

## Sodium pentapotassium pentanickel tetra(diphosphate), $\text{NaK}_5\text{Ni}_5(\text{P}_2\text{O}_7)_4$

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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{P}-\text{O}) = 0.002$  Å; disorder in main residue;  $R$  factor = 0.027;  $wR$  factor = 0.071; data-to-parameter ratio = 16.6.

The structure of the title compound,  $\text{NaK}_5\text{Ni}_5(\text{P}_2\text{O}_7)_4$ , is characterized by the presence of two crystallographically independent  $\text{P}_2\text{O}_7$  groups with different conformations. The conformation of the first  $\text{P}_2\text{O}_7$  group is eclipsed, whereas that of the second is staggered. All atoms are in general positions except for two nickel and one potassium ions which lie on symmetry centers. Moreover, the structure exhibits disorder of the cationic sites with one general position fully occupied equally by  $\text{Na}^+$  and  $\text{Ni}^{2+}$  cations. This mixed site is surrounded by five O atoms forming a square-based pyramid. The crystal structure consists of edge-sharing  $[\text{NiO}_6]$  octahedra forming infinite zigzag chains  $[\text{Ni}_3\text{O}_{14}]$  running parallel to  $[100]$ . Adjacent chains are connected through apices to  $\text{P}_2\text{O}_7$  groups and to another  $[\text{NiO}_6]$  or to a  $[\text{KO}_6]$  octahedron. The resulting three-dimensional framework presents intersecting tunnels running along the  $[010]$  and  $[001]$  directions in which the seven- and nine-coordinated potassium cations are located. The crystal structure of this new phosphate represents a new structural type.

### Related literature

For the crystal structure of nickel diphosphate, see: Lukaszewicz (1967); Pietraszko & Lukaszewicz (1968); Masse *et al.* (1979). For the structures of sodium and potassium nickel diphosphate, see: El Maadi *et al.* (1995); Erragh *et al.* (2000). For phosphates with mixed anions, see: Palkina & Maksimova (1980); Nagorny *et al.* (1996); Sanz *et al.* (1999). For bond-valence analysis, see: Brown & Altermatt (1985).

### Experimental

#### Crystal data

$\text{NaK}_5\text{Ni}_5(\text{P}_2\text{O}_7)_4$	$\gamma = 104.066$ (13)°
$M_r = 1207.80$	$V = 610.0$ (5) Å <sup>3</sup>
Triclinic, $P\bar{1}$	$Z = 1$
$a = 7.188$ (4) Å	Mo $K\alpha$ radiation
$b = 9.282$ (5) Å	$\mu = 5.31$ mm <sup>-1</sup>
$c = 10.026$ (5) Å	$T = 296$ K
$\alpha = 109.31$ (2)°	$0.20 \times 0.14 \times 0.11$ mm
$\beta = 90.019$ (12)°	

#### Data collection

Bruker APEXII CCD detector	13411 measured reflections
diffractometer	3608 independent reflections
Absorption correction: multi-scan	3195 reflections with $I > 2\sigma(I)$
( <i>SADABS</i> ; Sheldrick, 1999)	$R_{\text{int}} = 0.033$
$T_{\text{min}} = 0.511$ , $T_{\text{max}} = 0.638$	

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	218 parameters
$wR(F^2) = 0.071$	$\Delta\rho_{\text{max}} = 0.91$ e Å <sup>-3</sup>
$S = 1.03$	$\Delta\rho_{\text{min}} = -0.91$ e Å <sup>-3</sup>
3608 reflections	

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2200).

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## supporting information

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## Sodium pentapotassium pentanickel tetra(diphosphate), $\text{NaK}_5\text{Ni}_5(\text{P}_2\text{O}_7)_4$

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### S1. Comment

The most studied condensed phosphates are the diphosphates formerly called pyrophosphates. Most of these phosphates are polymorphic. The stability of each allotropic variety depends on several factors such as size and the electron affinity of the ions and synthesis conditions, in particular temperature and pressure. Thus in the case of  $\text{Ni}_2\text{P}_2\text{O}_7$ , we note the existence of four allotropic varieties: the form  $\alpha\text{-Ni}_2\text{P}_2\text{O}_7$  stable at room temperature and the  $\gamma\text{-Ni}_2\text{P}_2\text{O}_7$  determined by Lukaszewicz (1967), the high temperature form  $\beta\text{-Ni}_2\text{P}_2\text{O}_7$  obtained by Pietraszko & Lukaszewicz (1968) at 853 K and the  $\delta\text{-Ni}_2\text{P}_2\text{O}_7$  discovered by Masse *et al.* (1979). The addition of an alkali cation like Na or K in this system leads to new compounds with different structures. Indeed we find  $\text{K}_2\text{NiP}_2\text{O}_7$  investigated by El Maadi *et al.* (1995),  $\text{Na}_{7.39}\text{Ni}_{4.24}(\text{P}_2\text{O}_7)_4$  by Erragh *et al.* 2000) and three compounds with mixed anions:  $\text{K}_2\text{Ni}_4(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ ;  $\text{Na}_4\text{Ni}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$  and  $\text{Na}_4\text{Ni}_5(\text{PO}_4)_2(\text{P}_2\text{O}_7)_2$  respectively, developed by Palkina & Maksimova (1980); Nagorny *et al.* (1996) and Sanz *et al.* (1999) but to our knowledge no pyrophosphate with a mixture of two alkaline and nickel. The present work describes the synthesis method and the crystal structure of  $\text{NaK}_5\text{Ni}_5(\text{P}_2\text{O}_7)_4$  diphosphate from the X-ray diffraction data on single-crystal.

The partial three-dimensional plot in Fig.1 illustrates the connection ion-oxygen polyhedra in the crystal structure of the title compound. Among the 25 atoms include in the asymmetric unit of this structure, only three atoms (Ni1, Ni3 and K1) are in a special positions ( $\bar{1}$  symmetry). Furthermore, the structure is characterized by a cationic disorder in one general position fully occupied equally by Na1 and Ni4 atoms. This mixed site that will be noted M1 is surrounded by five oxygen atoms forming a square based pyramid. The conformations of the two crystallographically independent groups ( $\text{P}_2\text{O}_7$ ) P1—O4—P2 and P3—O14—P4 are eclipsed and staggered, respectively as indicated by the torsion angles O1—P1—P2—O5 = 3.5 (2) ° and O8—P3—P4—O12 = -24.6 (2) °. The distances P1—P2 = 2.902 Å, P3—P4 = 3.015 Å and angles P1—O4—P2 = 127.65 (11)°, P3—O14—P4 = 135.07 (13)° are within the limits generally observed in condensed phosphate crystal chemistry. All three nickel atoms Ni1, Ni2 and Ni3 are surrounded by a roughly octahedral arrangement of six oxygen atoms except that in the mixed site (M1O<sub>5</sub>). The potassium atoms K1, K2 and K3 are coordinated to six, seven and nine oxygen atoms, respectively.

The structure of  $\text{NaK}_5\text{Ni}_5(\text{P}_2\text{O}_7)_4$  consists of edge-sharing  $[\text{Ni}_1\text{O}_6]$  and  $[\text{Ni}_2\text{O}_6]$  octahedra forming an infinite zigzag chains  $[\text{Ni}_3\text{O}_{14}]$  running parallel to  $[100]$ , as shown in Fig. 2. Adjacent chains are connected by  $\text{P}_2\text{O}_7$  groups,  $\text{M1O}_5$  square-pyramid and  $[\text{Ni}_3\text{O}_6]$  or  $[\text{K1O}_6]$  octahedra *via* vertices in the way to build three-dimensional network.

The resulting 3-D framework presents intersecting tunnels running along the  $[010]$  and  $[001]$  directions, where the K2 and K3 potassium cations are located (Fig.2). Probably, the structure of this phosphate represents a new structural type.

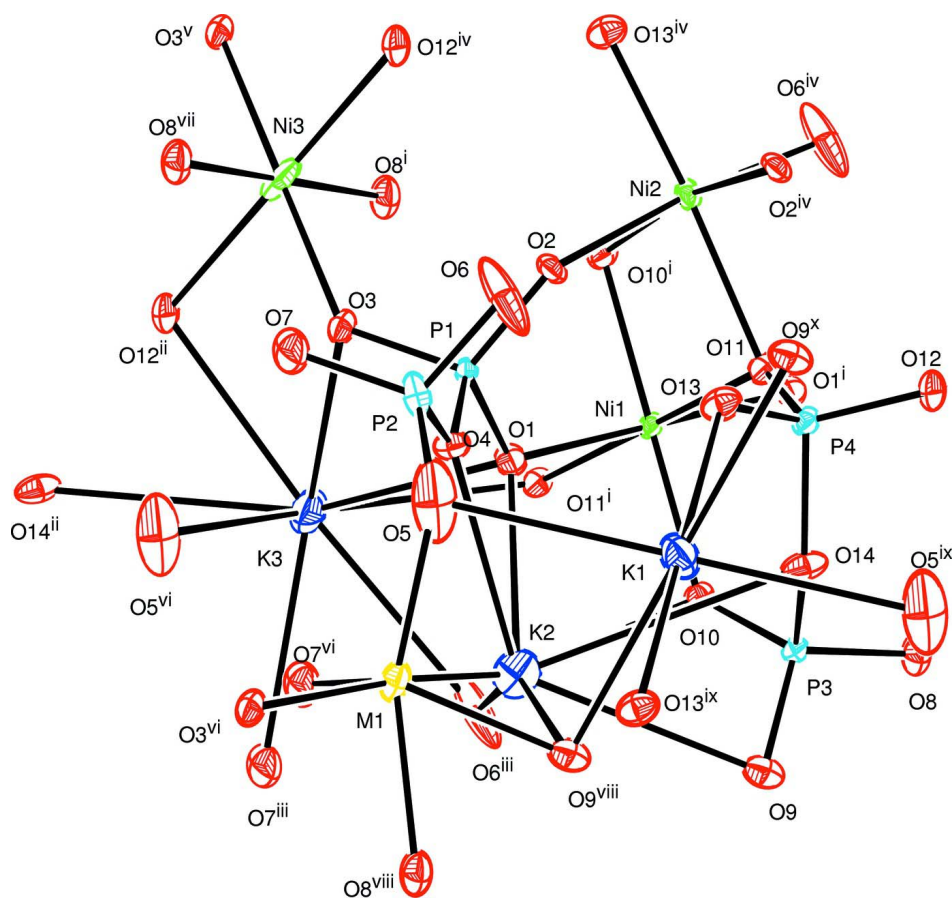
### S2. Experimental

$\text{NaK}_5\text{Ni}_5(\text{P}_2\text{O}_7)_4$  is obtained during the preparation of a mixture of triphosphate. Indeed, the powder of " $\text{NaK}_2\text{NiP}_3\text{O}_{10}$ " synthesized by wet process is introduced into a platinum crucible, and then gradually heated to a temperature above its

melting point (1073 K) for 2 h, followed by slow cooling of the order of 10 °K per hour up to 673 °K. Then the furnace is shuts down and the cooling is continued until room temperature. Small colourless single crystals were isolated from the mixture of phases. The study of crystal structure by X-ray diffraction leads to the formula of the new phosphate:  $\text{NaK}_5\text{Ni}_5(\text{P}_2\text{O}_7)_4$ .

### S3. Refinement

The atomic displacement factors of O5 and O6 atoms are very large compared to other oxygen atoms because the O5 is linked to Ni4 and Na1 occupying the disordered site and O6 is related to K2 and K3 that are in the tunnels. This explains the large displacement of these atoms. The highest peak and the deepest hole in the final Fourier map are at 0.76 Å and 0.49 Å, respectively, from Na1 and K2. The refinement of the occupancy rates of the mixed site of Na1 and Ni4 led to 0.5 for Na and 0.5 for Ni. These values are in good agreement with the charge balance and the bond valence analysis which gives occupation numbers of 0.60 for Ni and 0.40 for Na (Brown & Altermatt, 1985). The not significant bonds and angles were removed from the CIF file.



**Figure 1**

Plot of  $\text{NaK}_5\text{Ni}_5(\text{P}_2\text{O}_7)_4$  crystal structure showing polyhedra linkage. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $-x + 1, -y, -z$ ; (iii)  $-x + 1, -y + 1, -z$ ; (iv)  $x + 1, y + 1, z$ ; (v)  $x, y + 1, z$ ; (vi)  $-x + 1, -y + 1, -z + 1$ ; (vii)  $-x, -y, -z + 1$ ; (viii)  $-x + 1, -y, -z + 1$ ; (ix)  $x + 1, y, z$ ; (x)  $x - 1, y, z$ ; (xi)  $x - 1, y - 1, z$ ; (xii)  $x, y - 1, z$ .

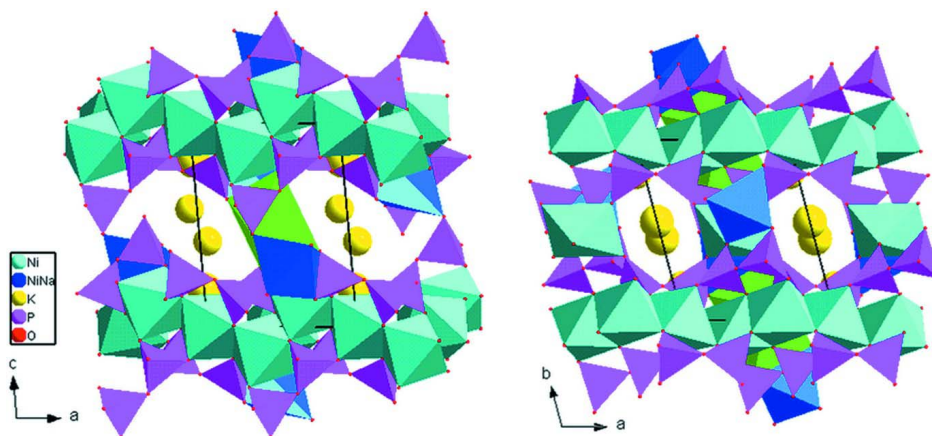


Figure 2

Projection views of the  $\text{NaK}_5\text{Ni}_5(\text{P}_2\text{O}_7)_4$  framework structure showing tunnels running along b and c directions where K2 and K3 atoms are located respectively.

### Sodium pentapotassium pentanickel tetra(diphosphate)

#### Crystal data

$\text{NaK}_5\text{Ni}_5(\text{P}_2\text{O}_7)_4$

$M_r = 1207.80$

Triclinic,  $P\bar{1}$

Hall symbol: -p 1

$a = 7.188$  (4) Å

$b = 9.282$  (5) Å

$c = 10.026$  (5) Å

$\alpha = 109.31$  (2)°

$\beta = 90.019$  (12)°

$\gamma = 104.066$  (13)°

$V = 610.0$  (5) Å<sup>3</sup>

$Z = 1$

$F(000) = 590$

$D_x = 3.288$  Mg m<sup>-3</sup>

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

Cell parameters from 3608 reflections

$\theta = 2.6$ – $30.2$ °

$\mu = 5.31$  mm<sup>-1</sup>

$T = 296$  K

Block, colourless

$0.20 \times 0.14 \times 0.11$  mm

#### Data collection

Bruker APEXII CCD detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  and  $\varphi$  scans

Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 1999)

$T_{\min} = 0.511$ ,  $T_{\max} = 0.638$

13411 measured reflections

3608 independent reflections

3195 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 30.2$ °,  $\theta_{\min} = 2.6$ °

$h = -10 \rightarrow 10$

$k = -13 \rightarrow 13$

$l = -14 \rightarrow 14$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.071$

$S = 1.03$

3608 reflections

218 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

$w = 1/[\sigma^2(F_o^2) + (0.034P)^2 + 1.127P]$

where  $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.91$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.91$  e Å<sup>-3</sup>

Extinction correction: *SHELXL97* (Sheldrick,  
2008),  $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0078 (9)

*Special details*

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

**Refinement.** Refinement of  $F^2$  against all reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on all data will be even larger.

*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)
Ni1	0.0000	0.0000	0.0000	0.00836 (10)	
Ni2	0.36001 (4)	-0.04138 (3)	-0.12590 (3)	0.01024 (8)	
Ni3	0.5000	0.5000	0.0000	0.02272 (13)	
Ni4	0.42559 (7)	0.37578 (6)	0.68239 (5)	0.01395 (11)	0.50
Na1	0.42559 (7)	0.37578 (6)	0.68239 (5)	0.01395 (11)	0.50
K1	0.5000	0.0000	0.5000	0.02299 (18)	
K2	0.05087 (10)	0.19327 (8)	0.42045 (7)	0.02536 (14)	
K3	0.00287 (10)	0.45372 (7)	0.18072 (8)	0.02541 (14)	
P1	0.36193 (8)	0.26003 (7)	0.17071 (6)	0.00759 (12)	
P2	0.65917 (10)	0.34427 (8)	0.39912 (7)	0.01475 (14)	
P3	-0.14668 (8)	-0.18481 (7)	0.22059 (6)	0.00879 (12)	
P4	0.25079 (8)	-0.18870 (7)	0.12603 (7)	0.00936 (12)	
O1	0.1486 (2)	0.1946 (2)	0.16422 (19)	0.0129 (3)	
O2	0.4605 (2)	0.1478 (2)	0.06750 (18)	0.0110 (3)	
O3	0.4162 (3)	0.4235 (2)	0.15797 (19)	0.0134 (3)	
O4	0.4368 (2)	0.2883 (2)	0.33014 (19)	0.0118 (3)	
O5	0.6436 (5)	0.3267 (3)	0.5429 (3)	0.0456 (8)	
O6	0.7578 (3)	0.2302 (3)	0.3004 (3)	0.0410 (7)	
O7	0.7412 (3)	0.5116 (2)	0.4030 (2)	0.0239 (4)	
O8	-0.2634 (3)	-0.3502 (2)	0.1363 (2)	0.0172 (4)	
O9	-0.2049 (3)	-0.1394 (2)	0.3710 (2)	0.0174 (4)	
O10	-0.1531 (2)	-0.0619 (2)	0.15276 (19)	0.0120 (3)	
O11	0.1762 (2)	-0.1410 (2)	0.00776 (19)	0.0107 (3)	
O12	0.2715 (3)	-0.3547 (2)	0.0742 (2)	0.0167 (4)	
O13	0.4217 (3)	-0.0687 (2)	0.21951 (19)	0.0143 (3)	
O14	0.0753 (3)	-0.1883 (2)	0.2327 (2)	0.0164 (4)	

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni1	0.00652 (18)	0.00716 (18)	0.0118 (2)	0.00142 (14)	0.00205 (15)	0.00396 (15)
Ni2	0.00772 (14)	0.00786 (14)	0.01396 (16)	0.00273 (11)	0.00143 (11)	0.00166 (11)
Ni3	0.0308 (3)	0.0183 (2)	0.0120 (2)	-0.0114 (2)	-0.0028 (2)	0.00858 (19)
Ni4	0.0144 (2)	0.0095 (2)	0.0161 (2)	-0.00049 (17)	-0.00043 (18)	0.00461 (18)
Na1	0.0144 (2)	0.0095 (2)	0.0161 (2)	-0.00049 (17)	-0.00043 (18)	0.00461 (18)
K1	0.0363 (5)	0.0181 (4)	0.0159 (4)	0.0108 (3)	0.0048 (3)	0.0049 (3)

K2	0.0255 (3)	0.0285 (3)	0.0226 (3)	0.0048 (3)	-0.0035 (2)	0.0110 (3)
K3	0.0256 (3)	0.0181 (3)	0.0365 (4)	0.0065 (2)	0.0080 (3)	0.0139 (3)
P1	0.0070 (2)	0.0060 (2)	0.0097 (3)	0.00174 (19)	0.0021 (2)	0.0025 (2)
P2	0.0162 (3)	0.0093 (3)	0.0164 (3)	0.0049 (2)	-0.0048 (2)	0.0001 (2)
P3	0.0081 (3)	0.0080 (3)	0.0102 (3)	0.0015 (2)	0.0023 (2)	0.0034 (2)
P4	0.0078 (3)	0.0087 (3)	0.0124 (3)	0.0021 (2)	0.0017 (2)	0.0047 (2)
O1	0.0082 (8)	0.0119 (8)	0.0164 (8)	0.0017 (6)	0.0021 (6)	0.0025 (7)
O2	0.0098 (8)	0.0098 (7)	0.0116 (8)	0.0037 (6)	0.0029 (6)	0.0004 (6)
O3	0.0178 (9)	0.0092 (8)	0.0141 (8)	0.0024 (7)	0.0027 (7)	0.0058 (7)
O4	0.0097 (8)	0.0142 (8)	0.0111 (8)	0.0020 (6)	0.0019 (6)	0.0049 (7)
O5	0.088 (2)	0.0238 (12)	0.0236 (12)	0.0141 (13)	-0.0258 (13)	0.0071 (10)
O6	0.0198 (11)	0.0277 (12)	0.0533 (16)	0.0167 (10)	-0.0176 (11)	-0.0223 (11)
O7	0.0176 (9)	0.0138 (9)	0.0312 (11)	-0.0018 (7)	0.0042 (8)	-0.0001 (8)
O8	0.0208 (9)	0.0105 (8)	0.0165 (9)	0.0004 (7)	-0.0026 (7)	0.0024 (7)
O9	0.0195 (9)	0.0202 (9)	0.0126 (8)	0.0070 (7)	0.0047 (7)	0.0043 (7)
O10	0.0106 (8)	0.0115 (8)	0.0174 (8)	0.0050 (6)	0.0044 (6)	0.0081 (7)
O11	0.0085 (7)	0.0118 (8)	0.0140 (8)	0.0033 (6)	0.0013 (6)	0.0066 (6)
O12	0.0211 (9)	0.0093 (8)	0.0218 (9)	0.0061 (7)	0.0042 (7)	0.0065 (7)
O13	0.0108 (8)	0.0177 (9)	0.0135 (8)	0.0005 (7)	0.0001 (6)	0.0062 (7)
O14	0.0102 (8)	0.0264 (10)	0.0195 (9)	0.0071 (7)	0.0051 (7)	0.0150 (8)

*Geometric parameters (Å, °)*

Ni1—O10 <sup>i</sup>	2.0403 (19)	K3—O6 <sup>x</sup>	2.953 (3)
Ni1—O10	2.0403 (19)	K3—O12 <sup>i</sup>	2.971 (3)
Ni1—O11	2.0487 (18)	K3—O3	3.053 (3)
Ni1—O11 <sup>i</sup>	2.0487 (18)	K3—O8 <sup>v</sup>	3.066 (2)
Ni1—O1	2.052 (2)	K3—O14 <sup>v</sup>	3.098 (3)
Ni1—O1 <sup>i</sup>	2.052 (2)	P1—O1	1.4986 (19)
Ni1—Ni2	2.9329 (14)	P1—O2	1.5178 (18)
Ni2—O2 <sup>ii</sup>	1.9963 (19)	P1—O3	1.5200 (19)
Ni2—O10 <sup>i</sup>	2.0171 (19)	P1—O4	1.602 (2)
Ni2—O6 <sup>ii</sup>	2.024 (2)	P2—O5	1.505 (3)
Ni2—O13 <sup>ii</sup>	2.0595 (19)	P2—O6	1.509 (2)
Ni2—O2	2.120 (2)	P2—O7	1.509 (2)
Ni2—O11	2.1504 (18)	P2—O4	1.631 (2)
Ni2—Ni2 <sup>ii</sup>	2.9960 (14)	P3—O8	1.514 (2)
Ni3—O3	1.9781 (19)	P3—O9	1.515 (2)
Ni3—O3 <sup>iii</sup>	1.9781 (19)	P3—O10	1.5178 (18)
Ni3—O8 <sup>i</sup>	2.070 (2)	P3—O14	1.609 (2)
Ni3—O8 <sup>iv</sup>	2.070 (2)	P4—O12	1.500 (2)
Ni3—O12 <sup>ii</sup>	2.342 (2)	P4—O13	1.508 (2)
Ni3—O12 <sup>v</sup>	2.342 (2)	P4—O11	1.5333 (19)
M1—O3 <sup>vi</sup>	2.079 (2)	P4—O14	1.654 (2)
M1—O7 <sup>vi</sup>	2.112 (2)	O2—Ni2 <sup>ii</sup>	1.9963 (19)
M1—O5	2.132 (4)	O3—M1 <sup>vi</sup>	2.079 (2)
M1—O8 <sup>vii</sup>	2.208 (2)	O6—Ni2 <sup>ii</sup>	2.024 (2)
M1—O9 <sup>vii</sup>	2.269 (2)	O6—K2 <sup>ix</sup>	2.574 (3)

K1—O13 <sup>viii</sup>	2.696 (2)	O6—K3 <sup>ix</sup>	2.953 (3)
K1—O13	2.696 (2)	O7—M1 <sup>vi</sup>	2.112 (2)
K1—O5 <sup>viii</sup>	2.839 (3)	O7—K2 <sup>vi</sup>	2.770 (2)
K1—O5	2.839 (3)	O7—K3 <sup>ix</sup>	2.915 (2)
K1—O9 <sup>ix</sup>	2.842 (2)	O8—Ni3 <sup>xi</sup>	2.070 (2)
K1—O9 <sup>vii</sup>	2.842 (2)	O8—M1 <sup>vii</sup>	2.208 (2)
K2—O6 <sup>x</sup>	2.574 (3)	O8—K3 <sup>xii</sup>	3.066 (2)
K2—O9 <sup>vii</sup>	2.609 (2)	O9—M1 <sup>vii</sup>	2.269 (2)
K2—O1	2.667 (2)	O9—K2 <sup>vii</sup>	2.609 (2)
K2—O7 <sup>vi</sup>	2.770 (2)	O9—K1 <sup>x</sup>	2.842 (2)
K2—O4	2.938 (2)	O10—Ni2 <sup>i</sup>	2.0171 (19)
K2—O10	3.011 (2)	O11—K3 <sup>i</sup>	2.865 (2)
K2—O9	3.064 (3)	O12—Ni3 <sup>xii</sup>	2.342 (2)
K3—O12 <sup>v</sup>	2.760 (2)	O12—K3 <sup>xii</sup>	2.760 (2)
K3—O1	2.805 (2)	O12—K3 <sup>i</sup>	2.971 (2)
K3—O11 <sup>i</sup>	2.865 (2)	O13—Ni2 <sup>ii</sup>	2.0595 (19)
K3—O7 <sup>x</sup>	2.915 (3)	O14—K3 <sup>xii</sup>	3.098 (3)
O10 <sup>i</sup> —Ni1—O10	180.00 (14)	O9 <sup>vii</sup> —K2—O4	89.43 (7)
O10 <sup>i</sup> —Ni1—O11	89.76 (7)	O1—K2—O4	51.46 (5)
O10—Ni1—O11	90.24 (7)	O7 <sup>vi</sup> —K2—O4	67.65 (6)
O10 <sup>i</sup> —Ni1—O11 <sup>i</sup>	90.24 (7)	O6 <sup>x</sup> —K2—O10	60.85 (7)
O10—Ni1—O11 <sup>i</sup>	89.76 (7)	O9 <sup>vii</sup> —K2—O10	124.00 (7)
O11—Ni1—O11 <sup>i</sup>	180.00 (7)	O1—K2—O10	58.11 (6)
O10 <sup>i</sup> —Ni1—O1	94.64 (8)	O7 <sup>vi</sup> —K2—O10	158.76 (6)
O10—Ni1—O1	85.36 (8)	O4—K2—O10	101.33 (6)
O11—Ni1—O1	95.94 (8)	O6 <sup>x</sup> —K2—O9	84.11 (8)
O11 <sup>i</sup> —Ni1—O1	84.06 (8)	O9 <sup>vii</sup> —K2—O9	81.83 (7)
O10 <sup>i</sup> —Ni1—O1 <sup>i</sup>	85.36 (8)	O1—K2—O9	105.24 (6)
O10—Ni1—O1 <sup>i</sup>	94.64 (8)	O7 <sup>vi</sup> —K2—O9	151.80 (7)
O11—Ni1—O1 <sup>i</sup>	84.06 (8)	O4—K2—O9	129.11 (6)
O11 <sup>i</sup> —Ni1—O1 <sup>i</sup>	95.94 (8)	O10—K2—O9	49.03 (5)
O1—Ni1—O1 <sup>i</sup>	180.00 (15)	O12 <sup>v</sup> —K3—O1	106.14 (7)
O2 <sup>ii</sup> —Ni2—O10 <sup>i</sup>	169.20 (7)	O12 <sup>v</sup> —K3—O11 <sup>i</sup>	117.27 (7)
O2 <sup>ii</sup> —Ni2—O6 <sup>ii</sup>	93.83 (9)	O1—K3—O11 <sup>i</sup>	57.90 (6)
O10 <sup>i</sup> —Ni2—O6 <sup>ii</sup>	89.84 (9)	O12 <sup>v</sup> —K3—O7 <sup>x</sup>	134.29 (7)
O2 <sup>ii</sup> —Ni2—O13 <sup>ii</sup>	89.76 (8)	O1—K3—O7 <sup>x</sup>	112.03 (6)
O10 <sup>i</sup> —Ni2—O13 <sup>ii</sup>	99.83 (8)	O11 <sup>i</sup> —K3—O7 <sup>x</sup>	104.10 (6)
O6 <sup>ii</sup> —Ni2—O13 <sup>ii</sup>	97.60 (11)	O12 <sup>v</sup> —K3—O6 <sup>x</sup>	172.29 (6)
O2 <sup>ii</sup> —Ni2—O2	86.65 (8)	O1—K3—O6 <sup>x</sup>	66.64 (6)
O10 <sup>i</sup> —Ni2—O2	88.70 (8)	O11 <sup>i</sup> —K3—O6 <sup>x</sup>	61.89 (7)
O6 <sup>ii</sup> —Ni2—O2	174.32 (10)	O7 <sup>x</sup> —K3—O6 <sup>x</sup>	50.52 (6)
O13 <sup>ii</sup> —Ni2—O2	88.07 (8)	O12 <sup>v</sup> —K3—O12 <sup>i</sup>	91.74 (7)
O2 <sup>ii</sup> —Ni2—O11	82.20 (7)	O1—K3—O12 <sup>i</sup>	106.98 (6)
O10 <sup>i</sup> —Ni2—O11	87.57 (7)	O11 <sup>i</sup> —K3—O12 <sup>i</sup>	51.26 (5)
O6 <sup>ii</sup> —Ni2—O11	91.53 (11)	O7 <sup>x</sup> —K3—O12 <sup>i</sup>	100.05 (8)
O13 <sup>ii</sup> —Ni2—O11	168.23 (7)	O6 <sup>x</sup> —K3—O12 <sup>i</sup>	93.03 (7)
O2—Ni2—O11	82.93 (8)	O12 <sup>v</sup> —K3—O3	58.80 (6)

O3—Ni3—O3 <sup>iii</sup>	180.00 (9)	O1—K3—O3	50.60 (5)
O3—Ni3—O8 <sup>i</sup>	93.37 (8)	O11 <sup>i</sup> —K3—O3	96.32 (6)
O3 <sup>iii</sup> —Ni3—O8 <sup>i</sup>	86.63 (8)	O7 <sup>x</sup> —K3—O3	137.10 (7)
O3—Ni3—O8 <sup>iv</sup>	86.63 (8)	O6 <sup>x</sup> —K3—O3	113.49 (6)
O3 <sup>iii</sup> —Ni3—O8 <sup>iv</sup>	93.37 (8)	O12 <sup>i</sup> —K3—O3	121.90 (6)
O8 <sup>i</sup> —Ni3—O8 <sup>iv</sup>	180.00 (17)	O12 <sup>v</sup> —K3—O8 <sup>v</sup>	83.94 (7)
O3—Ni3—O12 <sup>ii</sup>	97.37 (7)	O1—K3—O8 <sup>v</sup>	161.23 (6)
O3 <sup>iii</sup> —Ni3—O12 <sup>ii</sup>	82.63 (7)	O11 <sup>i</sup> —K3—O8 <sup>v</sup>	103.49 (6)
O8 <sup>i</sup> —Ni3—O12 <sup>ii</sup>	100.17 (8)	O7 <sup>x</sup> —K3—O8 <sup>v</sup>	67.60 (7)
O8 <sup>iv</sup> —Ni3—O12 <sup>ii</sup>	79.83 (8)	O6 <sup>x</sup> —K3—O8 <sup>v</sup>	103.75 (7)
O3—Ni3—O12 <sup>v</sup>	82.63 (7)	O12 <sup>i</sup> —K3—O8 <sup>v</sup>	56.06 (6)
O3 <sup>iii</sup> —Ni3—O12 <sup>v</sup>	97.37 (7)	O3—K3—O8 <sup>v</sup>	142.67 (6)
O8 <sup>i</sup> —Ni3—O12 <sup>v</sup>	79.83 (8)	O12 <sup>v</sup> —K3—O14 <sup>v</sup>	50.49 (6)
O8 <sup>iv</sup> —Ni3—O12 <sup>v</sup>	100.17 (8)	O1—K3—O14 <sup>v</sup>	149.36 (6)
O12 <sup>ii</sup> —Ni3—O12 <sup>v</sup>	180.0	O11 <sup>i</sup> —K3—O14 <sup>v</sup>	145.51 (6)
O3 <sup>vi</sup> —M1—O7 <sup>vi</sup>	97.28 (9)	O7 <sup>x</sup> —K3—O14 <sup>v</sup>	84.43 (6)
O3 <sup>vi</sup> —M1—O5	100.21 (10)	O6 <sup>x</sup> —K3—O14 <sup>v</sup>	134.95 (6)
O7 <sup>vi</sup> —M1—O5	107.23 (9)	O12 <sup>i</sup> —K3—O14 <sup>v</sup>	94.58 (6)
O3 <sup>vi</sup> —M1—O8 <sup>vii</sup>	80.71 (8)	O3—K3—O14 <sup>v</sup>	99.55 (5)
O7 <sup>vi</sup> —M1—O8 <sup>vii</sup>	100.81 (9)	O8 <sup>v</sup> —K3—O14 <sup>v</sup>	48.38 (6)
O5—M1—O8 <sup>vii</sup>	151.53 (8)	O1—P1—O2	113.34 (11)
O3 <sup>vi</sup> —M1—O9 <sup>vii</sup>	146.47 (7)	O1—P1—O3	112.74 (10)
O7 <sup>vi</sup> —M1—O9 <sup>vii</sup>	97.27 (9)	O2—P1—O3	111.86 (11)
O5—M1—O9 <sup>vii</sup>	104.03 (9)	O1—P1—O4	104.08 (10)
O8 <sup>vii</sup> —M1—O9 <sup>vii</sup>	66.96 (7)	O2—P1—O4	109.57 (10)
O13 <sup>viii</sup> —K1—O13	180.0	O3—P1—O4	104.53 (10)
O13 <sup>viii</sup> —K1—O5 <sup>viii</sup>	91.78 (7)	O5—P2—O6	112.93 (17)
O13—K1—O5 <sup>viii</sup>	88.22 (7)	O5—P2—O7	114.35 (14)
O13 <sup>viii</sup> —K1—O5	88.22 (7)	O6—P2—O7	112.17 (15)
O13—K1—O5	91.78 (7)	O5—P2—O4	104.13 (15)
O5 <sup>viii</sup> —K1—O5	180.00 (14)	O6—P2—O4	104.89 (12)
O13 <sup>viii</sup> —K1—O9 <sup>ix</sup>	104.71 (6)	O7—P2—O4	107.41 (11)
O13—K1—O9 <sup>ix</sup>	75.29 (6)	O8—P3—O9	109.31 (12)
O5 <sup>viii</sup> —K1—O9 <sup>ix</sup>	75.29 (9)	O8—P3—O10	114.40 (11)
O5—K1—O9 <sup>ix</sup>	104.71 (9)	O9—P3—O10	112.48 (11)
O13 <sup>viii</sup> —K1—O9 <sup>vii</sup>	75.29 (6)	O8—P3—O14	107.93 (11)
O13—K1—O9 <sup>vii</sup>	104.71 (6)	O9—P3—O14	105.88 (11)
O5 <sup>viii</sup> —K1—O9 <sup>vii</sup>	104.71 (9)	O10—P3—O14	106.35 (10)
O5—K1—O9 <sup>vii</sup>	75.29 (9)	O12—P4—O13	114.34 (12)
O9 <sup>ix</sup> —K1—O9 <sup>vii</sup>	180.0	O12—P4—O11	112.79 (11)
O6 <sup>x</sup> —K2—O9 <sup>vii</sup>	149.78 (9)	O13—P4—O11	114.65 (11)
O6 <sup>x</sup> —K2—O1	74.28 (9)	O12—P4—O14	105.83 (11)
O9 <sup>vii</sup> —K2—O1	135.37 (7)	O13—P4—O14	103.88 (11)
O6 <sup>x</sup> —K2—O7 <sup>vi</sup>	107.73 (8)	O11—P4—O14	103.90 (10)
O9 <sup>vii</sup> —K2—O7 <sup>vi</sup>	75.36 (8)	P1—O4—P2	127.65 (11)
O1—K2—O7 <sup>vi</sup>	102.63 (7)	P3—O14—P4	135.07 (13)
O6 <sup>x</sup> —K2—O4	119.96 (9)		



O1—P1—P2—O5

3.52 (17)

O8—P3—P4—O12

-24.60 (12)

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