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A new polymorph of $Lu(PO_3)_3$

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Key indicators: single-crystal X-ray study; T = 100 K; mean σ(Lu–O) = 0.005 Å; R factor = 0.033; wR factor = 0.061; data-to-parameter ratio = 26.2.

A new polymorph of lutetium polyphosphate, $Lu(PO_3)_3$, was found to be isotypic with the trigonal form of $Yb(PO_3)_3$. Two of the three Lu atoms occupy special positions (Wyckoff positions 3*a* and 3*b*, site symmetry $\overline{3}$). The atomic arrangement consists of infinite helical polyphosphate chains running along the *c* axis, with a repeat period of 12 PO_4 tetrahedra, joined with LuO_6 octahedra.

Related literature

For syntheses and optical properties, see: Briche *et al.* (2006); Jouini, Férid, Gacon, Grosvalet *et al.* (2003); Jouini, Férid, Gacon & Trabelsi-Ayadi (2003); Ternane *et al.* (2005); Graia *et al.* (2003); Anisimova *et al.* (1992). For the monoclinic polymorph of $Lu(PO_3)_3$, see: Höppe & Sedlmaier (2007); Yuan *et al.* (2008).

Experimental

Crystal data

$Lu(PO_3)_3$
M_r = 411.88
Trigonal, $R\overline{3}$
a = 20.9106 (6) Å
c = 12.0859 (7) Å
V = 4576.6 (3) Å^3
Z = 24
Mo $K\alpha$ radiation
μ = 13.59 mm^{-1}
T = 100 (2) K
0.18 × 0.18 × 0.17 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.102, T_{max} = 0.104
25139 measured reflections
4170 independent reflections
3609 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.060
S = 1.05
4170 reflections
159 parameters
$\Delta\rho_{max}$ = 2.34 e Å^{-3}
$\Delta\rho_{min}$ = −2.07 e Å^{-3}

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FI2065).

References

Anisimova, N. Y., Trunov, V. K., Karamanovskaya, N. B. & Chudinova, N. N. (1992). *Neorg. Mater.* **28**, 441–444.
Brandenburg, K. (2001). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Briche, S., Zambon, D., Boyer, D., Chadeyron, G. & Mahiou, R. (2006). *Opt. Mater.* **28**, 615–620.
Bruker (2005). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Graia, M., Driss, A. & Jouini, T. (2003). *Solid State Sci.* **5**, 393–402.
Höppe, H. A. & Sedlmaier, S. J. (2007). *Inorg. Chem.* **46**, 3467–3474.
Jouini, A., Férid, M., Gacon, J. C., Grosvalet, L., Thozet, A. & Trabelsi-Ayadi, M. (2003). *Mater. Res. Bull.* **38**, 1613–1622.
Jouini, A., Férid, M., Gacon, J. C. & Trabelsi-Ayadi, M. (2003). *Opt. Mater.* **24**, 175–180.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Ternane, R., Férid, M., Panczer, G., Trabelsi-Ayadi, M. & Boulon, G. (2005). *Opt. Mater.* **27**, 1832–1838.
Yuan, J. L., Zhang, H., Zhao, J. T., Chen, H. H., Yang, X. X. & Zhang, G. B. (2008). *Opt. Mater.* **30**, 1369–1374.

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A new polymorph of $Lu(PO_3)_3$

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S1. Comment

There is considerable scientific and technological interest in the synthesis, structure, and properties of yttrium and rare earth polyphosphates of the formula $Ln(PO_3)_3$, because these compounds offer thermal stability and richness of formulations and structures (Briche *et al.*, 2006, Jouini, Férid, Gacon, Grosvalet *et al.*, 2003, Jouini, Férid, Gacon & Trabelsi-Ayadi, 2003, Ternane *et al.*, 2005, Graia *et al.*, 2003). In this paper, we report the preparation and crystal structure refinement of the polyphosphate $Lu(PO_3)_3$, crystallizing in space group *R*-3 . The existence of the trigonal polymorph was originally reported by Anisimova for the $Yb(PO_3)_3$ polyphosphate (Anisimova *et al.*, 1992). The monoclinic polymorph of $Lu(PO_3)_3$ was recently reported by Höppe and Yuan (Höppe & Sedlmaier, 2007, Yuan *et al.*, 2008). The atomic arrangement of these structures is characterized by a three-dimensional framework built of $(PO_3)_n$ chains that are formed by corner-sharing of PO_4 tetrahedra. These two polymorphs differ by the polyphosphate chains configuration. The chains that were observed in monoclinic $Lu(PO_3)_3$ form infinite zigzag chains $(PO_3)_n$ that extend along *c* with a period of six tetrahedra. In trigonal $Lu(PO_3)_3$, the $(PO_3)_n$ chains are helical with a period of 12 tetrahedra (Fig.1) and are arranged about the 3_1 helical axis. The chains are joined to each other by LuO_6 octahedra (Fig 2.), no oxygen atom is shared between adjacent LuO_6 octahedra. Figure 3 shows the projection of $Lu(PO_3)_3$ with anisotropic displacement parameters drawn at the 50% probability level.

S2. Experimental

Single crystals of $Lu(PO_3)_3$ were grown by a flux method. Lutetium oxide was dissolved in an excess of phosphoric acid using the molar ratio Lu:*P* = 1:20. The resulting solution was heated in a vitreous graphite crucible at 573 K for 5 days. The obtained colourless crystals were then isolated from the acid solution using hot water.

S3. Refinement

The highest peak and the deepest hole are located 0.75Å and 0.57 Å, respectively from O10 and Lu3.

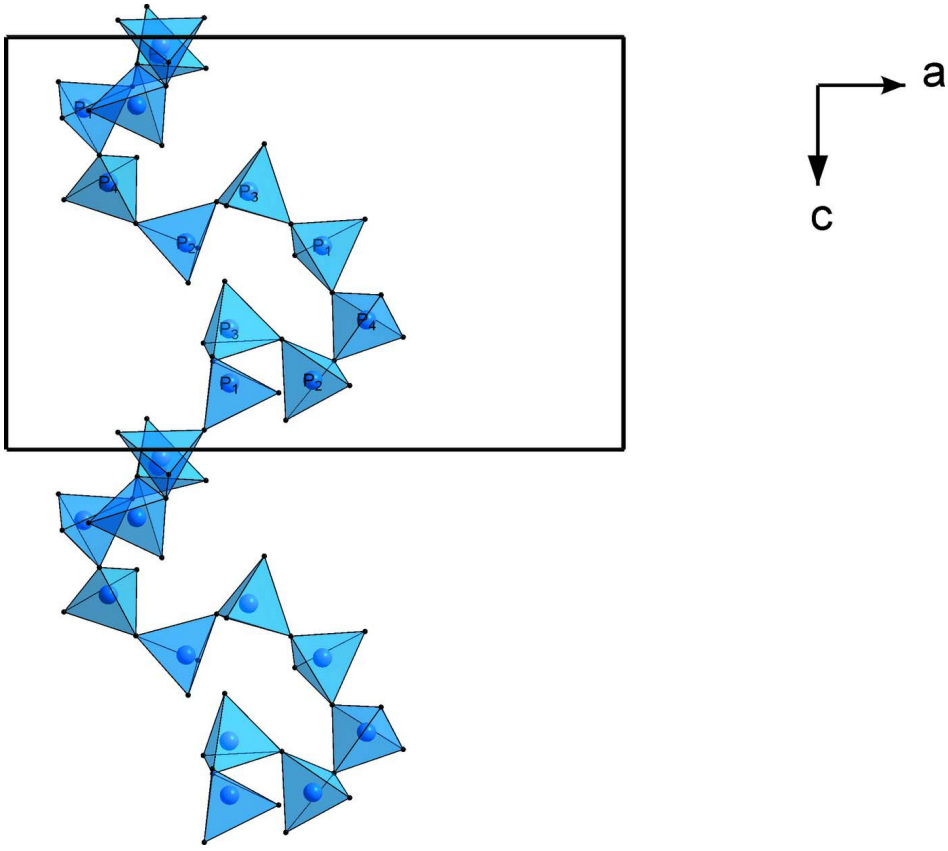

Figure 1

A projection of the helical $(PO_3)_n$ chains along b.

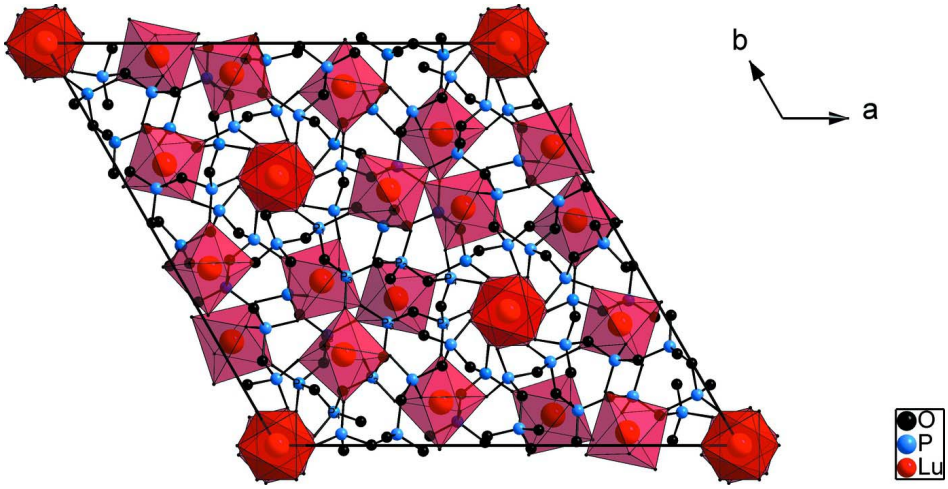

Figure 2

A projection of $Lu(PO_3)_3$ along *c*, showing the arrangement of the LuO_6 octahedra and PO_4 tetrahedra.

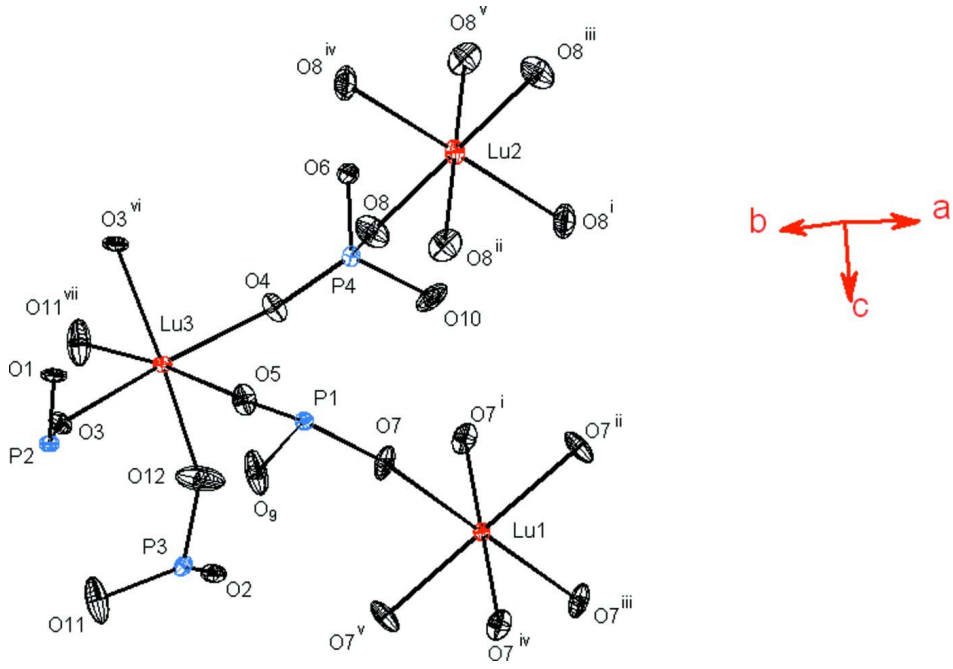

Figure 3

Projection of the $Lu(PO_3)_3$ polyphosphate, showing the lutetium coordination with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes : (i) -y, x-y, z; (ii) -x+y, -x, z; (iii)-x+1/3, -y+2/3, -z+2/3; (iv) y+1/3, -x+y+2/3, -z+2/3; (v) x-y+1/3, x+2/3, -z+2/3; (vi) -x, -y, -z; (vii) -x+y+1/3, -x+2/3, z+2/3.]

lutetium polyphosphate

Crystal data

$Lu(PO_3)_3$
$M_r = 411.88$
Trigonal, $R\overline{3}$
Hall symbol: -R 3
$a = 20.9106\ (6)$ Å
$c = 12.0859\ (7)$ Å
$V = 4576.6\ (3)$ Å^3
$Z = 24$
$F(000) = 4512$
$D_x = 3.587$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 2.8–34.1°$
$\mu = 13.59$ mm^{-1}
$T = 100$ K
Cube, colourless
0.18 × 0.18 × 0.17 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.102$, $T_{max} = 0.104$
25139 measured reflections
4170 independent reflections
3609 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 34.2°$, $\theta_{min} = 2.0°$
$h = -32\rightarrow32$
$k = -32\rightarrow32$
$l = -18\rightarrow18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.061$
$S = 1.05$
4170 reflections
159 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0212P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 2.34$ e Å^{-3}
$\Delta\rho_{min} = -2.07$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.000061 (8)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Lu1	0.6667	0.3333	0.3333	0.00741 (8)
Lu2	0.6667	0.3333	−0.1667	0.01207 (9)
Lu3	0.440661 (9)	0.365196 (10)	0.096806 (14)	0.00780 (5)
P1	0.63820 (6)	0.45920 (6)	0.16119 (9)	0.00821 (19)
P2	0.50313 (6)	0.54494 (6)	0.16810 (9)	0.0096 (2)
P3	0.39267 (6)	0.30556 (6)	0.37383 (10)	0.0111 (2)
P4	0.50120 (6)	0.25039 (6)	−0.01904 (10)	0.0107 (2)
O1	0.44368 (17)	0.46669 (17)	0.1552 (3)	0.0132 (6)
O2	0.34108 (18)	0.22020 (17)	0.3991 (3)	0.0132 (6)
O3	0.54706 (18)	0.58558 (18)	0.0709 (3)	0.0141 (6)
O4	0.45503 (18)	0.27392 (18)	0.0416 (3)	0.0168 (7)
O5	0.55847 (17)	0.42399 (18)	0.1374 (3)	0.0175 (7)
O6	0.45659 (17)	0.19780 (19)	−0.1185 (3)	0.0155 (7)
O7	0.66627 (18)	0.41823 (18)	0.2253 (3)	0.0190 (7)
O8	0.57293 (19)	0.3097 (2)	−0.0609 (3)	0.0247 (8)
O9	0.6655 (2)	0.5377 (2)	0.2137 (4)	0.0351 (11)
O10	0.5156 (2)	0.1948 (2)	0.0471 (3)	0.0315 (10)
O11	0.3569 (2)	0.3473 (2)	0.4088 (4)	0.0298 (9)
O12	0.4182 (3)	0.3127 (2)	0.2586 (3)	0.0364 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Lu1	0.00684 (11)	0.00684 (11)	0.00854 (19)	0.00342 (6)	0.000	0.000
Lu2	0.01014 (13)	0.01014 (13)	0.0159 (2)	0.00507 (6)	0.000	0.000

Lu3	0.00810 (8)	0.00796 (8)	0.00662 (8)	0.00347 (7)	0.00035 (6)	0.00000 (6)
P1	0.0086 (5)	0.0070 (5)	0.0084 (5)	0.0034 (4)	−0.0005 (4)	−0.0006 (4)
P2	0.0133 (5)	0.0095 (5)	0.0072 (5)	0.0065 (4)	−0.0008 (4)	−0.0007 (4)
P3	0.0150 (5)	0.0121 (5)	0.0095 (5)	0.0093 (4)	0.0006 (4)	0.0032 (4)
P4	0.0115 (5)	0.0132 (5)	0.0106 (5)	0.0084 (4)	−0.0009 (4)	0.0000 (4)
O1	0.0157 (15)	0.0117 (14)	0.0132 (15)	0.0076 (13)	0.0006 (12)	−0.0027 (12)
O2	0.0192 (16)	0.0124 (15)	0.0079 (14)	0.0077 (13)	0.0020 (12)	0.0008 (11)
O3	0.0216 (17)	0.0164 (16)	0.0055 (14)	0.0104 (14)	0.0015 (12)	−0.0001 (12)
O4	0.0141 (16)	0.0152 (16)	0.0215 (18)	0.0076 (13)	0.0028 (13)	−0.0036 (13)
O5	0.0089 (14)	0.0147 (16)	0.0269 (19)	0.0044 (13)	−0.0040 (13)	−0.0065 (14)
O6	0.0120 (15)	0.0265 (18)	0.0117 (15)	0.0125 (14)	−0.0042 (12)	−0.0051 (13)
O7	0.0154 (16)	0.0188 (17)	0.0264 (19)	0.0110 (14)	0.0048 (14)	0.0145 (14)
O8	0.0126 (16)	0.027 (2)	0.028 (2)	0.0050 (15)	0.0040 (14)	−0.0063 (16)
O9	0.023 (2)	0.030 (2)	0.060 (3)	0.0199 (18)	−0.019 (2)	−0.030 (2)
O10	0.063 (3)	0.025 (2)	0.021 (2)	0.033 (2)	−0.0207 (19)	−0.0072 (16)
O11	0.0202 (19)	0.0148 (17)	0.058 (3)	0.0114 (15)	0.0067 (18)	−0.0006 (18)
O12	0.063 (3)	0.022 (2)	0.0141 (19)	0.014 (2)	0.0127 (19)	0.0068 (15)

Geometric parameters (Å, º)

Lu1—O7^{i}	2.207 (3)	Lu3—O3^{x}	2.229 (3)
Lu1—O7^{ii}	2.207 (3)	P1—O5	1.475 (3)
Lu1—O7^{iii}	2.207 (3)	P1—O7	1.477 (3)
Lu1—O7^{iv}	2.207 (3)	P1—O10^{iii}	1.569 (4)
Lu1—O7	2.207 (3)	P1—O9	1.578 (4)
Lu1—O7^{v}	2.207 (3)	P2—O3	1.472 (3)
Lu2—O8^{vi}	2.180 (3)	P2—O1	1.488 (3)
Lu2—O8^{iv}	2.180 (3)	P2—O6^{xi}	1.585 (3)
Lu2—O8^{iii}	2.180 (3)	P2—O2^{ii}	1.593 (3)
Lu2—O8	2.180 (3)	P3—O11	1.467 (4)
Lu2—O8^{vii}	2.180 (3)	P3—O12	1.472 (4)
Lu2—O8^{viii}	2.180 (3)	P3—O9^{i}	1.573 (4)
Lu3—O11^{ix}	2.134 (3)	P3—O2	1.587 (3)
Lu3—O12	2.176 (4)	P4—O8	1.478 (4)
Lu3—O4	2.180 (3)	P4—O4	1.478 (3)
Lu3—O5	2.189 (3)	P4—O10	1.560 (4)
Lu3—O1	2.207 (3)	P4—O6	1.581 (3)
O7^{i}—Lu1—O7^{ii}	88.57 (14)	O4—Lu3—O5	87.21 (12)
O7^{i}—Lu1—O7^{iii}	180.0	O11^{ix}—Lu3—O1	91.99 (13)
O7^{ii}—Lu1—O7^{iii}	91.43 (14)	O12—Lu3—O1	95.32 (14)
O7^{i}—Lu1—O7^{iv}	91.43 (14)	O4—Lu3—O1	171.70 (12)
O7^{ii}—Lu1—O7^{iv}	180.0	O5—Lu3—O1	84.56 (12)
O7^{iii}—Lu1—O7^{iv}	88.57 (14)	O11^{ix}—Lu3—O3^{x}	88.69 (15)
O7^{i}—Lu1—O7	91.43 (14)	O12—Lu3—O3^{x}	174.96 (15)
O7^{ii}—Lu1—O7	91.43 (14)	O4—Lu3—O3^{x}	95.25 (12)
O7^{iii}—Lu1—O7	88.57 (14)	O5—Lu3—O3^{x}	96.14 (13)
O7^{iv}—Lu1—O7	88.57 (14)	O1—Lu3—O3^{x}	84.56 (12)

O7^{i}—Lu1—O7^{v}	88.57 (14)	O5—P1—O7	119.4 (2)
O7^{ii}—Lu1—O7^{v}	88.57 (14)	O5—P1—O10^{iii}	106.7 (2)
O7^{iii}—Lu1—O7^{v}	91.43 (14)	O7—P1—O10^{iii}	110.3 (2)
O7^{iv}—Lu1—O7^{v}	91.43 (14)	O5—P1—O9	109.15 (19)
O7—Lu1—O7^{v}	180.0	O7—P1—O9	110.6 (2)
O8^{vi}—Lu2—O8^{iv}	180.0	O10^{iii}—P1—O9	98.7 (3)
O8^{vi}—Lu2—O8^{iii}	90.92 (15)	O3—P2—O1	119.23 (19)
O8^{iv}—Lu2—O8^{iii}	89.08 (15)	O3—P2—O6^{xi}	105.71 (18)
O8^{vi}—Lu2—O8	90.92 (15)	O1—P2—O6^{xi}	109.44 (19)
O8^{iv}—Lu2—O8	89.08 (15)	O3—P2—O2^{ii}	112.19 (18)
O8^{iii}—Lu2—O8	89.08 (15)	O1—P2—O2^{ii}	106.01 (18)
O8^{vi}—Lu2—O8^{vii}	89.08 (15)	O6^{xi}—P2—O2^{ii}	103.12 (18)
O8^{iv}—Lu2—O8^{vii}	90.92 (15)	O11—P3—O12	118.6 (3)
O8^{iii}—Lu2—O8^{vii}	180.0	O11—P3—O9^{i}	105.0 (2)
O8—Lu2—O8^{vii}	90.92 (15)	O12—P3—O9^{i}	108.6 (3)
O8^{vi}—Lu2—O8^{viii}	89.08 (15)	O11—P3—O2	110.6 (2)
O8^{iv}—Lu2—O8^{viii}	90.92 (15)	O12—P3—O2	107.7 (2)
O8^{iii}—Lu2—O8^{viii}	90.92 (15)	O9^{i}—P3—O2	105.49 (19)
O8—Lu2—O8^{viii}	180.0	O8—P4—O4	116.6 (2)
O8^{vii}—Lu2—O8^{viii}	89.08 (15)	O8—P4—O10	107.9 (2)
O11^{ix}—Lu3—O12	86.28 (18)	O4—P4—O10	113.3 (2)
O11^{ix}—Lu3—O4	96.31 (13)	O8—P4—O6	108.8 (2)
O12—Lu3—O4	85.59 (14)	O4—P4—O6	110.62 (18)
O11^{ix}—Lu3—O5	173.76 (15)	O10—P4—O6	97.91 (19)
O12—Lu3—O5	88.86 (16)		

Symmetry codes: (i) $x-y+1/3, x-1/3, -z+2/3$; (ii) $y+1/3, -x+y+2/3, -z+2/3$; (iii) $-x+y+1, -x+1, z$; (iv) $-y+1, x-y, z$; (v) $-x+4/3, -y+2/3, -z+2/3$; (vi) $y+1/3, -x+y+2/3, -z-1/3$; (vii) $x-y+1/3, x-1/3, -z-1/3$; (viii) $-x+4/3, -y+2/3, -z-1/3$; (ix) $-x+y+1/3, -x+2/3, z-1/3$; (x) $-x+1, -y+1, -z$; (xi) $-y+2/3, x-y+1/3, z+1/3$.