5 (5)
O3 <sup>i</sup> —Zr2—O4 <sup>xi</sup>	84.5 (5)	O3 <sup>i</sup> —Ni2—O4 <sup>xi</sup>	84.5 (5)
O3 <sup>i</sup> —Zr2—O3 <sup>iii</sup>	92.1 (5)	O3 <sup>iii</sup> —Ni2—O4 <sup>xi</sup>	96.5 (5)
O3 <sup>i</sup> —Zr2—O4 <sup>xiii</sup>	170.8 (5)	O3 <sup>i</sup> —Ni2—O4 <sup>xiii</sup>	170.8 (5)
O3 <sup>i</sup> —Zr2—O3 <sup>v</sup>	92.1 (5)	O3 <sup>i</sup> —Ni2—O3 <sup>v</sup>	92.1 (5)
O3 <sup>iii</sup> —Zr2—O4 <sup>xi</sup>	96.5 (5)	O3—P1—O4	109.5 (8)
O4 <sup>xi</sup> —Zr2—O4 <sup>xiii</sup>	87.5 (5)	O1—P1—O2	108.1 (9)
O3 <sup>v</sup> —Zr2—O4 <sup>xi</sup>	170.8 (5)	O1—P1—O3	110.1 (9)
O3 <sup>iii</sup> —Zr2—O4 <sup>xiii</sup>	84.5 (5)	O1—P1—O4	109.9 (9)
O3 <sup>iii</sup> —Zr2—O3 <sup>v</sup>	92.1 (5)	O2—P1—O3	109.7 (8)
O3 <sup>v</sup> —Zr2—O4 <sup>xiii</sup>	96.5 (5)	O2—P1—O4	109.5 (9)
O1 <sup>xi</sup> —Ni1—O2 <sup>xii</sup>	93.2 (5)	Zr1—O1—P1	135.2 (10)
O1 <sup>xi</sup> —Ni1—O1 <sup>xiii</sup>	90.6 (6)	Ni1—O1—P1	135.2 (10)
O1 <sup>xi</sup> —Ni1—O2 <sup>xiv</sup>	175.9 (5)	Zr1 <sup>xv</sup> —O2—P1	168.8 (10)
O1 <sup>xiii</sup> —Ni1—O2 <sup>xii</sup>	87.7 (6)	Zr2 <sup>xvi</sup> —O3—P1	153.7 (9)
O2 <sup>xii</sup> —Ni1—O2 <sup>xiv</sup>	88.6 (5)	Zr2—O4—P1	156.8 (9)
O1 <sup>xiii</sup> —Ni1—O2 <sup>xiv</sup>	93.2 (5)	Ni2—O4—P1	156.8 (9)

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