# inorganic compounds

# A monoclinic polymorph of KY(PO$_3$)$_4$

## Karima Horchani-Naifer, Anis Jouini and Mokhtar Férid*

Unité de Recherches de Matériaux de Terres Rares, Centre National de Recherches en Sciences des Matériaux, BP 95 Hammam-Lif 2050, Tunisia
Correspondence e-mail: mokhtar.ferid@inrst.rnrt.tn

The title compound, potassium yttrium polyphosphate, KY(PO$_3$)$_4$, was synthesized using the flux method. The atomic arrangement consists of an infinite long-chain polyphosphate organization. Chains, with a period of four PO$_4$ tetrahedra, run along the *a*-axis direction. Two other polymorphs of this phosphate are known, in space groups *P*2$_1$/*n* and *C*2/*c*.

## Related literature

For related structures, see: Durif (1995); Hamady *et al.* (1995); Hong *et al.* (1975); Malinowski (1990); Malinowski *et al.* (1988); Palkina *et al.* (1977). For earlier work on KY(PO$_3$)$_4$, see: Jouini *et al.* (2003). For related literature, see: Sun *et al.* (2004).

## Experimental

### Crystal data

KY(PO$_3$)$_4$
$M_r$ = 443.89
Monoclinic, $P2_1$
$a$ = 7.2244 (3) Å
$b$ = 8.2825 (3) Å
$c$ = 7.854 (4) Å
$\beta$ = 91.735 (3)°

$V$ = 469.7 (2) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 7.40 mm$^{-1}$
$T$ = 298 (2) K
0.16 × 0.14 × 0.13 mm

### Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.321, $T_{max}$ = 0.376
3651 measured reflections

2011 independent reflections
1904 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.081
2 standard reflections
  every 150 reflections
  intensity decay: 2%

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.138
$S$ = 1.13
2011 reflections
165 parameters
1 restraint

$\Delta\rho_{max}$ = 1.19 e Å$^{-3}$
$\Delta\rho_{min}$ = −2.67 e Å$^{-3}$
Absolute structure: Flack (1983), with 867 Friedel pairs
Flack parameter: 0.002 (9)

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

## References

Brandenburg, K. (2001). *DIAMOND*. Crystal Impact GbR, University of Bonn, Germany.
Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.
Durif, A. (1995). *Crystal Chemistry of Condensed Phosphates*. New York: Plenum Press.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hamady, A., Jouini, T. & Driss, A. (1995). *Acta Cryst.* C**51**, 1970–1972.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Hong, H. Y.-P. (1975). *Mater. Res. Bull.* **10**, 1105–1110.
Jouini, A., Férid, M. & Trabelsi-Ayadi, M. (2003). *Thermochim. Acta*, **400**, 199–204.
Macíček, J. & Yordanov, A. (1992). *J. Appl. Cryst.* **25**, 73–80.
Malinowski, M. (1990). *J. Phys. Chem. Solids*, **51**, 59–64.
Malinowski, M., Jackier, B., Boulon, G. & Wolinski, W. (1988). *J. Lumin.* **39**, 301–311.
Palkina, K. K., Saiffuddinov, V. Z., Kuznetsov, V. G. & Chudinova, N. N. (1977). *Dokl. Akad. Nauk SSSR*, **237**, 837–839.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sun, T., Shen, G., Wang, X., Wang, R., Wei, J. & Shen, D. (2004). *Acta Cryst.* E**60**, i28–i30.

# supporting information

## A monoclinic polymorph of KY(PO$_3$)$_4$

### Karima Horchani-Naifer, Anis Jouini and Mokhtar Férid

### S1. Comment

Yttrium condensed phosphates have been considered as a crystal hosts for optical materials when doped with lanthanides, due to there high-temperature chemical stability, high yield intrinsic fluorescence and minimal trapping of excitation, rendering them attractive materials for investigations of the energy transfer phenomena and fluorescence quenching(Malinowski, 1990; Malinowski *et al.*, 1988). The literature dealing with these compounds was rather confusing for some time, between cyclic or chain condensed phosphates, but it is currently well established that the $M^I$Y(PO$_3$)$_4$ compounds are polyphosphates with infinite chain and $M^I$YP$_4$O$_{12}$ are cyclotetraphosphates (with $M^I=$ monovalent cation) (Durif, 1995). In our laboratory we have synthesized the potassium and yttrium polyphosphates to establish the solid–liquid equilibrium diagram of the KPO$_3$–Y(PO$_3$)$_3$ system (Jouini *et al.*, 2003). Three allotropic phases with the space groups $P2_1$, $P2_1/n$ and $C2/c$ were isolated and characterized. The three monoclinic allotropes are: i) KY(PO$_3$)$_4$ polyphosphate with the $P2_1$ space group, isostructural with KNd(PO$_3$)$_4$ (Hong, 1975). ii) KY(PO$_3$)$_4$ polyphosphate belongs to $P2_1/n$ space group, and is isostructural with TlNd(PO$_3$)$_4$ (Palkina *et al.*, 1977). In these two forms the phosphate anion has a chain structure. iii) The third allotropic form is KYP$_4$O$_{12}$ which crystallizes in the $C2/c$ space group, only this structure was investigated (Hamady, 1995). This paper is devoted to the crystal structure of the first polymorph KY(PO$_3$)$_4$ ($P2_1$). The atomic arrangement of this srtucture is characterized by a three-dimensional framework built of (PO$_3$)$_n$ chains that are formed by corner-sharing of PO$_4$ tetrahedra (Figs 1,2). The chains run along the $a$ axis , with four PO$_4$ tetrahedra in a repeating unit. KY(PO$_3$)$_4$ is isostructural with KNd(PO$_3$)$_4$ , but not with CsLa(PO$_3$)$_4$ (Sun *et al.*, 2004) although they belong to the same space group, $P2_1$. In the latter, the infinite screw (PO$_3$)$_n$ chains are repeated after every eighth PO$_4$ group along the b axis. The chains (two per unit cell) are joined to each other by YO$_8$ polyhedra (Fig 3.), no O atom is shared with the adjacent YO$_8$ polyhedra. The K atoms are in an eightfold coordination.

### S2. Experimental

Single crystal of KY(PO$_3$)$_4$ was prepared by flux method. Homogeneous solution of potassium carbonate K$_2$CO$_3$ (6 g) and yttrium oxide Y$_2$O$_3$ (0.5 g) containing a large excess of orthophosphoric acid H$_3$PO$_4$ (16 ml, 85% concentration) was heated in a vitreous carbon crucible at 473 K for 1 day. Then the temperature of the furnace was slowly raised to the predermined temperature in the range of 573–623 K for 7 days. Crystals were separated from the excess phosphoric acid by washing the product in boiling water.
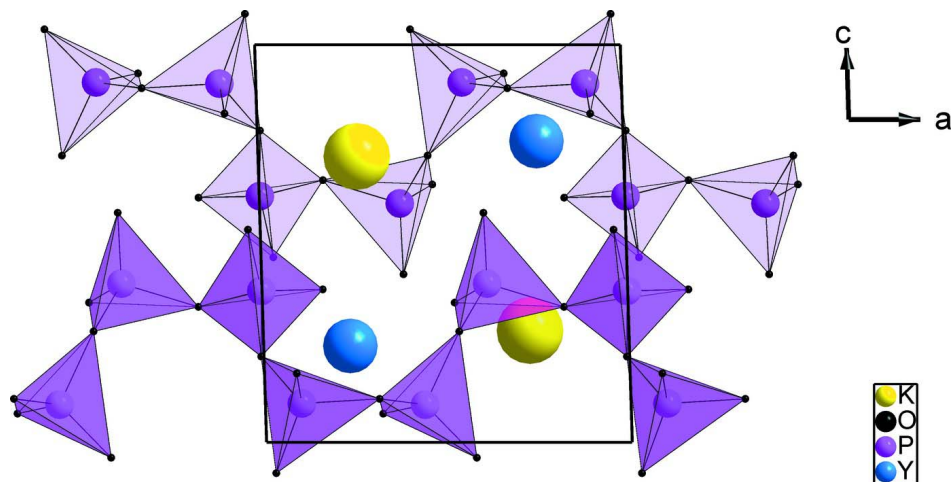
### S3. Refinement

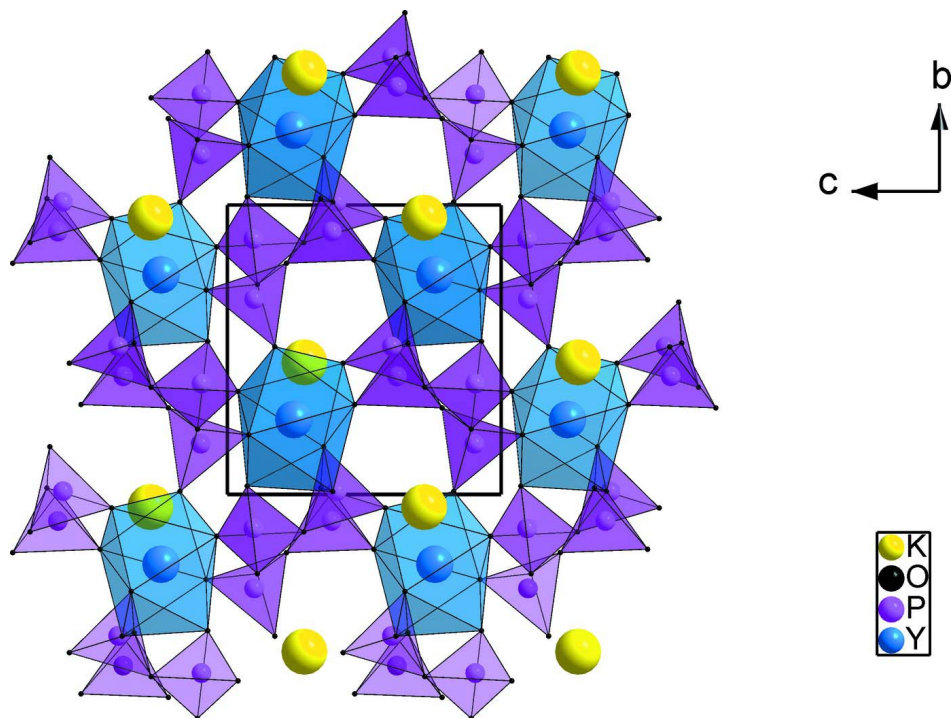The highest peak and the deepest hole are located 0.09Å and 0.85 Å from Y.
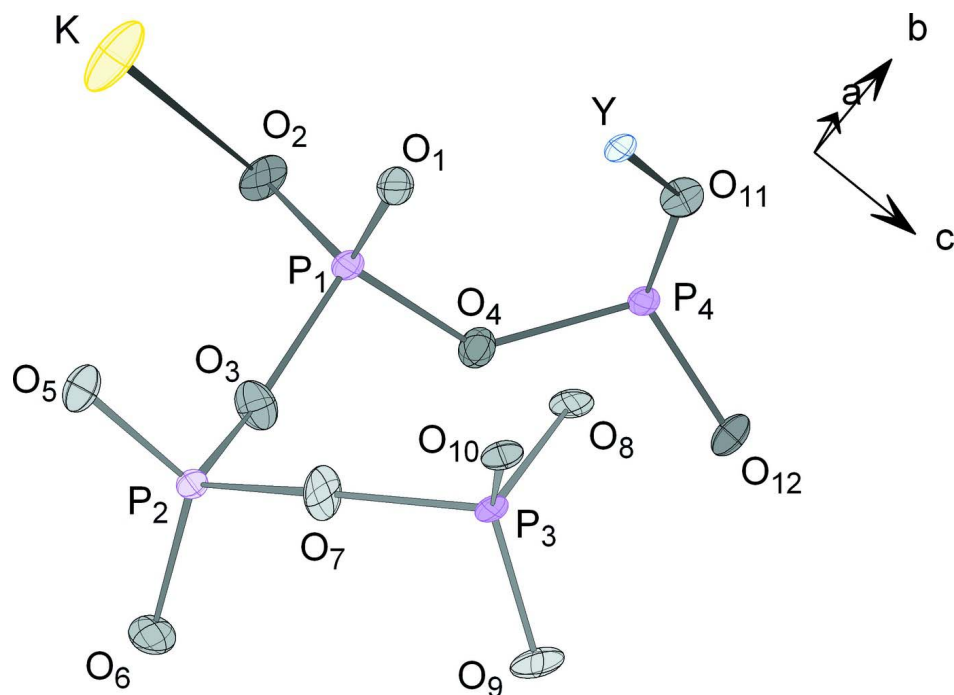
**Figure 1**

Projection of $KY(PO_3)_4$ with anisotropic displacement parameters drawn at the 50% probability level.



**Figure 2**

The structural arrangement of $KY(PO_3)_4$ along the *b* axis.

**Figure 3**

Projection of KY(PO₃)₄ along the *a* axis, showing isolated YO₈ polyhedra joined to (PO₃)n chains.

**Potassium yttrium polyphosphate**

*Crystal data*

| | |
|---|---|
| $KY(PO_3)_4$ | $F(000) = 428$ |
| $M_r = 443.89$ | $D_x = 3.138$ Mg m$^{-3}$ |
| Monoclinic, $P2_1$ | Melting point: 760 K |
| Hall symbol: P 2yb | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 7.2244$ (3) Å | Cell parameters from 25 reflections |
| $b = 8.2825$ (3) Å | $\theta = 2.6$–27.5° |
| $c = 7.854$ (4) Å | $\mu = 7.40$ mm$^{-1}$ |
| $\beta = 91.735$ (3)° | $T = 298$ K |
| $V = 469.7$ (2) Å$^3$ | Prism, colourless |
| $Z = 2$ | $0.16 \times 0.14 \times 0.13$ mm |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | 2011 independent reflections |
| Radiation source: fine-focus sealed tube | 1904 reflections with $I > 2\sigma(I)$ |
| Graphite monochromator | $R_{int} = 0.081$ |
| $\omega/2\theta$ scans | $\theta_{max} = 27.5°$, $\theta_{min} = 2.6°$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | $h = -7\rightarrow9$ |
| | $k = -8\rightarrow10$ |
| $T_{min} = 0.321$, $T_{max} = 0.376$ | $l = -8\rightarrow10$ |
| 3651 measured reflections | 2 standard reflections every 150 reflections |
| | intensity decay: 2% |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0908P)^2]$ |
| Least-squares matrix: full | where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)] = 0.048$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $wR(F^2) = 0.138$ | $\Delta\rho_{max} = 1.19$ e Å$^{-3}$ |
| $S = 1.13$ | $\Delta\rho_{min} = -2.67$ e Å$^{-3}$ |
| 2011 reflections | Extinction correction: *SHELXL97* (Sheldrick, |
| 165 parameters | 2008), Fc$^*$=kFc[1+0.001xFc$^2\lambda^3$/sin(2$\theta$)]$^{-1/4}$ |
| 1 restraint | Extinction coefficient: 0.065 (7) |
| Primary atom site location: structure-invariant direct methods | Absolute structure: Flack (1983), with 867 Friedel pairs |
| Secondary atom site location: difference Fourier map | Absolute structure parameter: 0.002 (9) |

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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$^2$ > 2sigma(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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Y | 0.23704 (8) | 0.75897 (9) | 0.24245 (8) | 0.0086 (3) |
| K | 0.2703 (3) | 0.4566 (3) | −0.2812 (3) | 0.0303 (6) |
| P1 | 0.4367 (3) | 0.3830 (2) | 0.0947 (3) | 0.0091 (4) |
| P2 | 0.0994 (3) | 0.1755 (2) | 0.0978 (2) | 0.0086 (4) |
| P3 | −0.0018 (3) | 0.4085 (2) | 0.3809 (2) | 0.0088 (4) |
| P4 | 0.6161 (3) | 0.5114 (2) | 0.3992 (2) | 0.0084 (4) |
| O1 | 0.3212 (8) | 0.5292 (7) | 0.0721 (7) | 0.0140 (12) |
| O2 | 0.5736 (8) | 0.3558 (8) | −0.0387 (8) | 0.0184 (13) |
| O3 | 0.3126 (7) | 0.2261 (7) | 0.1093 (8) | 0.0169 (13) |
| O4 | 0.5360 (8) | 0.3706 (7) | 0.2789 (7) | 0.0139 (12) |
| O5 | 0.0239 (8) | 0.2062 (7) | −0.0776 (7) | 0.0150 (12) |
| O6 | 0.0880 (8) | 0.0105 (7) | 0.1732 (7) | 0.0163 (12) |
| O7 | −0.0076 (8) | 0.2991 (7) | 0.2159 (8) | 0.0189 (13) |
| O8 | 0.1660 (7) | 0.5100 (7) | 0.3846 (7) | 0.0124 (11) |
| O9 | −0.0337 (8) | 0.3109 (7) | 0.5348 (8) | 0.0167 (12) |
| O10 | −0.1755 (8) | 0.5225 (7) | 0.3407 (7) | 0.0121 (11) |
| O11 | 0.5258 (8) | 0.6648 (7) | 0.3514 (7) | 0.0138 (11) |
| O12 | 0.6118 (7) | 0.4535 (7) | 0.5773 (7) | 0.0121 (11) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Y | 0.0092 (4) | 0.0103 (4) | 0.0067 (4) | −0.0004 (3) | 0.0048 (2) | −0.0001 (2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| K | 0.0180 (10) | 0.0601 (16) | 0.0129 (8) | 0.0108 (9) | 0.0031 (7) | −0.0019 (10) |
| P1 | 0.0100 (9) | 0.0098 (10) | 0.0080 (9) | −0.0003 (7) | 0.0044 (7) | −0.0004 (6) |
| P2 | 0.0084 (9) | 0.0095 (9) | 0.0082 (9) | −0.0008 (6) | 0.0034 (7) | −0.0004 (7) |
| P3 | 0.0090 (9) | 0.0107 (10) | 0.0070 (9) | −0.0009 (7) | 0.0055 (7) | 0.0003 (7) |
| P4 | 0.0086 (9) | 0.0088 (9) | 0.0081 (8) | 0.0003 (6) | 0.0032 (7) | 0.0001 (6) |
| O1 | 0.018 (3) | 0.012 (3) | 0.012 (3) | 0.001 (2) | 0.003 (2) | −0.001 (2) |
| O2 | 0.021 (3) | 0.021 (3) | 0.014 (3) | 0.007 (2) | 0.011 (2) | −0.001 (2) |
| O3 | 0.010 (3) | 0.018 (3) | 0.023 (3) | −0.003 (2) | 0.000 (2) | −0.004 (2) |
| O4 | 0.016 (3) | 0.015 (3) | 0.011 (3) | 0.001 (2) | −0.002 (2) | 0.000 (2) |
| O5 | 0.014 (3) | 0.020 (3) | 0.011 (3) | 0.004 (2) | 0.002 (2) | −0.003 (2) |
| O6 | 0.019 (3) | 0.011 (3) | 0.019 (3) | 0.003 (2) | −0.002 (2) | 0.004 (2) |
| O7 | 0.018 (3) | 0.020 (3) | 0.019 (3) | 0.003 (2) | 0.008 (2) | −0.010 (2) |
| O8 | 0.008 (3) | 0.016 (3) | 0.013 (3) | −0.004 (2) | 0.004 (2) | 0.004 (2) |
| O9 | 0.017 (3) | 0.019 (3) | 0.015 (3) | 0.003 (2) | 0.010 (2) | 0.007 (2) |
| O10 | 0.011 (3) | 0.015 (3) | 0.011 (3) | −0.002 (2) | 0.005 (2) | 0.003 (2) |
| O11 | 0.012 (3) | 0.015 (3) | 0.014 (3) | 0.003 (2) | 0.000 (2) | 0.002 (2) |
| O12 | 0.010 (2) | 0.019 (3) | 0.008 (2) | 0.005 (2) | 0.002 (2) | 0.000 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Y—O2[i] | 2.282 (6) | P1—O1 | 1.479 (6) |
| Y—O5[ii] | 2.296 (6) | P1—O2 | 1.480 (6) |
| Y—O9[iii] | 2.358 (6) | P1—O3 | 1.585 (6) |
| Y—O11 | 2.363 (5) | P1—O4 | 1.599 (5) |
| Y—O12[iv] | 2.387 (5) | P2—O5 | 1.488 (6) |
| Y—O6[v] | 2.400 (6) | P2—O6 | 1.492 (6) |
| Y—O8 | 2.408 (6) | P2—O3 | 1.597 (6) |
| Y—O1 | 2.415 (6) | P2—O7 | 1.597 (6) |
| Y—K[i] | 3.921 (2) | P3—O8 | 1.474 (6) |
| K—O12[vi] | 2.736 (6) | P3—O9 | 1.478 (6) |
| K—O8[vi] | 2.744 (6) | P3—O7 | 1.581 (6) |
| K—O6[ii] | 2.785 (6) | P3—O10 | 1.594 (6) |
| K—O1 | 2.852 (6) | P4—O11 | 1.472 (6) |
| K—O9[vi] | 2.859 (7) | P4—O12 | 1.480 (6) |
| K—O11[vii] | 2.892 (7) | P4—O10[viii] | 1.590 (6) |
| K—O2 | 2.979 (6) | P4—O4 | 1.598 (6) |
| K—O5 | 3.194 (6) | | |
| | | | |
| O2[i]—Y—O5[ii] | 99.8 (2) | O9[vi]—K—O11[vii] | 86.49 (17) |
| O2[i]—Y—O9[iii] | 148.9 (2) | O12[vi]—K—O2 | 66.57 (16) |
| O5[ii]—Y—O9[iii] | 86.2 (2) | O8[vi]—K—O2 | 146.32 (18) |
| O2[i]—Y—O11 | 80.1 (2) | O6[ii]—K—O2 | 121.50 (18) |
| O5[ii]—Y—O11 | 147.3 (2) | O1—K—O2 | 50.68 (17) |
| O9[iii]—Y—O11 | 110.8 (2) | O9[vi]—K—O2 | 138.0 (2) |
| O2[i]—Y—O12[iv] | 84.6 (2) | O11[vii]—K—O2 | 61.22 (17) |
| O5[ii]—Y—O12[iv] | 144.7 (2) | O12[vi]—K—O5 | 136.07 (19) |
| O9[iii]—Y—O12[iv] | 73.79 (19) | O8[vi]—K—O5 | 116.25 (17) |
| O11—Y—O12[iv] | 67.98 (19) | O6[ii]—K—O5 | 54.12 (17) |

| | | | |
|---|---|---|---|
| O2$^i$—Y—O6$^v$ | 79.1 (2) | O1—K—O5 | 72.96 (18) |
| O5$^{ii}$—Y—O6$^v$ | 71.5 (2) | O9$^{vi}$—K—O5 | 63.10 (17) |
| O9$^{iii}$—Y—O6$^v$ | 74.0 (2) | O11$^{vii}$—K—O5 | 81.22 (17) |
| O11—Y—O6$^v$ | 138.9 (2) | O2—K—O5 | 84.71 (17) |
| O12$^{iv}$—Y—O6$^v$ | 75.09 (19) | O1—P1—O2 | 115.3 (4) |
| O2$^i$—Y—O8 | 140.1 (2) | O1—P1—O3 | 111.2 (3) |
| O5$^{ii}$—Y—O8 | 85.16 (19) | O2—P1—O3 | 108.5 (4) |
| O9$^{iii}$—Y—O8 | 70.5 (2) | O1—P1—O4 | 113.4 (3) |
| O11—Y—O8 | 75.39 (19) | O2—P1—O4 | 109.9 (3) |
| O12$^{iv}$—Y—O8 | 113.77 (19) | O3—P1—O4 | 97.0 (3) |
| O6$^v$—Y—O8 | 138.4 (2) | O5—P2—O6 | 120.0 (3) |
| O2$^i$—Y—O1 | 73.9 (2) | O5—P2—O3 | 109.5 (3) |
| O5$^{ii}$—Y—O1 | 75.7 (2) | O6—P2—O3 | 106.4 (3) |
| O9$^{iii}$—Y—O1 | 136.7 (2) | O5—P2—O7 | 104.9 (3) |
| O11—Y—O1 | 72.9 (2) | O6—P2—O7 | 108.9 (4) |
| O12$^{iv}$—Y—O1 | 137.92 (19) | O3—P2—O7 | 106.4 (3) |
| O6$^v$—Y—O1 | 132.6 (2) | O8—P3—O9 | 116.4 (4) |
| O8—Y—O1 | 69.1 (2) | O8—P3—O7 | 110.1 (3) |
| O12$^{vi}$—K—O8$^{vi}$ | 80.69 (17) | O9—P3—O7 | 110.9 (4) |
| O12$^{vi}$—K—O6$^{ii}$ | 169.5 (2) | O8—P3—O10 | 107.9 (3) |
| O8$^{vi}$—K—O6$^{ii}$ | 91.99 (17) | O9—P3—O10 | 110.2 (3) |
| O12$^{vi}$—K—O1 | 107.81 (17) | O7—P3—O10 | 100.1 (3) |
| O8$^{vi}$—K—O1 | 156.9 (2) | O11—P4—O12 | 120.0 (3) |
| O6$^{ii}$—K—O1 | 76.31 (17) | O11—P4—O10$^{viii}$ | 107.0 (3) |
| O12$^{vi}$—K—O9$^{vi}$ | 118.63 (18) | O12—P4—O10$^{viii}$ | 109.8 (3) |
| O8$^{vi}$—K—O9$^{vi}$ | 53.15 (16) | O11—P4—O4 | 109.3 (3) |
| O6$^{ii}$—K—O9$^{vi}$ | 60.95 (18) | O12—P4—O4 | 107.7 (3) |
| O1—K—O9$^{vi}$ | 130.90 (19) | O10$^{viii}$—P4—O4 | 101.5 (3) |
| O12$^{vi}$—K—O11$^{vii}$ | 56.23 (17) | P1—O3—P2 | 139.3 (4) |
| O8$^{vi}$—K—O11$^{vii}$ | 94.54 (19) | P4—O4—P1 | 129.2 (4) |
| O6$^{ii}$—K—O11$^{vii}$ | 132.5 (2) | P3—O7—P2 | 147.4 (4) |
| O1—K—O11$^{vii}$ | 108.06 (18) | P4$^{ix}$—O10—P3 | 130.9 (4) |

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