

The type IV polymorph of  $\text{KEu}(\text{PO}_3)_4$ Abdelghani Oudahmane,<sup>a</sup> Mohamed Daoud,<sup>a</sup>  
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Received 10 November 2009; accepted 16 November 2009

Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{P}-\text{O}) = 0.002$  Å;  $R$  factor = 0.030;  $wR$  factor = 0.072; data-to-parameter ratio = 38.0.

Single crystals of  $\text{KEu}(\text{PO}_3)_4$ , potassium europium(III) polyphosphate, were obtained by solid-state reactions. This monoclinic form is the second polymorph described for this composition and belongs to type IV of long-chain polyphosphates with general formula  $A^I B^{III}(\text{PO}_3)_4$ . It is isotypic with its  $\text{KEr}(\text{PO}_3)_4$  and  $\text{KDy}(\text{PO}_3)_4$  homologues. The crystal structure is built of infinite helical chains of corner-sharing  $\text{PO}_4$  tetrahedra with a repeating unit of eight tetrahedra. These chains are further linked by isolated  $\text{EuO}_8$  square antiprisms, forming a three-dimensional framework. The  $\text{K}^+$  ions are located in pseudo-hexagonal channels running along  $[\bar{2}01]$  and are surrounded by nine O atoms in a distorted environment.

## Related literature

Besides crystals of the title compound, crystals of the type III polymorph (Hu *et al.*, 1984) have also been obtained. For isotypic  $AB(\text{PO}_3)_4$  structures, where  $A$  is an alkali metal, Tl or  $\text{NH}_4^+$ , and  $B$  is a rare earth element, see: Palkina *et al.* (1977) for  $\text{TlNd}$ ; Maksimova *et al.* (1978) for  $\text{RbNd}$ ; Dago *et al.* (1980) for  $\text{KEr}$ ; Maksimova *et al.* (1981) for  $\text{CsNd}$ ; Maksimova *et al.* (1982) for  $\text{RbHo}$ ; Horchani *et al.* (2004) for  $\text{RbEr}$ ; Rekik *et al.* (2004) for  $\text{KGd}$ ; Naili & Mhiri (2005) for  $\text{CsGd}$ ; Ben Zarkouna *et al.* (2006) for  $(\text{NH}_4)\text{Gd}$ ; Khliissa & Férid (2006) for  $\text{RbTb}$ ; Ettis *et al.* (2006) for  $\text{RbGd}$ ; Chehimi-Moumen & Férid (2007) for  $\text{KDy}$ ; Horchani-Naifer & Férid (2007) for  $\text{CsPr}$ ; Zhu *et al.* (2009) for  $\text{CsEu}$ . For a review on the crystal chemistry of polyphosphates, see: Durif (1995). Jaouadi *et al.* (2003) have discussed the main crystal chemical characteristics of the seven  $AB(\text{PO}_3)_4$  structure types. For applications of rare earth polyphosphates, see: Rashchi & Finch (2000); Barsukov *et al.* (2004). For general background, see: Porai-Koshits & Aslanov (1972). For ionic radii, see: Shannon (1976).

## Experimental

## Crystal data

$\text{KEu}(\text{PO}_3)_4$	$V = 968.73(2) \text{ \AA}^3$
$M_r = 506.94$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 10.3723(1) \text{ \AA}$	$\mu = 7.63 \text{ mm}^{-1}$
$b = 8.9721(1) \text{ \AA}$	$T = 296 \text{ K}$
$c = 10.8320(1) \text{ \AA}$	$0.12 \times 0.11 \times 0.10 \text{ mm}$
$\beta = 106.053(1)^\circ$	

## Data collection

Bruker APEXII CCD diffractometer	24299 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2008)	6201 independent reflections
$T_{\min} = 0.466$ , $T_{\max} = 0.513$	5023 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.045$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	163 parameters
$wR(F^2) = 0.072$	$\Delta\rho_{\text{max}} = 1.72 \text{ e \AA}^{-3}$
$S = 1.04$	$\Delta\rho_{\text{min}} = -2.04 \text{ e \AA}^{-3}$
6201 reflections	

## Table 1

Selected bond lengths (Å).

P1—O7	1.480 (2)	P3—O6	1.482 (2)
P1—O4 <sup>i</sup>	1.483 (2)	P3—O2	1.4873 (19)
P1—O12	1.588 (2)	P3—O11	1.6005 (19)
P1—O3 <sup>ii</sup>	1.5968 (19)	P3—O1	1.6033 (19)
P2—O10 <sup>iii</sup>	1.4795 (19)	P4—O9	1.4784 (19)
P2—O5	1.483 (2)	P4—O8 <sup>v</sup>	1.484 (2)
P2—O11 <sup>iii</sup>	1.6015 (18)	P4—O1	1.601 (2)
P2—O3 <sup>iv</sup>	1.602 (2)	P4—O12 <sup>iii</sup>	1.601 (2)

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

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: DIAMOND (Brandenburg, 1999); 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: WM2282).

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**supplementary materials**

*Acta Cryst.* (2009). E65, i91-i92 [ doi:10.1107/S1600536809048788 ]

## The type IV polymorph of $\text{KEu}(\text{PO}_3)_4$

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### Comment

Rare earth polyphosphates are interesting materials and bear potential applications (Rashchi & Finch, 2000; Barsukov *et al.*, 2004). The title compound is a member of a large family of polyphosphates with general formula  $A^I B^{III}(\text{PO}_3)_4$  (where  $A^I$  is a monovalent cation: Li, Na, K, Rb, Cs, Tl,  $\text{NH}_4$ , Ag and  $B^{III}$  is a trivalent cation: Ln, Y, Bi). It is now well known that these compounds are classified into seven structural types usually labelled by roman numerals from I to VII. A short recapitulation of the main crystal chemical characteristics of these seven structural types has recently been given by Jaouadi *et al.* (2003). The  $\text{KEu}(\text{PO}_3)_4$  polymorph described in this article belongs to the IV structural type.

In the crystal structure the  $\text{Eu}^{3+}$  ion is eight-coordinated by the oxygen atoms and its 8-coordination polyhedron is better described as a square antiprism than a dodecahedron according to the criteria of Porai-Koshits & Aslanov (1972) ( $\delta_1 = 10.37^\circ$ ,  $\delta_2 = 10.85^\circ$ ,  $\delta_3 = 47.97^\circ$ ,  $\delta_4 = 53.54^\circ$ ). The Eu—O distances range from 2.3199 (19) Å to 2.4827 (19) Å with an average  $\langle \text{Eu—O} \rangle$  distance of 2.399 Å that is slightly shorter than the sum of the ionic radii *i.e.* 2.466 Å (Shannon, 1976). The structure of this type IV polymorph is built of infinite helical chains of corner-sharing  $\text{PO}_4$  tetrahedra further linked by isolated  $\text{EuO}_8$  square antiprisms. The  $(\text{PO}_3)_\infty$  chains exhibit a repeating unit of eight  $\text{PO}_4$  tetrahedra (Fig. 1) and are running along the [101] direction. The three-dimensional framework resulting from the edge-sharing between the  $\text{PO}_4$  tetrahedra and the  $\text{EuO}_8$  square antiprisms exhibits pseudo hexagonal channels where the  $\text{K}^+$  ions reside. The  $\text{K}^+$  ion is 9-coordinated by oxygen atoms with distances ranging from 2.789 (2) Å to 3.370 (3) Å. By sharing corners, the  $\text{KO}_9$  coordination polyhedra form corrugated chains running along the [010] direction (Fig. 2). Whereas the K atoms are separated by 6.599 (2) Å within the chain, the shortest K—K distance in the structure, 4.770 (2) Å, occurs between two adjacent  $(\text{KO}_9)_\infty$  chains. This shortest distance corresponds to the separation between two  $\text{K}^+$  ions within the channels of the structure running along the  $[\bar{2}01]$  direction. This separation distance  $A^I—A^I$  is strongly dependent on the nature of the  $A^I$  element and decreases as the size of the  $A^I$  element increases. For instance, in the  $A^I\text{Gd}(\text{PO}_3)_4$  homologue series, where  $A^I = \text{K}, \text{Rb}, \text{Cs}$ , this  $A^I—A^I$  shortest distance varies from 4.801 Å for K to 4.211 Å for Cs (4.524 Å for Rb). For  $\text{CsEu}(\text{PO}_3)_4$  the shortest Cs—Cs distance is equal to 4.237 Å (Zhu *et al.* 2009).

For isotopic  $AB(\text{PO}_3)_4$  structures, where  $A$  is an alkali metal, Tl or  $\text{NH}_4^+$ , and  $B$  is a rare earth element, see: Palkina *et al.* (1977) for TlNd, Maksimova *et al.* (1978) for RbNd, Dago *et al.* (1980) for KEr, Maksimova *et al.* (1981) for CsNd, Maksimova *et al.* (1982) for RbHo, Horchani *et al.* (2004) for RbEr, Rekik *et al.* (2004) for KGd, Naïli & Mhiri (2005) for CsGd, Ben Zarkouna *et al.* (2006) for  $(\text{NH}_4)\text{Gd}$ , Khliissa & Férid (2006) for RbTb, Ettis *et al.* (2006) for RbGd, Chehimi-Moumen & Férid (2007) for KDy, Horchani-Naifer & Férid (2007) for CsPr, and Zhu *et al.* (2009) for CsEu. For a review on the crystal chemistry of polyphosphates, see: Durif (1995).

## Experimental

Crystals of the title compound were synthesized by reacting  $\text{Eu}_2\text{O}_3$  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 34:57:9 was used for the synthesis. The mixture was heated at 473 K for 6 h, then at 573 K for 6 h and finally at 873 K for 24 h. The furnace was then cooled down first to 773 K at the rate of  $2 \text{ K}\cdot\text{h}^{-1}$  and then to room temperature at the rate of  $\text{K}\cdot\text{h}^{-1}$ . Single crystals were extracted from the batch by washing with hot water. Besides crystals of the title compound, crystals of the type III polymorph (Hu *et al.*, 1984)) have also been obtained.

## Refinement

The highest residual peak in the final difference Fourier map was located  $0.68 \text{ \AA}$  from atom Eu and the deepest hole was located  $0.45 \text{ \AA}$  from atom K.

## Figures

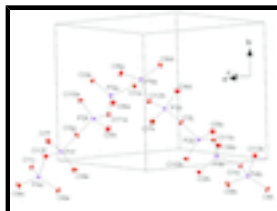


Fig. 1. ORTEP-3 view of the repeating unit with eight  $\text{PO}_4$  tetrahedra, leading to helical  $(\text{PO}_3)_\infty$  chains. Displacement ellipsoids are drawn at the 50 % probability level. Symmetry codes: (a)  $-1/2+x, 3/2-y, 1/2+z$ ; (b)  $-1+x, -1+y, z$ ; (c)  $x, -1+y, 1+z$ ; (d)  $-1+x, y, z$ ; (e)  $-1/2+x, 1/2-y, 1/2+z$ ; (f)  $3-x, 1-y, 1-z$ ; (g)  $2-x, 1-y, 1-z$ ; (h)  $5/2-x, -1/2+y, 1/2-z$ ; (i)  $-3/2+x, 1/2-y, -1/2+z$ ; (j)  $3/2-x, -1/2+y, 1/2-z$ ; (k)  $2-x, 1-y, -z$ .

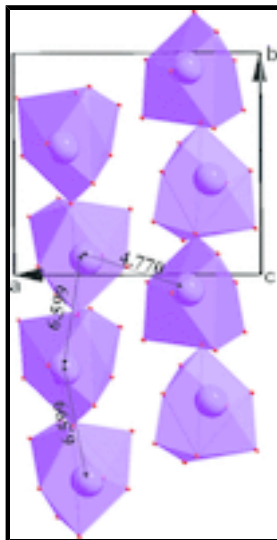


Fig. 2. Partial view of infinite chains of corner-sharing  $\text{KO}_9$  polyhedra.

## potassium europium(III) polyphosphate

### Crystal data

$\text{KEu}(\text{PO}_3)_4$

$M_r = 506.94$

Monoclinic,  $P2_1/n$

Hall symbol:  $-P 2_1n$

$F_{000} = 952$

$D_x = 3.476 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 6203 reflections

$a = 10.3723 (1) \text{ \AA}$	$\theta = 2.6\text{--}40.6^\circ$
$b = 8.9721 (1) \text{ \AA}$	$\mu = 7.63 \text{ mm}^{-1}$
$c = 10.8320 (1) \text{ \AA}$	$T = 296 \text{ K}$
$\beta = 106.053 (1)^\circ$	Hexagonal prism, colourless
$V = 968.733 (17) \text{ \AA}^3$	$0.12 \times 0.11 \times 0.10 \text{ mm}$
$Z = 4$	

### Data collection

Bruker APEXII CCD diffractometer	6201 independent reflections
Radiation source: fine-focus sealed tube	5023 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.045$
Detector resolution: $8.3333 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 40.6^\circ$
$T = 296 \text{ K}$	$\theta_{\text{min}} = 3.1^\circ$
$\omega$ and $\varphi$ scans	$h = -18 \rightarrow 18$
Absorption correction: multi-scan (SADABS; Bruker, 2008)	$k = -16 \rightarrow 16$
$T_{\text{min}} = 0.466$ , $T_{\text{max}} = 0.513$	$l = -19 \rightarrow 5$
24299 measured reflections	

### Refinement

Refinement on $F^2$	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.030$	$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2 + 1.1689P]$
$wR(F^2) = 0.072$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{\text{max}} = 0.002$
6201 reflections	$\Delta\rho_{\text{max}} = 1.72 \text{ e \AA}^{-3}$
163 parameters	$\Delta\rho_{\text{min}} = -2.04 \text{ e \AA}^{-3}$
	Extinction correction: none

### 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 ( $\text{\AA}^2$ )

$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
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## supplementary materials

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K	0.79467 (11)	0.57090 (14)	0.04227 (10)	0.0395 (2)
Eu	0.500385 (11)	0.772652 (13)	0.184899 (12)	0.00645 (3)
P1	0.85428 (6)	0.90558 (7)	0.24010 (7)	0.00615 (10)
P2	0.54001 (6)	0.82848 (7)	-0.14102 (7)	0.00607 (10)
P3	0.24938 (6)	1.02436 (7)	0.22927 (6)	0.00609 (10)
P4	0.17657 (6)	0.89469 (7)	-0.01962 (6)	0.00626 (10)
O1	0.14215 (17)	0.9549 (2)	0.10673 (19)	0.0085 (3)
O2	0.35389 (19)	0.9131 (2)	0.29039 (19)	0.0093 (3)
O3	-0.02278 (19)	0.7943 (2)	0.2518 (2)	0.0103 (3)
O4	0.6017 (2)	0.5368 (2)	0.1754 (2)	0.0117 (3)
O5	0.5648 (2)	0.7615 (2)	-0.0114 (2)	0.0117 (3)
O6	0.17180 (19)	1.0919 (2)	0.3112 (2)	0.0106 (3)
O7	0.73783 (19)	0.8192 (2)	0.2547 (2)	0.0134 (4)
O8	0.5691 (2)	0.7074 (2)	0.4090 (2)	0.0114 (3)
O9	0.31707 (19)	0.8419 (2)	0.0175 (2)	0.0121 (3)
O10	0.53947 (19)	1.0334 (2)	0.1765 (2)	0.0121 (3)
O11	0.31589 (17)	1.1548 (2)	0.1668 (2)	0.0092 (3)
O12	0.8309 (2)	0.9497 (2)	0.0936 (2)	0.0125 (3)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
K	0.0363 (5)	0.0581 (6)	0.0243 (4)	0.0047 (4)	0.0085 (4)	-0.0045 (4)
Eu	0.00596 (4)	0.00617 (4)	0.00701 (5)	0.00051 (3)	0.00144 (3)	0.00084 (4)
P1	0.0054 (2)	0.0053 (2)	0.0068 (2)	-0.00011 (17)	0.0002 (2)	0.00105 (19)
P2	0.0060 (2)	0.0053 (2)	0.0071 (2)	-0.00059 (17)	0.0021 (2)	-0.00025 (19)
P3	0.0057 (2)	0.0065 (2)	0.0062 (3)	0.00066 (17)	0.0020 (2)	-0.00024 (19)
P4	0.0052 (2)	0.0077 (2)	0.0050 (2)	-0.00047 (17)	0.00004 (19)	0.00081 (19)
O1	0.0071 (6)	0.0106 (7)	0.0078 (7)	-0.0029 (5)	0.0023 (6)	-0.0027 (6)
O2	0.0094 (7)	0.0093 (7)	0.0087 (8)	0.0032 (5)	0.0015 (6)	0.0013 (6)
O3	0.0108 (7)	0.0104 (7)	0.0101 (8)	0.0053 (6)	0.0036 (6)	0.0047 (6)
O4	0.0163 (8)	0.0086 (7)	0.0117 (8)	0.0013 (6)	0.0063 (7)	0.0015 (6)
O5	0.0135 (8)	0.0155 (8)	0.0074 (8)	0.0021 (6)	0.0048 (7)	0.0014 (6)
O6	0.0114 (7)	0.0126 (7)	0.0095 (8)	0.0022 (6)	0.0059 (7)	-0.0018 (6)
O7	0.0073 (7)	0.0148 (8)	0.0173 (10)	-0.0029 (6)	0.0019 (7)	0.0051 (7)
O8	0.0114 (7)	0.0125 (8)	0.0093 (8)	0.0046 (6)	0.0011 (6)	0.0038 (6)
O9	0.0083 (7)	0.0193 (9)	0.0080 (8)	0.0053 (6)	0.0011 (6)	0.0024 (7)
O10	0.0099 (7)	0.0060 (6)	0.0212 (10)	0.0017 (5)	0.0059 (7)	0.0020 (7)
O11	0.0060 (6)	0.0077 (6)	0.0146 (9)	-0.0005 (5)	0.0040 (6)	0.0009 (6)
O12	0.0191 (9)	0.0087 (7)	0.0069 (8)	-0.0009 (6)	-0.0009 (7)	0.0026 (6)

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

K—O4	2.789 (2)	P1—O7	1.480 (2)
K—O5	2.860 (2)	P1—O4 <sup>vi</sup>	1.483 (2)
K—O6 <sup>i</sup>	2.874 (2)	P1—O12	1.588 (2)
K—O2 <sup>i</sup>	2.961 (2)	P1—O3 <sup>iii</sup>	1.5968 (19)
K—O10 <sup>ii</sup>	3.075 (3)	P1—K <sup>vi</sup>	3.4868 (13)

K—O3 <sup>iii</sup>	3.221 (2)	P2—O10 <sup>iv</sup>	1.4795 (19)
K—O7 <sup>ii</sup>	3.234 (3)	P2—O5	1.483 (2)
K—O11 <sup>iv</sup>	3.326 (2)	P2—O11 <sup>iv</sup>	1.6015 (18)
K—O7	3.370 (3)	P2—O3 <sup>i</sup>	1.602 (2)
K—P3 <sup>i</sup>	3.4008 (12)	P3—O6	1.482 (2)
K—P1 <sup>ii</sup>	3.4868 (13)	P3—O2	1.4873 (19)
Eu—O9	2.3199 (19)	P3—O11	1.6005 (19)
Eu—O4	2.3775 (19)	P3—O1	1.6033 (19)
Eu—O10	2.3799 (18)	P3—K <sup>vii</sup>	3.4008 (12)
Eu—O5	2.401 (2)	P4—O9	1.4784 (19)
Eu—O7	2.4045 (19)	P4—O8 <sup>viii</sup>	1.484 (2)
Eu—O8	2.406 (2)	P4—O1	1.601 (2)
Eu—O6 <sup>v</sup>	2.4214 (18)	P4—O12 <sup>iv</sup>	1.601 (2)
Eu—O2	2.4827 (19)		
O4—K—O5	59.57 (6)	O5—Eu—O2	141.68 (7)
O4—K—O6 <sup>i</sup>	100.70 (7)	O7—Eu—O2	118.10 (7)
O5—K—O6 <sup>i</sup>	89.02 (7)	O8—Eu—O2	72.99 (6)
O4—K—O2 <sup>i</sup>	147.48 (7)	O6 <sup>v</sup> —Eu—O2	77.51 (6)
O5—K—O2 <sup>i</sup>	99.06 (6)	O7—P1—O4 <sup>vi</sup>	118.08 (13)
O6 <sup>i</sup> —K—O2 <sup>i</sup>	51.47 (5)	O7—P1—O12	109.51 (12)
O4—K—O10 <sup>ii</sup>	76.15 (6)	O4 <sup>vi</sup> —P1—O12	110.78 (11)
O5—K—O10 <sup>ii</sup>	118.26 (7)	O7—P1—O3 <sup>iii</sup>	108.73 (11)
O6 <sup>i</sup> —K—O10 <sup>ii</sup>	143.04 (7)	O4 <sup>vi</sup> —P1—O3 <sup>iii</sup>	110.13 (12)
O2 <sup>i</sup> —K—O10 <sup>ii</sup>	135.75 (6)	O12—P1—O3 <sup>iii</sup>	97.66 (11)
O4—K—O3 <sup>iii</sup>	94.01 (6)	O10 <sup>iv</sup> —P2—O5	121.60 (13)
O5—K—O3 <sup>iii</sup>	93.77 (6)	O10 <sup>iv</sup> —P2—O11 <sup>iv</sup>	110.86 (11)
O6 <sup>i</sup> —K—O3 <sup>iii</sup>	164.29 (7)	O5—P2—O11 <sup>iv</sup>	106.08 (11)
O2 <sup>i</sup> —K—O3 <sup>iii</sup>	112.83 (6)	O10 <sup>iv</sup> —P2—O3 <sup>i</sup>	107.58 (12)
O10 <sup>ii</sup> —K—O3 <sup>iii</sup>	46.46 (5)	O5—P2—O3 <sup>i</sup>	109.67 (12)
O4—K—O7 <sup>ii</sup>	49.24 (5)	O11 <sup>iv</sup> —P2—O3 <sup>i</sup>	98.65 (10)
O5—K—O7 <sup>ii</sup>	108.54 (6)	O6—P3—O2	117.21 (12)
O6 <sup>i</sup> —K—O7 <sup>ii</sup>	97.63 (6)	O6—P3—O11	108.85 (11)
O2 <sup>i</sup> —K—O7 <sup>ii</sup>	138.36 (6)	O2—P3—O11	109.42 (10)
O10 <sup>ii</sup> —K—O7 <sup>ii</sup>	52.04 (5)	O6—P3—O1	106.70 (11)
O3 <sup>iii</sup> —K—O7 <sup>ii</sup>	96.13 (6)	O2—P3—O1	111.17 (11)
O4—K—O11 <sup>iv</sup>	105.76 (6)	O11—P3—O1	102.44 (11)
O5—K—O11 <sup>iv</sup>	46.23 (5)	O9—P4—O8 <sup>viii</sup>	119.05 (12)
O6 <sup>i</sup> —K—O11 <sup>iv</sup>	78.27 (6)	O9—P4—O1	108.15 (11)
O2 <sup>i</sup> —K—O11 <sup>iv</sup>	57.13 (5)	O8 <sup>viii</sup> —P4—O1	109.93 (11)
O10 <sup>ii</sup> —K—O11 <sup>iv</sup>	138.47 (6)	O9—P4—O12 <sup>iv</sup>	108.86 (12)
O3 <sup>iii</sup> —K—O11 <sup>iv</sup>	92.53 (6)	O8 <sup>viii</sup> —P4—O12 <sup>iv</sup>	110.62 (12)



## supplementary materials

O7 <sup>ii</sup> —K—O11 <sup>iv</sup>	153.96 (6)	O1—P4—O12 <sup>iv</sup>	98.17 (11)
O4—K—O7	55.48 (6)	P4—O1—P3	124.84 (11)
O5—K—O7	56.64 (6)	P3—O2—Eu	126.82 (12)
O6 <sup>i</sup> —K—O7	144.25 (6)	P3—O2—K <sup>vii</sup>	93.80 (9)
O2 <sup>i</sup> —K—O7	135.83 (6)	Eu—O2—K <sup>vii</sup>	139.28 (8)
O10 <sup>ii</sup> —K—O7	63.35 (5)	P1 <sup>ix</sup> —O3—P2 <sup>vii</sup>	130.06 (14)
O3 <sup>iii</sup> —K—O7	44.54 (5)	P1 <sup>ix</sup> —O3—K <sup>ix</sup>	91.84 (9)
O7 <sup>ii</sup> —K—O7	85.78 (3)	P2 <sup>vii</sup> —O3—K <sup>ix</sup>	97.17 (9)
O11 <sup>iv</sup> —K—O7	83.30 (6)	P1 <sup>ii</sup> —O4—Eu	138.08 (12)
O9—Eu—O4	118.75 (7)	P1 <sup>ii</sup> —O4—K	105.27 (10)
O9—Eu—O10	79.54 (7)	Eu—O4—K	108.28 (7)
O4—Eu—O10	142.30 (6)	P2—O5—Eu	143.49 (12)
O9—Eu—O5	71.81 (7)	P2—O5—K	110.57 (10)
O4—Eu—O5	71.94 (7)	Eu—O5—K	105.40 (8)
O10—Eu—O5	85.13 (7)	P3—O6—Eu <sup>x</sup>	144.03 (13)
O9—Eu—O7	138.27 (7)	P3—O6—K <sup>vii</sup>	97.49 (9)
O4—Eu—O7	75.03 (7)	Eu <sup>x</sup> —O6—K <sup>vii</sup>	118.48 (8)
O10—Eu—O7	70.79 (7)	P1—O7—Eu	148.46 (13)
O5—Eu—O7	76.95 (8)	P1—O7—K <sup>vi</sup>	87.05 (10)
O9—Eu—O8	143.51 (7)	Eu—O7—K <sup>vi</sup>	92.57 (7)
O4—Eu—O8	79.39 (7)	P1—O7—K	88.34 (10)
O10—Eu—O8	105.75 (7)	Eu—O7—K	91.59 (7)
O5—Eu—O8	143.72 (7)	K <sup>vi</sup> —O7—K	175.37 (7)
O7—Eu—O8	74.50 (7)	P4 <sup>xi</sup> —O8—Eu	130.26 (12)
O9—Eu—O6 <sup>v</sup>	75.16 (7)	P4—O9—Eu	146.27 (13)
O4—Eu—O6 <sup>v</sup>	75.02 (7)	P2 <sup>iv</sup> —O10—Eu	138.15 (12)
O10—Eu—O6 <sup>v</sup>	142.48 (6)	P2 <sup>iv</sup> —O10—K <sup>vi</sup>	106.53 (11)
O5—Eu—O6 <sup>v</sup>	112.01 (7)	Eu—O10—K <sup>vi</sup>	97.15 (7)
O7—Eu—O6 <sup>v</sup>	143.80 (7)	P3—O11—P2 <sup>iv</sup>	132.40 (12)
O8—Eu—O6 <sup>v</sup>	80.43 (7)	P3—O11—K <sup>iv</sup>	136.15 (9)
O9—Eu—O2	75.52 (7)	P2 <sup>iv</sup> —O11—K <sup>iv</sup>	88.55 (8)
O4—Eu—O2	143.69 (7)	P1—O12—P4 <sup>iv</sup>	133.66 (14)
O10—Eu—O2	69.57 (7)		

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

Fig. 1

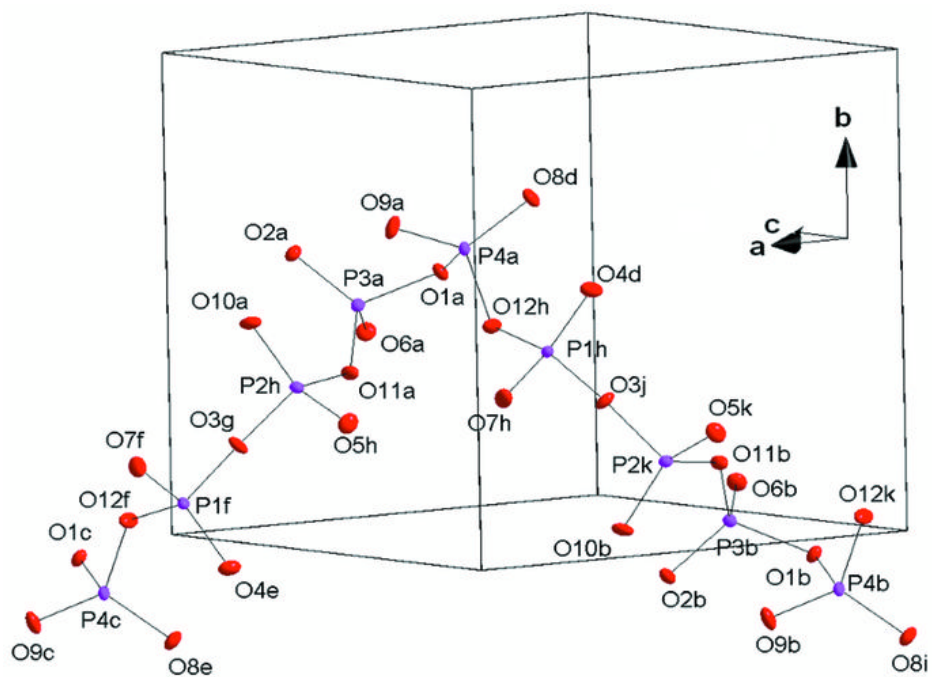


Fig. 2

