

Lutetium(III) cyclotetraphosphate

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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{Lu}-\text{O}) = 0.003$ Å;

R factor = 0.020; wR factor = 0.038; data-to-parameter ratio = 17.5.

Single crystals of the title compound, tetralutetium(III) tris(cyclotetraphosphate), $\text{Lu}_4(\text{P}_4\text{O}_{12})_3$, were obtained by solid-state reaction. The cubic structure is isotypic with its Al^{III} and Sc^{III} analogues and is built up from four-membered $(\text{P}_4\text{O}_{12})^{4-}$ phosphate ring anions ($\bar{4}$ symmetry), isolated from each other and further linked through isolated LuO_6 octahedra (.3. symmetry) *via* corner sharing. Each LuO_6 octahedron is linked to six $(\text{P}_4\text{O}_{12})^{4-}$ rings, while each $(\text{P}_4\text{O}_{12})^{4-}$ ring is linked to eight LuO_6 octahedra.

Related literature

The title compound belongs to a structural type discovered a long time ago through the $\text{Al}_4(\text{P}_4\text{O}_{12})_3$ member, the structure of which was first investigated by Hendricks & Wyckoff (1927) and then described by Pauling & Sherman (1937). Since then, five isotypic compounds have been characterized: $\text{Cr}_4(\text{P}_4\text{O}_{12})_3$ (Rémy & Boullé, 1964); $\text{Ti}_4(\text{P}_4\text{O}_{12})_3$ (Liebau & Williams, 1964); $\text{Fe}_4(\text{P}_4\text{O}_{12})_3$ (d'Yvoire *et al.*, 1962); $\text{Sc}_4(\text{P}_4\text{O}_{12})_3$ (Bagieu-Beucher, 1976; Mezentseva *et al.*, 1977; Bagieu-Beucher & Guitel, 1978; Smolin *et al.* 1978) and $\text{Yb}_4(\text{P}_4\text{O}_{12})_3$ (Chudinova, 1979). For a review of the crystal chemistry of cyclotetraphosphates, see: Durif (1995). For other polymorphs of composition $\text{Lu}(\text{PO}_3)_3$, see: Höpfe & Sedlmaier (2007); Yuan *et al.* (2008); Bejaoui *et al.* (2008).

Experimental

Crystal data

$\text{Lu}_4(\text{P}_4\text{O}_{12})_3$	$Z = 4$
$M_r = 1647.52$	Mo $K\alpha$ radiation
Cubic, $I\bar{4}3d$	$\mu = 13.08$ mm ⁻¹
$a = 14.6920$ (6) Å	$T = 296$ K
$V = 3171.3$ (2) Å ³	$0.18 \times 0.10 \times 0.08$ mm

Data collection

Bruker APEXII CCD diffractometer	3088 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2008)	717 independent reflections
$T_{\text{min}} = 0.534$, $T_{\text{max}} = 0.746$	659 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$	$\Delta\rho_{\text{max}} = 0.90$ e Å ⁻³
$wR(F^2) = 0.038$	$\Delta\rho_{\text{min}} = -0.67$ e Å ⁻³
$S = 1.03$	Absolute structure: Flack (1983),
717 reflections	272 Friedel pairs
41 parameters	Flack parameter: 0.000 (15)

Table 1

Selected bond lengths (Å).

Lu—O ³ⁱ	2.182 (3)	Lu—O2	2.185 (4)
Lu—O ³ⁱⁱ	2.182 (3)	P—O ²ⁱⁱⁱ	1.464 (4)
Lu—O3	2.182 (3)	P—O3	1.481 (4)
Lu—O ²ⁱ	2.185 (4)	P—O ^{1iv}	1.583 (3)
Lu—O ²ⁱⁱ	2.185 (4)	P—O1	1.594 (3)

Symmetry codes: (i) $-z + 1, x - \frac{1}{2}, -y + \frac{1}{2}$; (ii) $y + \frac{1}{2}, -z + \frac{1}{2}, -x + 1$; (iii) $-z + 1, -x + \frac{3}{2}, y$; (iv) $-y + \frac{5}{4}, x - \frac{3}{4}, -z + \frac{3}{4}$.

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* (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: WM2342).

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Comment

The title compound is the third polymorph of composition $\text{Lu}(\text{PO}_3)_3$ besides the monoclinic form described by Höpfe & Sedlmaier (2007) and Yuan *et al.* (2008) and the trigonal form more recently reported by Bejaoui *et al.* (2008). The title compound is also the less dense polymorph with a calculated density of 3.451 Mg m^{-3} versus 3.587 Mg m^{-3} for the trigonal and 3.708 Mg m^{-3} for the monoclinic form and is probably the highest temperature form. This cyclotetraphosphate belongs to a structural type (cubic, with space group $I\bar{4}3d$) known since 1927 through the archetype $\text{Al}_4(\text{P}_4\text{O}_{12})_3$ determined by Hendricks & Wyckoff (1927). Then Pauling & Sherman (1937) gave the first description of the structure and reported roughly estimated atomic coordinates deduced from geometrical considerations. Since this time only five members of this family, viz. $\text{Cr}_4^{\text{III}}(\text{P}_4\text{O}_{12})_3$ (Rémy & Boullé, 1964), $\text{Ti}_4^{\text{III}}(\text{P}_4\text{O}_{12})_3$ (Liebau & Williams, 1964), $\text{Fe}_4^{\text{III}}(\text{P}_4\text{O}_{12})_3$ (d'Yvoire *et al.*, 1962), $\text{Sc}_4^{\text{III}}(\text{P}_4\text{O}_{12})_3$ (Bagieu-Beucher, 1976; Mezentseva *et al.*, 1977 and Smolin *et al.*, 1978) and $\text{Yb}_4^{\text{III}}(\text{P}_4\text{O}_{12})_3$ (Chudinova, 1979), have been identified. Corresponding unit cell parameters are listed in Durif (1995). Among these isotypic compounds only the structure of the $\text{Sc}_4(\text{P}_4\text{O}_{12})_3$ cyclotetraphosphate has almost simultaneously been refined from single-crystal data by Bagieu-Beucher & Guittel (1978) and Smolin *et al.* (1978). Their refinements confirmed the description of Pauling & Sherman (1937) according to which all the crystallographically independent atoms except the A^{III} element (.3. symmetry) are in general positions. The structure is built of four-membered phosphate ring anions $(\text{P}_4\text{O}_{12})^{4-}$ (Fig. 1), isolated from each other and further linked by LuO_6 octahedra by sharing corners. Each LuO_6 octahedron is linked to six $(\text{P}_4\text{O}_{12})^{4-}$ rings (Fig. 2a) while each $(\text{P}_4\text{O}_{12})^{4-}$ ring is linked to eight LuO_6 octahedra (Fig. 2b) through oxygen atoms with shorter P—O distances (1.464 (4) and 1.481 (4) Å). The $(\text{P}_4\text{O}_{12})^{4-}$ ring anions are located around the 12a Wyckoff positions of space group $I\bar{4}3d$ and exhibit $\bar{4}$ symmetry. Comparison of the $(\text{P}_4\text{O}_{12})^{4-}$ ring anions in both $\text{Sc}_4(\text{P}_4\text{O}_{12})_3$ and $\text{Lu}_4(\text{P}_4\text{O}_{12})_3$ structures shows these two ring anions being geometrically quite identical with alternating upward- and downward-pointing tetrahedra and P—O—P angles of 137.1° and $136.9(2)^\circ$, respectively. The P—O distances in the PO_4 groups are identical within their e.s.d.. The four bridging oxygen atoms of these ring anions are located at the apices of a flattened tetrahedron with characteristic angles of 148.22° and 94.30° for Sc and 147.95° and 94.37° for the Lu cyclotetraphosphate. The LuO_6 octahedron is very slightly distorted along a threefold axis, resulting in two sets of Lu—O distances equal to 2.182 (3) and 2.185 (4) Å, respectively.

Experimental

Single crystals of the title compound were obtained by solid state reaction while attempting to synthesized a long chain polyphosphate by reacting Lu_2O_3 with $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ and Rb_2CO_3 in an alumina boat. A mixture of these reagents in the molar ratio 27 : 85.5 : 8.7 was used for the synthesis. The mixture was successively heated at 473 K for 24 hours, then at 573 K for 24 additional hours and finally at 813 K for 24 hours. Then the sample was cooled down to 683 K at the rate of 3 K h^{-1} and maintained at this temperature for 36 hours. Finally, the sample was cooled down to room temperature by shutting the

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muffle furnace off. Single crystals were extracted from the batch by washing with hot water and filtering. The crystals were dried at 353 K in an oven. A translucent octahedral crystal of the title compound was selected for the structure refinement.

Refinement

The highest residual peak in the final difference Fourier map was located 0.87 Å from atom Lu and the deepest hole was located 0.99 Å from atom Lu.

Figures

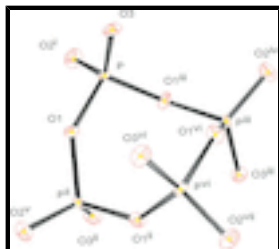


Fig. 1. ORTEP-3 view of the four-membered phosphate (P_4O_{12})⁴⁻ ring anion. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) 1-z, 3/2-x, y ; (ii) 3/4+y, 5/4-x, 3/4-z ; (iii) 5/4-y, -3/4+x, 3/4-z ; (iv) -1/4+x, 1/4-z, 3/4-y ; (v) 9/4-x, 1/4+z, 3/4-y ; (vi) 2-x, 1/2-y, z ; (vii) 1+z, -1+x, y.

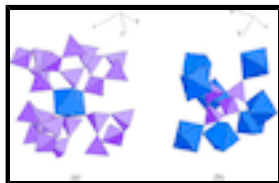


Fig. 2. Partial view of the $\text{Lu}_4(\text{P}_4\text{O}_{12})_3$ structure showing: (a) the connections between the LuO_6 octahedron and the (P_4O_{12})⁴⁻ ring anions, (b) the connections between the (P_4O_{12})⁴⁻ ring anion and the LuO_6 octahedra.

Tetralutetium(III) tris(cyclotetraphosphate)

Crystal data

$\text{Lu}_4(\text{P}_4\text{O}_{12})_3$

$M_r = 1647.52$

Cubic, $\bar{I}43d$

Hall symbol: I -4bd 2c 3

$a = 14.6920$ (6) Å

$V = 3171.3$ (2) Å³

$Z = 4$

$F(000) = 3008$

$D_x = 3.451$ Mg m⁻³

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

Cell parameters from 1548 reflections

$\theta = 3.4\text{--}30.3^\circ$

$\mu = 13.08$ mm⁻¹

$T = 296$ K

Truncated octahedron, colourless

$0.18 \times 0.10 \times 0.08$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

Detector resolution: 8.3333 pixels mm⁻¹

ϕ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2008)

$T_{\min} = 0.534$, $T_{\max} = 0.746$

717 independent reflections

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

$R_{\text{int}} = 0.034$

$\theta_{\max} = 30.4^\circ$, $\theta_{\min} = 3.9^\circ$

$h = -16 \rightarrow 11$

$k = -6 \rightarrow 20$

$l = -19 \rightarrow 9$

3088 measured reflections

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.020$

$wR(F^2) = 0.038$

$S = 1.03$

717 reflections

41 parameters

0 restraints

0 constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

$w = 1/[\sigma^2(F_o^2) + (0.0088P)^2]$

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

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

$\Delta\rho_{\max} = 0.90 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.67 \text{ e } \text{Å}^{-3}$

Absolute structure: Flack (1983), 272 Friedel pairs

Flack parameter: 0.000 (15)

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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Lu	0.896610 (13)	0.396610 (13)	0.103390 (13)	0.00602 (8)
P	0.95737 (9)	0.37294 (9)	0.33447 (9)	0.0077 (2)
O1	1.0613 (2)	0.3432 (2)	0.3430 (2)	0.0128 (7)
O2	1.0325 (2)	0.3642 (3)	0.0522 (2)	0.0188 (8)
O3	0.9295 (2)	0.3498 (3)	0.2404 (2)	0.0142 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Lu	0.00602 (8)	0.00602 (8)	0.00602 (8)	0.00039 (8)	-0.00039 (8)	-0.00039 (8)
P	0.0097 (5)	0.0051 (6)	0.0082 (6)	0.0017 (5)	-0.0008 (5)	0.0015 (4)
O1	0.0113 (15)	0.0146 (18)	0.0123 (17)	0.0007 (15)	-0.0025 (14)	0.0054 (17)
O2	0.0103 (17)	0.024 (2)	0.022 (2)	0.0016 (18)	0.0015 (16)	-0.0014 (18)
O3	0.0202 (19)	0.0141 (19)	0.0084 (16)	0.0012 (16)	-0.0050 (15)	0.0023 (16)

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Geometric parameters (Å, °)

Lu—O3 ⁱ	2.182 (3)	P—O2 ⁱⁱⁱ	1.464 (4)
Lu—O3 ⁱⁱ	2.182 (3)	P—O3	1.481 (4)
Lu—O3	2.182 (3)	P—O1 ^{iv}	1.583 (3)
Lu—O2 ⁱ	2.185 (4)	P—O1	1.594 (3)
Lu—O2 ⁱⁱ	2.185 (4)	O1—P ^v	1.583 (3)
Lu—O2	2.185 (4)	O2—P ^{vi}	1.464 (4)
O3 ⁱ —Lu—O3 ⁱⁱ	89.06 (14)	O3—Lu—O2	92.64 (13)
O3 ⁱ —Lu—O3	89.06 (14)	O2 ⁱ —Lu—O2	87.72 (15)
O3 ⁱⁱ —Lu—O3	89.06 (14)	O2 ⁱⁱ —Lu—O2	87.72 (15)
O3 ⁱ —Lu—O2 ⁱ	92.64 (13)	O2 ⁱⁱⁱ —P—O3	118.0 (2)
O3 ⁱⁱ —Lu—O2 ⁱ	178.26 (14)	O2 ⁱⁱⁱ —P—O1 ^{iv}	107.3 (2)
O3—Lu—O2 ⁱ	90.59 (14)	O3—P—O1 ^{iv}	111.5 (2)
O3 ⁱ —Lu—O2 ⁱⁱ	90.59 (14)	O2 ⁱⁱⁱ —P—O1	109.2 (2)
O3 ⁱⁱ —Lu—O2 ⁱⁱ	92.64 (13)	O3—P—O1	106.0 (2)
O3—Lu—O2 ⁱⁱ	178.26 (14)	O1 ^{iv} —P—O1	103.9 (2)
O2 ⁱ —Lu—O2 ⁱⁱ	87.72 (15)	P ^v —O1—P	136.9 (2)
O3 ⁱ —Lu—O2	178.26 (14)	P ^{vi} —O2—Lu	164.9 (2)
O3 ⁱⁱ —Lu—O2	90.59 (14)	P—O3—Lu	148.2 (2)

Symmetry codes: (i) $-z+1, x-1/2, -y+1/2$; (ii) $y+1/2, -z+1/2, -x+1$; (iii) $-z+1, -x+3/2, y$; (iv) $-y+5/4, x-3/4, -z+3/4$; (v) $y+3/4, -x+5/4, -z+3/4$; (vi) $-y+3/2, z, -x+1$.

Fig. 1

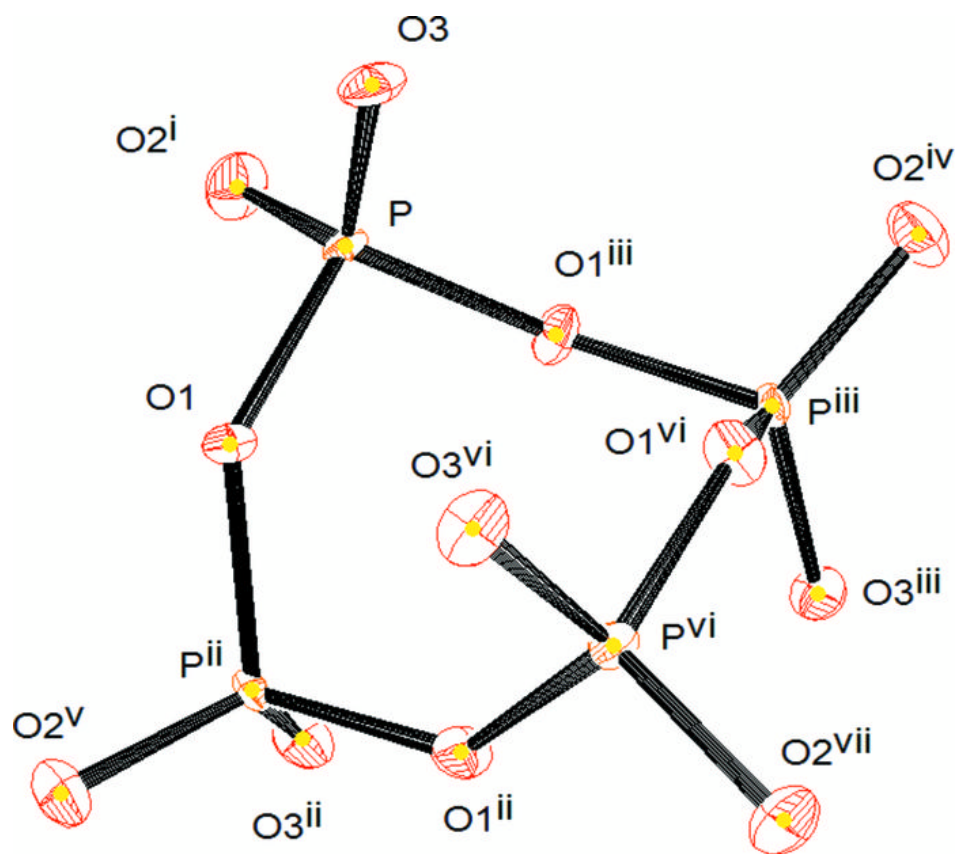


Fig. 2

