

## KPr(PO<sub>3</sub>)<sub>4</sub>

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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{P}-\text{O}) = 0.001$  Å;  $R$  factor = 0.018;  $wR$  factor = 0.043; data-to-parameter ratio = 82.0.

Single crystals of the title compound, potassium praseodymium(III) polyphosphate, were obtained by solid-state reaction. The monoclinic non-centrosymmetric structure is isotypic with all other  $KLn(\text{PO}_3)_4$  analogues from  $Ln = \text{La}$  to  $\text{Er}$ , inclusive. The crystal structure of these long-chain polyphosphates is built up from infinite crenelated polyphosphate chains of corner-sharing  $\text{PO}_4$  tetrahedra with a repeating unit of four tetrahedra. These chains, running along [100], are arranged in a pseudo-tetragonal rod packing and are further linked by isolated  $\text{PrO}_8$  square antiprisms [ $\text{Pr}-\text{O} = 2.3787$  (9)– $2.5091$  (8) Å], forming a three-dimensional framework. The  $\text{K}^+$  ions reside in channels parallel to [010] and exhibit a highly distorted coordination sphere by eight O atoms at distances ranging from 2.7908 (9) to 3.1924 (11) Å.

### Related literature

Long-chain polyphosphates with general formula  $A^I B^{III}(\text{PO}_3)_4$  have been classified into seven structural types, labelled from I to VII (Jaoudi *et al.*, 2003). All  $KLn(\text{PO}_3)_4$  polyphosphates ( $Ln$  is a trivalent rare earth element) reported up to now adopt type III except for  $\text{KYb}(\text{PO}_3)_4$  (Palkina *et al.*, 1981). For corresponding isotypic crystal structures, see: Zhu *et al.* (2009) for Ce and Eu; Horchani-Naifer *et al.* (2008) for Y; Parreu *et al.* (2006) for Gd and Nd; Xing *et al.* (1987) for Tb; Ninghai *et al.* (1984) for Eu; Lin *et al.* (1983) for La; Krutik *et al.* (1980) for Er; Hong *et al.* (1975) for Nd. For a review of the crystal chemistry of phosphates, see: Durif (1995). For the cyclophosphate structure with the same composition,  $\text{KPr}(\text{PO}_3)_4$ , see: Zhou *et al.* (1987).

### Experimental

#### Crystal data

|                             |                                   |
|-----------------------------|-----------------------------------|
| $\text{KPr}(\text{PO}_3)_4$ | $V = 494.37$ (3) Å <sup>3</sup>   |
| $M_r = 495.89$              | $Z = 2$                           |
| Monoclinic, $P2_1$          | Mo $K\alpha$ radiation            |
| $a = 7.2872$ (2) Å          | $\mu = 6.06$ mm <sup>-1</sup>     |
| $b = 8.4570$ (3) Å          | $T = 296$ K                       |
| $c = 8.0268$ (2) Å          | $0.29 \times 0.21 \times 0.16$ mm |
| $\beta = 91.994$ (1)°       |                                   |

#### Data collection

|  |   |
|--|---|
| Bruker APEXII CCD diffractometer                         | 45940 measured reflections              |
| Absorption correction: multi-scan (SADABS; Bruker, 2008) | 13443 independent reflections           |
| $T_{\min} = 0.448$ , $T_{\max} = 0.751$                  | 13257 reflections with $I > 2\sigma(I)$ |
|  | $R_{\text{int}} = 0.034$                |

#### Refinement

|                                 |   |
|---------------------------------|---|
| $R[F^2 > 2\sigma(F^2)] = 0.018$ | $\Delta\rho_{\text{max}} = 2.86$ e Å <sup>-3</sup>  |
| $wR(F^2) = 0.043$               | $\Delta\rho_{\text{min}} = -2.42$ e Å <sup>-3</sup> |
| $S = 1.07$                      | Absolute structure: Flack (1983),                   |
| 13443 reflections               | 6278 Friedel pairs                                  |
| 164 parameters                  | Flack parameter: 0.022 (3)                          |
| 1 restraint                     |   |

**Table 1**

Selected bond lengths (Å).

|                    |            |                      |            |
|--------------------|------------|----------------------|------------|
| P1–O6              | 1.4841 (8) | P3–O3 <sup>ii</sup>  | 1.4806 (8) |
| P1–O12             | 1.4850 (8) | P3–O4                | 1.4832 (8) |
| P1–O5              | 1.5881 (7) | P3–O5                | 1.5902 (8) |
| P1–O10             | 1.5887 (9) | P3–O1 <sup>iii</sup> | 1.5980 (8) |
| P2–O11             | 1.4810 (9) | P4–O8 <sup>iv</sup>  | 1.4777 (8) |
| P2–O7 <sup>i</sup> | 1.4822 (8) | P4–O9 <sup>v</sup>   | 1.4829 (8) |
| P2–O1              | 1.5926 (8) | P4–O2                | 1.5874 (8) |
| P2–O2              | 1.5941 (8) | P4–O10               | 1.5973 (9) |

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

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: CaRine (Boudias & Monceau, 1998) and ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2370).

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## supporting information

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**KPr(PO<sub>3</sub>)<sub>4</sub>**

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**S1. Comment**

Long chains polyphosphates with general formula  $A^I B^{III}(\text{PO}_3)_4$  have been classified into seven structural types, labelled from I to VII (Durif, 1995; Jaoudi *et al.* 2003). All long-chains polyphosphates of formula  $KLn(\text{PO}_3)_4$  ( $Ln$  = rare earth elements) reported up to now (Zhu *et al.*, 2009; Horchani-Naifer *et al.*, 2008; Parreu *et al.*, 2006; Xing *et al.*, 1987; Ninghai *et al.*, 1984; Lin *et al.*, 1983; Krutik *et al.*, 1980; Hong *et al.*, 1975) adopt type III except for  $\text{KYb}(\text{PO}_3)_4$  (Palkina *et al.* 1981) which is the only presently known member of type V. Most of these potassium polyphosphates are dimorphic and crystallize with both the type III and the type IV polymorphs.  $\text{KCe}(\text{PO}_3)_4$  which has been shown to crystallize with either the type II and the type III is the first exception. The second exception is concerned with the Er member of this series presenting the type VII polymorph besides both type III and type IV polymorphs. Moreover, type III long-chain polyphosphates do not exist for monovalent cations other than  $\text{K}^+$ . The structure of the title compound also fits in this type III isotypic series.

The crystal structure of the title compound is built from crenelated chains with a repeating unit of four corner-sharing tetrahedra, as displayed in Fig. 1. The chains are further linked by isolated  $\text{PrO}_8$  square antiprisms to form the three-dimensional framework. Each  $\text{PrO}_8$  polyhedron (Pr—O distances range from 2.3787 (9) to 2.5091 (8) Å) is connected through vertices to four  $(\text{PO}_3)_\infty$  chains stacked in a pseudo-tetragonal rod packing as shown in Fig. 2. Figure 2 also shows that within this pseudo-tetragonal rod packing, two adjacent chains are twisted by *ca.* 90° whereas two opposite chains are parallel. The relative disposition of the chains running along the [100] direction accounts for the strong non-centrosymmetric character of the structure. Figure 3 displays details of the connections between the  $\text{PrO}_8$  square antiprisms and the four chains surrounding each antiprism. One of the four chains (labelled  $C_1$ ) is attached in a tridentate fashion on a triangular face of the square antiprism whereas the opposite and parallel chain (labelled  $C_2$ ) is connected only through a vertex (Fig. 3a). The two other chains which are adjacent to the first one are attached in a bidentate fashion. The first of these two chains (labelled  $C_3$ ) is linked through a bidentate diphosphate group attached on one side of one square face of the square antiprism (Fig. 3b). The second chain (labelled  $C_4$ ) is connected at the ends of one diagonal of the second square face of the antiprism (Fig. 3c) through corners of the terminal  $\text{PO}_4$  groups of the crenel-shaped tetraphosphate group corresponding to the repeating unit of the chain. This polyhedral linkage delimits channels running along [010] where the  $\text{K}^+$  ions lie in a highly distorted environment defined by eight oxygen atoms at distances ranging from 2.7908 (9) to 3.1924 (11) Å.

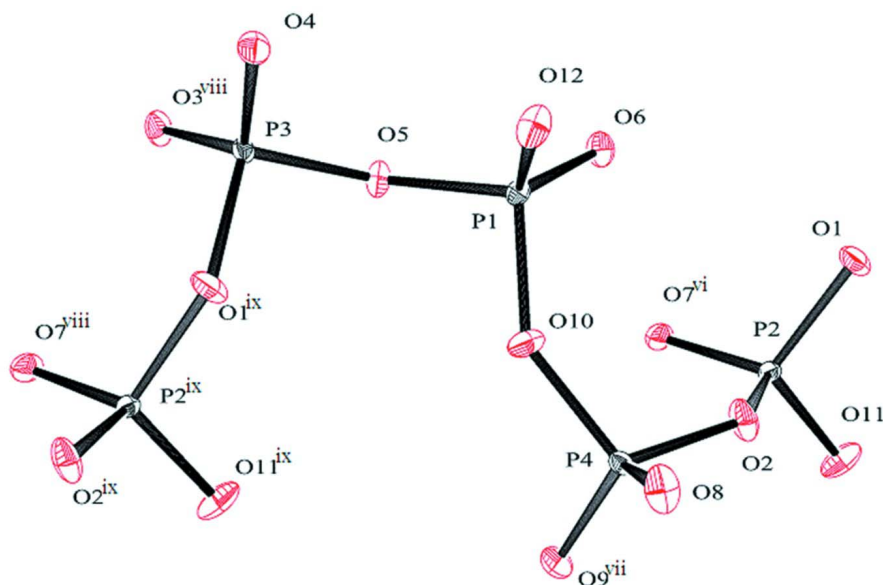
For the cyclophosphate structure with the same composition  $\text{KPr}(\text{PO}_3)_4$ , see: (Zhou *et al.*, 1987).

## S2. Experimental

Crystals of the title compound were synthesized by reacting  $\text{Pr}_6\text{O}_{11}$  with  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  and  $\text{K}_2\text{CO}_3$  in a platinum crucible. A mixture of these reagents in the molar ratio 14: 66: 20 was used for the synthesis. The mixture has first been heated at 473 K for 12 h and then the temperature has been increased up to 573 K and maintained for 12 h before to be raised at 853 K and kept for 24 additional hours. At the end of this heating step, the muffle furnace was cooled down first to 673 K at the rate of 2 K h<sup>-1</sup> and subsequently to room temperature by switching the power off. Single crystals were extracted from the batch by leaching with hot water.

## S3. Refinement

The highest residual peak in the final difference Fourier map was located 0.46 Å from atom Pr and the deepest hole was located 0.47 Å from atom K.



**Figure 1**

View of the repeating unit of the  $(\text{PO}_3)_\infty$  chains. Displacement ellipsoids are drawn at the 50% probability level.

[Symmetry codes: (vi)  $-x + 1, y + 1/2, -z + 1$ ; (vii)  $x, y, z - 1$ ; (viii)  $-x, y + 1/2, -z + 1$ ; (ix)  $x - 1, y, z$ .]

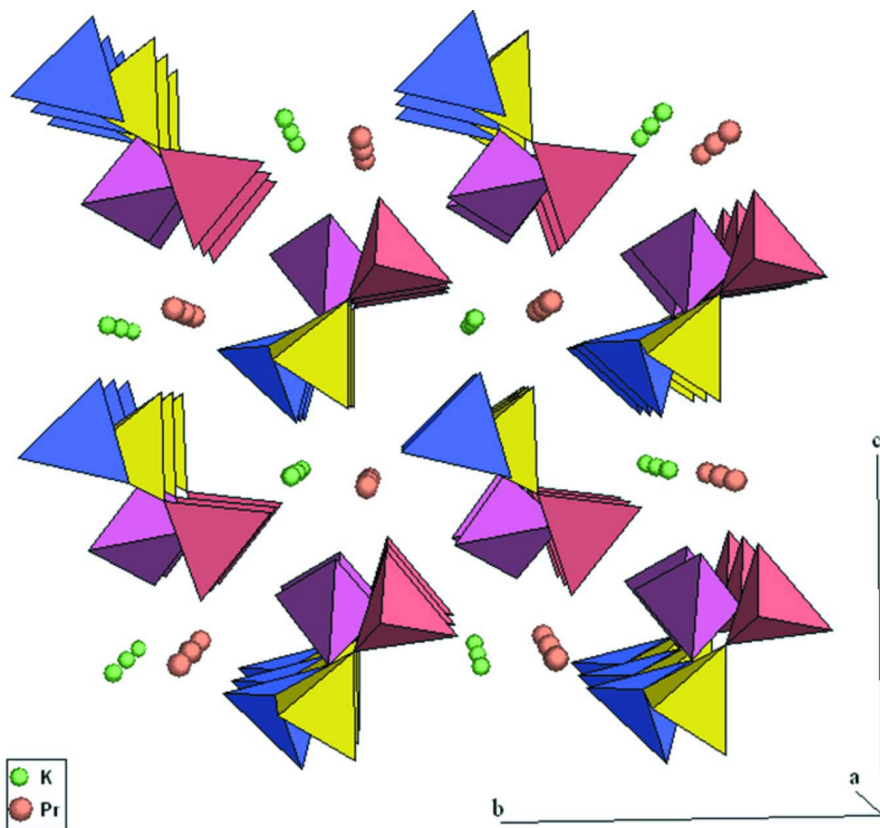
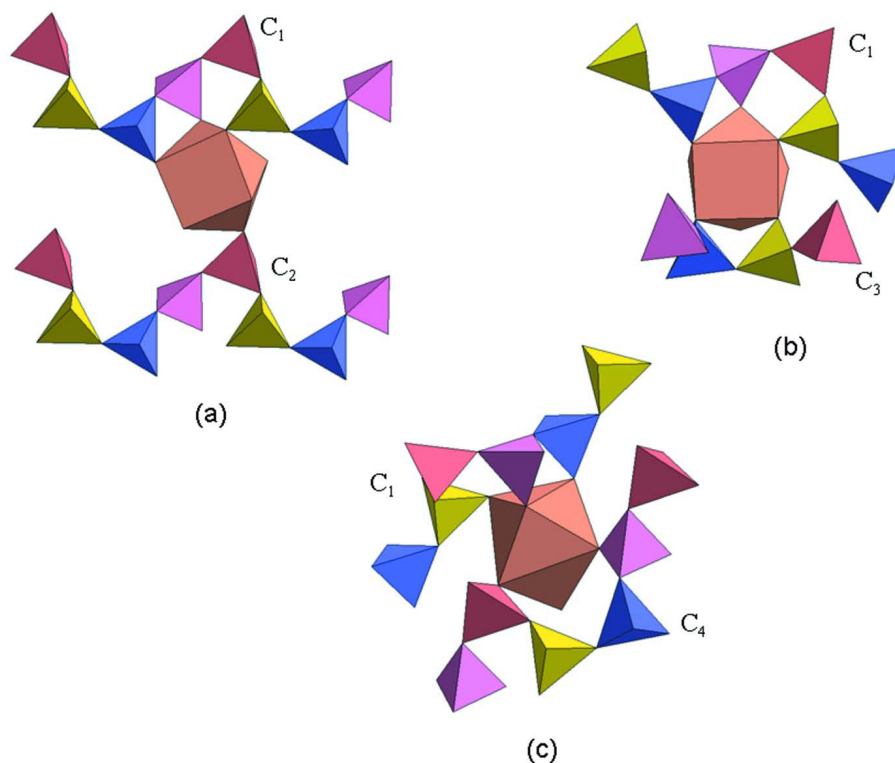


Figure 2

Projection along [100] showing the pseudo-tetragonal rod packing of the infinite (PO<sub>3</sub>) chains.



**Figure 3**

Details of the connections between the  $(\text{PO}_3)_\infty$  chains and the  $\text{PrO}_8$  square antiprisms: a) view showing the tridentate attachment of one chain ( $C_1$ ) and the connection of the second chain ( $C_2$ ) parallel and opposite to the first one. b) view showing the bidentate attachment of the third chain ( $C_3$ ) adjacent and orthogonal to the first one. c) view showing the bidentate attachment of the fourth chain ( $C_4$ ) also orthogonal and adjacent to the first one.

### Potassium praseodymium polyphosphate

#### Crystal data

$\text{KPr}(\text{PO}_3)_4$   
 $M_r = 495.89$   
 Monoclinic,  $P2_1$   
 Hall symbol: P 2yb  
 $a = 7.2872(2) \text{ \AA}$   
 $b = 8.4570(3) \text{ \AA}$   
 $c = 8.0268(2) \text{ \AA}$   
 $\beta = 91.994(1)^\circ$   
 $V = 494.37(3) \text{ \AA}^3$   
 $Z = 2$

$F(000) = 468$   
 $D_x = 3.331 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 9960 reflections  
 $\theta = 2.8\text{--}57.3^\circ$   
 $\mu = 6.06 \text{ mm}^{-1}$   
 $T = 296 \text{ K}$   
 Prism, green  
 $0.29 \times 0.21 \times 0.16 \text{ mm}$

#### Data collection

Bruker APEXII CCD  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 Detector resolution:  $8.3333 \text{ pixels mm}^{-1}$   
 $\omega$  and  $\varphi$  scans

Absorption correction: multi-scan  
 (*SADABS*; Bruker, 2008)  
 $T_{\min} = 0.448$ ,  $T_{\max} = 0.751$   
 45940 measured reflections  
 13443 independent reflections  
 13257 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.034$

$\theta_{\max} = 57.4^\circ$ ,  $\theta_{\min} = 3.7^\circ$   
 $h = -17 \rightarrow 17$

$k = -19 \rightarrow 20$   
 $l = -18 \rightarrow 18$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.018$   
 $wR(F^2) = 0.043$   
 $S = 1.07$   
 13443 reflections  
 164 parameters  
 1 restraint  
 0 constraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 $w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 0.0715P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.004$   
 $\Delta\rho_{\max} = 2.86 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -2.42 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: *SHELXL97* (Sheldrick,  
 2008),  $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.0305 (6)  
 Absolute structure: Flack (1983), 6278 Friedel  
 pairs  
 Absolute structure parameter: 0.022 (3)

*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.

**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  $F^2 > \sigma(F^2)$  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>      | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|---------------|---------------|----------------------------------|
| K   | 0.77227 (5)   | 0.31500 (7)   | 0.72001 (4)   | 0.02909 (8)                      |
| Pr  | 0.265282 (4)  | 0.119995 (8)  | 0.757982 (4)  | 0.00552 (1)                      |
| P1  | 0.50137 (3)   | 0.26677 (3)   | 0.38019 (3)   | 0.00690 (3)                      |
| P2  | 0.93476 (3)   | 0.24280 (3)   | 0.09865 (3)   | 0.00685 (3)                      |
| P3  | 0.12252 (3)   | 0.37267 (3)   | 0.39531 (3)   | 0.00674 (3)                      |
| P4  | 0.60346 (3)   | 0.04117 (3)   | 0.10444 (3)   | 0.00675 (3)                      |
| O1  | 1.04301 (12)  | 0.23711 (10)  | 0.27436 (11)  | 0.01360 (11)                     |
| O2  | 0.81354 (11)  | 0.08886 (10)  | 0.12702 (13)  | 0.01412 (12)                     |
| O3  | -0.03801 (11) | 0.02642 (9)   | 0.65100 (11)  | 0.01191 (10)                     |
| O4  | 0.11151 (11)  | 0.31458 (11)  | 0.56903 (9)   | 0.01188 (10)                     |
| O5  | 0.33093 (10)  | 0.38001 (9)   | 0.34329 (10)  | 0.01061 (9)                      |
| O6  | 0.66909 (10)  | 0.36646 (10)  | 0.38630 (10)  | 0.01127 (9)                      |
| O7  | 0.18250 (12)  | -0.11539 (10) | 0.92653 (10)  | 0.01172 (10)                     |
| O8  | 0.41427 (12)  | 0.38104 (10)  | 0.82424 (13)  | 0.01527 (12)                     |
| O9  | 0.53826 (12)  | 0.07174 (11)  | 0.93036 (10)  | 0.01395 (12)                     |
| O10 | 0.49263 (14)  | 0.16280 (13)  | 0.21526 (13)  | 0.01754 (15)                     |
| O11 | 1.06463 (16)  | 0.21154 (13)  | -0.03535 (13) | 0.01866 (16)                     |
| O12 | 0.46952 (13)  | 0.16652 (11)  | 0.52829 (11)  | 0.01411 (12)                     |

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

|     | $U^{11}$     | $U^{22}$    | $U^{33}$     | $U^{12}$      | $U^{13}$      | $U^{23}$      |
|-----|--------------|-------------|--------------|---------------|---------------|---------------|
| K   | 0.01717 (11) | 0.0542 (3)  | 0.01579 (10) | 0.00955 (13)  | -0.00159 (8)  | -0.00090 (12) |
| Pr  | 0.00546 (1)  | 0.00563 (1) | 0.00548 (1)  | -0.00032 (1)  | 0.00021 (1)   | 0.00006 (1)   |
| P1  | 0.00666 (7)  | 0.00665 (7) | 0.00750 (7)  | 0.00002 (5)   | 0.00174 (5)   | 0.00055 (5)   |
| P2  | 0.00649 (6)  | 0.00695 (7) | 0.00716 (7)  | -0.00010 (5)  | 0.00069 (5)   | -0.00144 (5)  |
| P3  | 0.00623 (6)  | 0.00685 (7) | 0.00704 (7)  | 0.00079 (5)   | -0.00105 (5)  | 0.00031 (5)   |
| P4  | 0.00704 (7)  | 0.00576 (6) | 0.00735 (7)  | -0.00051 (5)  | -0.00141 (5)  | -0.00019 (5)  |
| O1  | 0.0159 (3)   | 0.0098 (2)  | 0.0145 (3)   | 0.0010 (2)    | -0.0082 (2)   | -0.00244 (18) |
| O2  | 0.0083 (2)   | 0.0108 (2)  | 0.0229 (3)   | -0.00354 (17) | -0.0037 (2)   | 0.0027 (2)    |
| O3  | 0.0102 (2)   | 0.0084 (2)  | 0.0168 (3)   | -0.00284 (17) | -0.00320 (19) | -0.00037 (18) |
| O4  | 0.0114 (2)   | 0.0160 (3)  | 0.0082 (2)   | 0.0013 (2)    | 0.00038 (16)  | 0.00301 (18)  |
| O5  | 0.00730 (18) | 0.0111 (2)  | 0.0135 (2)   | 0.00173 (16)  | 0.00166 (16)  | 0.00354 (18)  |
| O6  | 0.00779 (19) | 0.0116 (2)  | 0.0145 (2)   | -0.00191 (17) | 0.00084 (16)  | 0.00167 (19)  |
| O7  | 0.0141 (2)   | 0.0103 (2)  | 0.0106 (2)   | -0.00433 (19) | -0.00116 (18) | 0.00117 (17)  |
| O8  | 0.0131 (3)   | 0.0090 (2)  | 0.0235 (4)   | 0.00183 (19)  | -0.0015 (2)   | -0.0067 (2)   |
| O9  | 0.0143 (3)   | 0.0186 (3)  | 0.0087 (2)   | 0.0028 (2)    | -0.00406 (18) | 0.0001 (2)    |
| O10 | 0.0157 (3)   | 0.0201 (3)  | 0.0169 (3)   | 0.0020 (3)    | 0.0016 (2)    | -0.0106 (3)   |
| O11 | 0.0206 (4)   | 0.0191 (3)  | 0.0171 (3)   | 0.0030 (3)    | 0.0121 (3)    | -0.0029 (3)   |
| O12 | 0.0141 (3)   | 0.0144 (3)  | 0.0142 (3)   | 0.0033 (2)    | 0.0059 (2)    | 0.0074 (2)    |

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

|                      |             |                       |             |
|----------------------|-------------|-----------------------|-------------|
| K—O4 <sup>i</sup>    | 2.7908 (9)  | P2—O7 <sup>vi</sup>   | 1.4822 (8)  |
| K—O6                 | 2.7909 (9)  | P2—O1                 | 1.5926 (8)  |
| K—O8                 | 2.8231 (10) | P2—O2                 | 1.5941 (8)  |
| K—O3 <sup>i</sup>    | 2.8684 (10) | P2—K <sup>vii</sup>   | 3.2805 (4)  |
| K—O7 <sup>ii</sup>   | 2.9050 (9)  | P3—O3 <sup>viii</sup> | 1.4806 (8)  |
| K—O12                | 2.9285 (11) | P3—O4                 | 1.4832 (8)  |
| K—O11 <sup>iii</sup> | 2.9781 (13) | P3—O5                 | 1.5902 (8)  |
| K—O9                 | 3.1924 (11) | P3—O1 <sup>ix</sup>   | 1.5980 (8)  |
| K—P2 <sup>iii</sup>  | 3.2805 (4)  | P4—O8 <sup>v</sup>    | 1.4777 (8)  |
| K—P1                 | 3.3360 (4)  | P4—O9 <sup>vii</sup>  | 1.4829 (8)  |
| Pr—O11 <sup>iv</sup> | 2.3787 (9)  | P4—O2                 | 1.5874 (8)  |
| Pr—O9                | 2.4180 (8)  | P4—O10                | 1.5973 (9)  |
| Pr—O12               | 2.4414 (8)  | O1—P3 <sup>i</sup>    | 1.5980 (8)  |
| Pr—O3                | 2.4731 (7)  | O3—P3 <sup>x</sup>    | 1.4806 (8)  |
| Pr—O4                | 2.4791 (8)  | O3—K <sup>ix</sup>    | 2.8684 (10) |
| Pr—O6 <sup>v</sup>   | 2.4912 (8)  | O4—K <sup>ix</sup>    | 2.7908 (9)  |
| Pr—O7                | 2.4928 (8)  | O6—Pr <sup>vi</sup>   | 2.4912 (8)  |
| Pr—O8                | 2.5091 (8)  | O7—P2 <sup>v</sup>    | 1.4822 (8)  |
| P1—O6                | 1.4841 (8)  | O7—K <sup>xi</sup>    | 2.9051 (9)  |
| P1—O12               | 1.4850 (8)  | O8—P4 <sup>vi</sup>   | 1.4776 (8)  |
| P1—O5                | 1.5881 (7)  | O9—P4 <sup>iii</sup>  | 1.4829 (8)  |
| P1—O10               | 1.5887 (9)  | O11—Pr <sup>xii</sup> | 2.3787 (9)  |
| P2—O11               | 1.4810 (9)  | O11—K <sup>vii</sup>  | 2.9782 (13) |



|   |             |   |              |
|---|-------------|---|--------------|
| O4 <sup>i</sup> —K—O6                   | 78.26 (2)   | O12—Pr—O8                               | 75.38 (3)    |
| O4 <sup>i</sup> —K—O8                   | 166.08 (3)  | O3—Pr—O8                                | 136.89 (3)   |
| O6—K—O8                                 | 91.87 (3)   | O4—Pr—O8                                | 74.26 (3)    |
| O4 <sup>i</sup> —K—O3 <sup>i</sup>      | 58.32 (3)   | O6 <sup>v</sup> —Pr—O8                  | 140.10 (3)   |
| O6—K—O3 <sup>i</sup>                    | 93.61 (3)   | O7—Pr—O8                                | 134.32 (3)   |
| O8—K—O3 <sup>i</sup>                    | 133.01 (3)  | O11 <sup>iv</sup> —Pr—K <sup>ix</sup>   | 48.64 (3)    |
| O4 <sup>i</sup> —K—O7 <sup>ii</sup>     | 110.62 (3)  | O9—Pr—K <sup>ix</sup>                   | 147.29 (2)   |
| O6—K—O7 <sup>ii</sup>                   | 157.42 (3)  | O12—Pr—K <sup>ix</sup>                  | 116.78 (2)   |
| O8—K—O7 <sup>ii</sup>                   | 75.23 (3)   | O3—Pr—K <sup>ix</sup>                   | 46.23 (2)    |
| O3 <sup>i</sup> —K—O7 <sup>ii</sup>     | 108.78 (3)  | O4—Pr—K <sup>ix</sup>                   | 44.44 (2)    |
| O4 <sup>i</sup> —K—O12                  | 115.71 (3)  | O6 <sup>v</sup> —Pr—K <sup>ix</sup>     | 120.771 (19) |
| O6—K—O12                                | 52.38 (2)   | O7—Pr—K <sup>ix</sup>                   | 97.96 (2)    |
| O8—K—O12                                | 63.48 (3)   | O8—Pr—K <sup>ix</sup>                   | 91.99 (2)    |
| O3 <sup>i</sup> —K—O12                  | 83.86 (3)   | O11 <sup>iv</sup> —Pr—K                 | 120.16 (3)   |
| O7 <sup>ii</sup> —K—O12                 | 131.14 (3)  | O9—Pr—K                                 | 51.68 (2)    |
| O4 <sup>i</sup> —K—O11 <sup>iii</sup>   | 70.23 (2)   | O12—Pr—K                                | 45.47 (3)    |
| O6—K—O11 <sup>iii</sup>                 | 147.28 (3)  | O3—Pr—K                                 | 155.08 (2)   |
| O8—K—O11 <sup>iii</sup>                 | 120.66 (3)  | O4—Pr—K                                 | 94.44 (2)    |
| O3 <sup>i</sup> —K—O11 <sup>iii</sup>   | 62.54 (3)   | O6 <sup>v</sup> —Pr—K                   | 97.156 (19)  |
| O7 <sup>ii</sup> —K—O11 <sup>iii</sup>  | 50.31 (2)   | O7—Pr—K                                 | 127.02 (2)   |
| O12—K—O11 <sup>iii</sup>                | 136.81 (3)  | O8—Pr—K                                 | 43.25 (2)    |
| O4 <sup>i</sup> —K—O9                   | 136.58 (3)  | K <sup>ix</sup> —Pr—K                   | 130.558 (15) |
| O6—K—O9                                 | 118.49 (3)  | O6—P1—O12                               | 116.70 (5)   |
| O8—K—O9                                 | 56.95 (3)   | O6—P1—O5                                | 107.54 (5)   |
| O3 <sup>i</sup> —K—O9                   | 79.85 (3)   | O12—P1—O5                               | 110.52 (5)   |
| O7 <sup>ii</sup> —K—O9                  | 70.04 (3)   | O6—P1—O10                               | 110.55 (5)   |
| O12—K—O9                                | 66.11 (2)   | O12—P1—O10                              | 110.38 (6)   |
| O11 <sup>iii</sup> —K—O9                | 81.08 (3)   | O5—P1—O10                               | 99.78 (5)    |
| O4 <sup>i</sup> —K—P2 <sup>iii</sup>    | 96.054 (18) | O6—P1—K                                 | 55.97 (3)    |
| O6—K—P2 <sup>iii</sup>                  | 174.10 (2)  | O12—P1—K                                | 61.30 (4)    |
| O8—K—P2 <sup>iii</sup>                  | 94.00 (2)   | O5—P1—K                                 | 121.03 (3)   |
| O3 <sup>i</sup> —K—P2 <sup>iii</sup>    | 81.93 (2)   | O10—P1—K                                | 138.98 (4)   |
| O7 <sup>ii</sup> —K—P2 <sup>iii</sup>   | 26.858 (16) | O11—P2—O7 <sup>vi</sup>                 | 115.17 (6)   |
| O12—K—P2 <sup>iii</sup>                 | 130.40 (2)  | O11—P2—O1                               | 109.17 (6)   |
| O11 <sup>iii</sup> —K—P2 <sup>iii</sup> | 26.821 (17) | O7 <sup>vi</sup> —P2—O1                 | 114.25 (5)   |
| O9—K—P2 <sup>iii</sup>                  | 64.676 (17) | O11—P2—O2                               | 109.22 (6)   |
| O4 <sup>i</sup> —K—P1                   | 98.784 (19) | O7 <sup>vi</sup> —P2—O2                 | 111.14 (5)   |
| O6—K—P1                                 | 26.147 (16) | O1—P2—O2                                | 96.24 (5)    |
| O8—K—P1                                 | 74.92 (2)   | O11—P2—K <sup>vii</sup>                 | 65.14 (5)    |
| O3 <sup>i</sup> —K—P1                   | 90.78 (2)   | O7 <sup>vi</sup> —P2—K <sup>vii</sup>   | 62.31 (3)    |
| O7 <sup>ii</sup> —K—P1                  | 150.12 (2)  | O1—P2—K <sup>vii</sup>                  | 167.90 (4)   |
| O12—K—P1                                | 26.409 (16) | O2—P2—K <sup>vii</sup>                  | 95.76 (4)    |
| O11 <sup>iii</sup> —K—P1                | 153.20 (3)  | O3 <sup>viii</sup> —P3—O4               | 119.42 (5)   |
| O9—K—P1                                 | 92.400 (19) | O3 <sup>viii</sup> —P3—O5               | 107.01 (5)   |
| P2 <sup>iii</sup> —K—P1                 | 156.78 (2)  | O4—P3—O5                                | 110.07 (4)   |
| O4 <sup>i</sup> —K—P4 <sup>vi</sup>     | 148.57 (3)  | O3 <sup>viii</sup> —P3—O1 <sup>ix</sup> | 109.79 (4)   |
| O6—K—P4 <sup>vi</sup>                   | 96.19 (2)   | O4—P3—O1 <sup>ix</sup>                  | 107.65 (5)   |
| O8—K—P4 <sup>vi</sup>                   | 21.809 (17) | O5—P3—O1 <sup>ix</sup>                  | 101.41 (5)   |

|  |              |   |            |
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| O3 <sup>i</sup> —K—P4 <sup>vi</sup>    | 152.95 (2)   | O3 <sup>viii</sup> —P3—K <sup>ix</sup>  | 90.09 (4)  |
| O7 <sup>ii</sup> —K—P4 <sup>vi</sup>   | 65.122 (18)  | O5—P3—K <sup>ix</sup>                   | 150.30 (3) |
| O12—K—P4 <sup>vi</sup>                 | 82.33 (2)    | O1 <sup>ix</sup> —P3—K <sup>ix</sup>    | 95.04 (4)  |
| O11 <sup>iii</sup> —K—P4 <sup>vi</sup> | 115.28 (2)   | O8 <sup>v</sup> —P4—O9 <sup>vii</sup>   | 119.69 (6) |
| O9—K—P4 <sup>vi</sup>                  | 73.308 (19)  | O8 <sup>v</sup> —P4—O2                  | 106.59 (5) |
| P2 <sup>iii</sup> —K—P4 <sup>vi</sup>  | 89.502 (11)  | O9 <sup>vii</sup> —P4—O2                | 109.84 (5) |
| P1—K—P4 <sup>vi</sup>                  | 87.099 (10)  | O8 <sup>v</sup> —P4—O10                 | 108.77 (6) |
| O4 <sup>i</sup> —K—P3 <sup>i</sup>     | 20.271 (16)  | O9 <sup>vii</sup> —P4—O10               | 105.12 (6) |
| O6—K—P3 <sup>i</sup>                   | 58.589 (17)  | O2—P4—O10                               | 106.09 (5) |
| O8—K—P3 <sup>i</sup>                   | 147.16 (3)   | O8 <sup>v</sup> —P4—K <sup>v</sup>      | 45.22 (4)  |
| O3 <sup>i</sup> —K—P3 <sup>i</sup>     | 68.374 (19)  | O9 <sup>vii</sup> —P4—K <sup>v</sup>    | 103.55 (4) |
| O7 <sup>ii</sup> —K—P3 <sup>i</sup>    | 126.64 (2)   | O2—P4—K <sup>v</sup>                    | 145.07 (4) |
| O12—K—P3 <sup>i</sup>                  | 102.092 (19) | O10—P4—K <sup>v</sup>                   | 73.90 (4)  |
| O11 <sup>iii</sup> —K—P3 <sup>i</sup>  | 90.45 (2)    | P2—O1—P3 <sup>i</sup>                   | 132.40 (6) |
| O9—K—P3 <sup>i</sup>                   | 147.36 (2)   | P4—O2—P2                                | 136.74 (6) |
| P2 <sup>iii</sup> —K—P3 <sup>i</sup>   | 115.882 (11) | P3 <sup>x</sup> —O3—Pr                  | 136.64 (5) |
| P1—K—P3 <sup>i</sup>                   | 81.085 (10)  | P3 <sup>x</sup> —O3—K <sup>ix</sup>     | 126.63 (4) |
| P4 <sup>vi</sup> —K—P3 <sup>i</sup>    | 137.479 (17) | Pr—O3—K <sup>ix</sup>                   | 95.26 (3)  |
| O11 <sup>iv</sup> —Pr—O9               | 99.75 (4)    | P3—O4—Pr                                | 139.19 (5) |
| O11 <sup>iv</sup> —Pr—O12              | 151.63 (3)   | P3—O4—K <sup>ix</sup>                   | 119.05 (4) |
| O9—Pr—O12                              | 87.04 (3)    | Pr—O4—K <sup>ix</sup>                   | 97.10 (3)  |
| O11 <sup>iv</sup> —Pr—O3               | 77.45 (4)    | P1—O5—P3                                | 132.48 (5) |
| O9—Pr—O3                               | 148.45 (3)   | P1—O6—Pr <sup>vi</sup>                  | 130.14 (5) |
| O12—Pr—O3                              | 110.50 (3)   | P1—O6—K                                 | 97.89 (4)  |
| O11 <sup>iv</sup> —Pr—O4               | 86.26 (3)    | Pr <sup>vi</sup> —O6—K                  | 122.05 (3) |
| O9—Pr—O4                               | 143.85 (3)   | P2 <sup>v</sup> —O7—Pr                  | 136.16 (5) |
| O12—Pr—O4                              | 72.87 (3)    | P2 <sup>v</sup> —O7—K <sup>xi</sup>     | 90.83 (4)  |
| O3—Pr—O4                               | 67.70 (3)    | Pr—O7—K <sup>xi</sup>                   | 132.10 (3) |
| O11 <sup>iv</sup> —Pr—O6 <sup>v</sup>  | 137.47 (3)   | P4 <sup>vi</sup> —O8—Pr                 | 147.72 (6) |
| O9—Pr—O6 <sup>v</sup>                  | 87.33 (3)    | P4 <sup>vi</sup> —O8—K                  | 112.97 (5) |
| O12—Pr—O6 <sup>v</sup>                 | 69.86 (3)    | Pr—O8—K                                 | 99.24 (3)  |
| O3—Pr—O6 <sup>v</sup>                  | 75.34 (3)    | P4 <sup>iii</sup> —O9—Pr                | 143.02 (6) |
| O4—Pr—O6 <sup>v</sup>                  | 112.14 (3)   | P4 <sup>iii</sup> —O9—K                 | 116.82 (5) |
| O11 <sup>iv</sup> —Pr—O7               | 73.45 (4)    | Pr—O9—K                                 | 91.87 (3)  |
| O9—Pr—O7                               | 76.38 (3)    | P1—O10—P4                               | 144.49 (7) |
| O12—Pr—O7                              | 134.75 (3)   | P2—O11—Pr <sup>xii</sup>                | 171.29 (7) |
| O3—Pr—O7                               | 72.70 (3)    | P2—O11—K <sup>vii</sup>                 | 88.04 (5)  |
| O4—Pr—O7                               | 138.54 (3)   | Pr <sup>xii</sup> —O11—K <sup>vii</sup> | 94.52 (4)  |
| O6 <sup>v</sup> —Pr—O7                 | 67.60 (3)    | P1—O12—Pr                               | 144.39 (5) |
| O11 <sup>iv</sup> —Pr—O8               | 80.66 (4)    | P1—O12—K                                | 92.29 (5)  |
| O9—Pr—O8                               | 71.69 (3)    | Pr—O12—K                                | 98.06 (3)  |

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