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An orthorhombic polymorph of cerium(III) ultraphosphate, CeP₅O₁₄Jing Zhu,^{a*} Wen-Dan Cheng^b and Hao Zhang^b

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{P}-\text{O}) = 0.007$ Å; R factor = 0.048; wR factor = 0.094; data-to-parameter ratio = 12.7.

Cerium(III) ultraphosphate, CeP₅O₁₄, was synthesized by a high-temperature solution reaction between CeO₂ and NH₄H₂PO₄ in a Ce–P molar ratio of 1:12. Colourless crystals of the orthorhombic polymorph were obtained by cooling the melt of the mixture. The structure contains (P₅O₁₄)³⁻ anionic ribbons linked by distorted CeO₈ polyhedra.

Related literature

For applications of rare-earth ultraphosphates, see: Cole *et al.* (2000); Katrusiak & Kaczmarek (1995); Kobayashi *et al.* (1976); Schulz *et al.* (1974). For a discussion of structure types in this chemical system, see: Averbuch-Pouchot & Durif (1992). For the triclinic polymorph of CeP₅O₁₄, see: Rzaigui *et al.* (1984).

Experimental

Crystal data

CeP ₅ O ₁₄	$V = 1047.97(18)$ Å ³
$M_r = 518.97$	$Z = 4$
Orthorhombic, $Pmna$	Mo $K\alpha$ radiation
$a = 13.1252(12)$ Å	$\mu = 5.19$ mm ⁻¹
$b = 8.7991(9)$ Å	$T = 293(2)$ K
$c = 9.0741(9)$ Å	$0.08 \times 0.08 \times 0.05$ mm

Data collection

Rigaku Mercury CCD diffractometer	7608 measured reflections
Absorption correction: multi-scan (<i>CrystalClear</i> ; Molecular Structure Corporation & Rigaku, 2001)	1262 independent reflections
$T_{\min} = 0.663$, $T_{\max} = 0.771$	1212 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.072$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	99 parameters
$wR(F^2) = 0.094$	$\Delta\rho_{\text{max}} = 1.70$ e Å ⁻³
$S = 1.00$	$\Delta\rho_{\text{min}} = -1.08$ e Å ⁻³
1262 reflections	

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 2005); 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: B12303).

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supplementary materials

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An orthorhombic polymorph of cerium(III) ultraphosphate, CeP₅O₁₄

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Comment

Rare-earth ultraphosphates, LnP₅O₁₄ (Ln = rare-earth element), have attracted wide interest because of their potential applications in the laser domain (Schulz *et al.*, 1974; Kobayashi *et al.*, 1976; Katrusiak & Kaczmarek, 1995; Cole *et al.*, 2000). These compounds can be generally classified into four structure types: monoclinic (*P2₁/a*), monoclinic (*C2/c*), orthorhombic (*Pnma*), and triclinic (*P1*) (Averbuch-Pouchot & Durif, 1992). In this chemical system, many of the compounds are isotypic, and some are polymorphic. However, many polymorphs of ultraphosphates LnP₅O₁₄ have not been realised to date. Herein, we present the synthesis and crystal structure of an orthorhombic polymorph of CeP₅O₁₄.

In the structure (Figs. 1 and 2), the Ce³⁺ cation plays an important bridging role, connecting neighbouring (P₅O₁₄)³⁻ anionic ribbons. The CeO₈ polyhedron is corner-sharing with eight PO₄ tetrahedra, with the Ce—O bond distances ranging from 2.436 (5) to 2.534 (8) Å. The shortest Ce—Ce distance is 5.2271 (9) Å. The (P₅O₁₄)³⁻ anionic ribbon may be described as two PO₄ infinite chains linked by P(2)O₄ tetrahedra, as shown in Fig. 3. P(1)O₄, P(3)O₄, and P(4)O₄ tetrahedra are corner-shared to form screwed infinite chains along the *b* axis. P(2)O₄ tetrahedra are corner-shared with two surrounding PO₄ infinite chains along the *a* axis. Thus, a (P₅O₁₄)³⁻ anionic ribbon is observed parallel to *b*.

Experimental

The title compound was prepared by a high-temperature solution reaction, using analytical reagent CeO₂ and NH₄H₂PO₄ in a molar ratio corresponding to Ce/P = 1:12. Starting mixtures were finely ground in an agate mortar to ensure optimal homogeneity and reactivity, then placed in a platinum crucible and heated at 373 K for 4 h. Afterwards, the mixtures were reground and heated to 973 K for 24 h. Finally, the temperature was cooled to 773 K at a rate of 2 K/h and air-quenched to room temperature. A few colourless, block-shaped crystals were obtained from the melt of the mixture.

Refinement

The position of the Ce atom was obtained using direct methods, and the remaining atoms were located in successive difference Fourier syntheses. The chemical composition of the single crystal was confirmed by energy-dispersive X-ray (EDX) analysis, and no impurity elements were detected.

Figures



Fig. 1. Asymmetric unit with displacement ellipsoids shown at 50% probability.

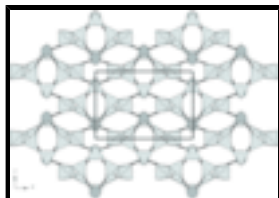


Fig. 2. Projection of the structure along the *b* axis. The tetrahedra represent PO₄ groups and the gray circles represent Ce³⁺ cations.



Fig. 3. (P₅O₁₄)³⁻ anionic ribbon running parallel to the *b* axis.

Cerium(III) ultraphosphate

Crystal data

CeP₅O₁₄

M_r = 518.97

Orthorhombic, *Pmna*

Hall symbol: -P 2ac 2

a = 13.1252 (12) Å

b = 8.7991 (9) Å

c = 9.0741 (9) Å

V = 1047.97 (18) Å³

Z = 4

*F*₀₀₀ = 980

D_x = 3.289 Mg m⁻³

Mo *Kα* radiation

λ = 0.71073 Å

Cell parameters from 2047 reflections

θ = 2.3–27.5°

μ = 5.19 mm⁻¹

T = 293 (2) K

Block, colourless

0.08 × 0.08 × 0.05 mm

Data collection

Rigaku Mercury CCD
diffractometer

1262 independent reflections

Radiation source: fine-focus sealed tube

1212 reflections with *I* > 2σ(*I*)

Monochromator: graphite

*R*_{int} = 0.072

T = 293(2) K

*θ*_{max} = 27.5°

ω scans

*θ*_{min} = 2.3°

Absorption correction: multi-scan

(CrystalClear; Molecular Structure Corporation & Rigaku, 2001)

h = -17→16

$T_{\min} = 0.663$, $T_{\max} = 0.771$
7608 measured reflections

$k = -11 \rightarrow 11$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

$$w = 1/[\sigma^2(F_o^2) + 37.6801P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$R[F^2 > 2\sigma(F^2)] = 0.048$$

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

$$wR(F^2) = 0.094$$

$$\Delta\rho_{\max} = 1.70 \text{ e } \text{\AA}^{-3}$$

$$S = 1.00$$

$$\Delta\rho_{\min} = -1.08 \text{ e } \text{\AA}^{-3}$$

1262 reflections

Extinction correction: SHELXL97 (Sheldrick, 2008),

$$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

99 parameters

Extinction coefficient: 0.0114 (15)

Primary atom site location: structure-invariant direct methods

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ce	0.5000	0.72337 (7)	0.68985 (6)	0.00797 (19)
P1	0.2936 (2)	0.5000	0.5000	0.0113 (6)
P2	0.0000	0.3121 (3)	0.7524 (3)	0.0091 (5)
P3	0.3233 (2)	0.0000	0.5000	0.0102 (5)
P4	0.16332 (14)	0.2351 (2)	0.54996 (19)	0.0098 (4)
O1	0.1129 (4)	0.2256 (7)	0.4081 (6)	0.0189 (12)
O2	0.3474 (4)	0.5859 (7)	0.6151 (6)	0.0182 (12)
O3	0.2451 (5)	0.1123 (8)	0.5815 (6)	0.0295 (16)
O4	0.0000	0.4655 (9)	0.6859 (9)	0.0155 (16)
O5	0.2151 (5)	0.3901 (7)	0.5849 (7)	0.0307 (17)
O6	0.3778 (4)	-0.0799 (6)	0.6175 (6)	0.0165 (12)
O7	0.0000	0.2893 (10)	0.9131 (8)	0.0176 (17)
O8	0.0934 (4)	0.2133 (6)	0.6876 (6)	0.0161 (11)

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ce	0.0074 (3)	0.0090 (3)	0.0075 (3)	0.000	0.000	0.0003 (2)
P1	0.0062 (11)	0.0135 (13)	0.0143 (13)	0.000	0.000	-0.0033 (11)
P2	0.0089 (12)	0.0120 (13)	0.0063 (11)	0.000	0.000	-0.0008 (10)
P3	0.0080 (11)	0.0124 (13)	0.0102 (12)	0.000	0.000	-0.0013 (10)
P4	0.0059 (8)	0.0152 (10)	0.0083 (8)	0.0002 (7)	0.0001 (6)	-0.0019 (7)
O1	0.021 (3)	0.023 (3)	0.013 (2)	0.006 (3)	-0.008 (2)	-0.001 (2)
O2	0.014 (3)	0.023 (3)	0.018 (3)	-0.006 (2)	-0.003 (2)	0.000 (2)
O3	0.029 (3)	0.050 (4)	0.010 (3)	0.028 (3)	0.001 (2)	-0.004 (3)
O4	0.019 (4)	0.012 (4)	0.016 (4)	0.000	0.000	-0.005 (3)
O5	0.034 (4)	0.031 (4)	0.027 (3)	-0.027 (3)	0.019 (3)	-0.015 (3)
O6	0.016 (3)	0.017 (3)	0.016 (3)	0.006 (2)	-0.002 (2)	0.001 (2)
O7	0.021 (4)	0.024 (4)	0.008 (3)	0.000	0.000	-0.002 (3)
O8	0.017 (3)	0.017 (3)	0.014 (2)	0.007 (2)	0.005 (2)	0.004 (2)

Geometric parameters (\AA , $^\circ$)

Ce—O2	2.436 (5)	P2—O8 ^{ix}	1.614 (5)
Ce—O2 ⁱ	2.436 (5)	P2—O8	1.614 (5)
Ce—O6 ⁱⁱ	2.449 (5)	P3—O6 ^x	1.464 (5)
Ce—O6 ⁱⁱⁱ	2.449 (5)	P3—O6	1.464 (5)
Ce—O7 ^{iv}	2.513 (7)	P3—O3 ^x	1.606 (6)
Ce—O1 ^v	2.514 (5)	P3—O3	1.606 (6)
Ce—O1 ^{vi}	2.514 (5)	P4—O1	1.450 (5)
Ce—O4 ^{vii}	2.534 (8)	P4—O3	1.549 (6)
P1—O2	1.470 (6)	P4—O5	1.557 (6)
P1—O2 ^{viii}	1.470 (6)	P4—O8	1.562 (5)
P1—O5 ^{viii}	1.609 (6)	O1—Ce ^{iv}	2.514 (5)
P1—O5	1.609 (6)	O4—Ce ^{xi}	2.534 (7)
P2—O7	1.472 (8)	O6—Ce ^{xii}	2.449 (5)
P2—O4	1.479 (8)	O7—Ce ^{vi}	2.513 (7)
O2—Ce—O2 ⁱ	110.6 (3)	O2 ^{viii} —P1—O5 ^{viii}	106.0 (3)
O2—Ce—O6 ⁱⁱ	144.55 (18)	O2—P1—O5	106.0 (3)
O2 ⁱ —Ce—O6 ⁱⁱ	74.82 (19)	O2 ^{viii} —P1—O5	109.8 (3)
O2—Ce—O6 ⁱⁱⁱ	74.82 (19)	O5 ^{viii} —P1—O5	100.4 (6)
O2 ⁱ —Ce—O6 ⁱⁱⁱ	144.55 (18)	O7—P2—O4	121.9 (5)
O6 ⁱⁱ —Ce—O6 ⁱⁱⁱ	81.8 (3)	O7—P2—O8 ^{ix}	106.7 (3)
O2—Ce—O7 ^{iv}	72.54 (17)	O4—P2—O8 ^{ix}	110.1 (3)
O2 ⁱ —Ce—O7 ^{iv}	72.54 (17)	O7—P2—O8	106.7 (3)
O6 ⁱⁱ —Ce—O7 ^{iv}	76.3 (2)	O4—P2—O8	110.1 (3)
O6 ⁱⁱⁱ —Ce—O7 ^{iv}	76.3 (2)	O8 ^{ix} —P2—O8	98.9 (4)

O2—Ce—O1 ^v	142.43 (19)	O6 ^x —P3—O6	121.5 (5)
O2 ⁱ —Ce—O1 ^v	79.83 (19)	O6 ^x —P3—O3 ^x	105.8 (3)
O6 ⁱⁱ —Ce—O1 ^v	72.48 (18)	O6—P3—O3 ^x	110.6 (3)
O6 ⁱⁱⁱ —Ce—O1 ^v	118.08 (19)	O6 ^x —P3—O3	110.6 (3)
O7 ^{iv} —Ce—O1 ^v	142.65 (14)	O6—P3—O3	105.8 (3)
O2—Ce—O1 ^{vi}	79.83 (19)	O3 ^x —P3—O3	100.5 (5)
O2 ⁱ —Ce—O1 ^{vi}	142.43 (19)	O1—P4—O3	116.1 (3)
O6 ⁱⁱ —Ce—O1 ^{vi}	118.08 (19)	O1—P4—O5	115.5 (4)
O6 ⁱⁱⁱ —Ce—O1 ^{vi}	72.48 (18)	O3—P4—O5	105.7 (4)
O7 ^{iv} —Ce—O1 ^{vi}	142.65 (14)	O1—P4—O8	115.8 (3)
O1 ^v —Ce—O1 ^{vi}	72.2 (3)	O3—P4—O8	100.0 (3)
O2—Ce—O4 ^{vii}	71.29 (16)	O5—P4—O8	101.6 (3)
O2 ⁱ —Ce—O4 ^{vii}	71.29 (16)	P4—O1—Ce ^{iv}	163.4 (4)
O6 ⁱⁱ —Ce—O4 ^{vii}	138.78 (13)	P1—O2—Ce	148.0 (4)
O6 ⁱⁱⁱ —Ce—O4 ^{vii}	138.78 (14)	P4—O3—P3	141.9 (4)
O7 ^{iv} —Ce—O4 ^{vii}	113.9 (3)	P2—O4—Ce ^{xi}	129.5 (5)
O1 ^v —Ce—O4 ^{vii}	79.0 (2)	P4—O5—P1	135.1 (4)
O1 ^{vi} —Ce—O4 ^{vii}	79.0 (2)	P3—O6—Ce ^{xii}	148.7 (3)
O2—P1—O2 ^{viii}	122.6 (5)	P2—O7—Ce ^{vi}	174.7 (6)
O2—P1—O5 ^{viii}	109.8 (3)	P4—O8—P2	132.2 (4)

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

Fig. 1

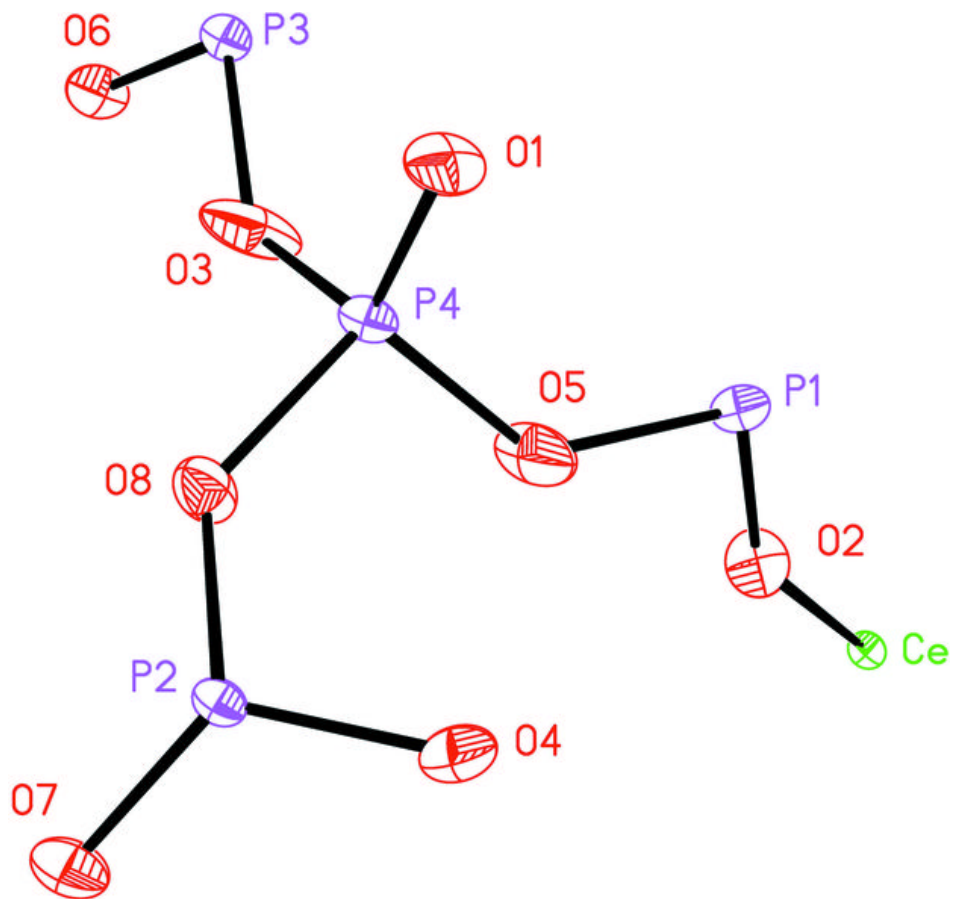


Fig. 2

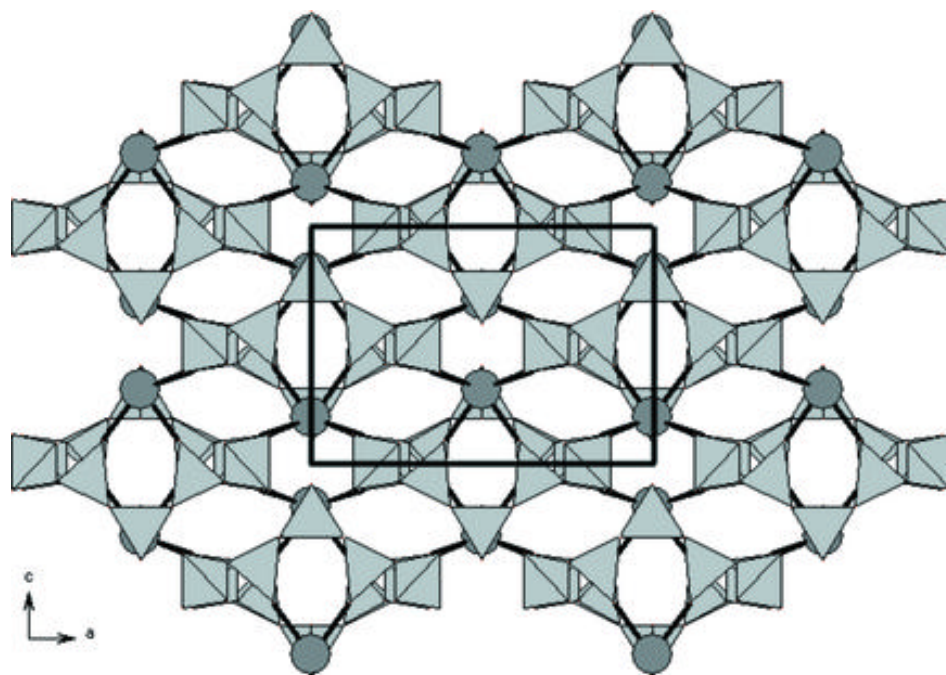


Fig. 3

