inorganic compounds

An orthorhombic polymorph of the ultraphosphate YP$_5$O$_{14}$

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Single crystals of yttrium pentaphosphate(V), YP$_5$O$_{14}$, were obtained by solid-state reaction. The orthorhombic title compound belongs to the family of ultraphosphates and is the second polymorph of this composition. It is isotypic with its Ho and Er analogues. The structure contains two bridging Q^2-type PO$_4$ tetrahedra and one branching Q^3-type PO$_4$ tetrahedron, leading to infinite ultraphosphate ribbons running along the a axis. The coordination polyhedron around the Y^{3+} cation may be described as distorted bicapped trigonal-prismatic. The YO$_8$ polyhedra are isolated from each other. They are linked by corner-sharing to the O atoms of six Q^2-type and of two Q^3-type PO$_4$ tetrahedra into a three-dimensional framework.

Related literature

Besides crystals of the title compound, crystals of the monoclinic polymorph were also obtained (Mbarek *et al.*, 2009). For isotypic structures, see: Durif (1972) for the Ho member; Katrusiak & Kaczmarek (1995) and Dimitrova *et al.* (2004) for the Er member. For a review of the crystal chemistry of ultraphosphates, see: Durif (1995). For applications of rare earth ultraphosphates, see: Rao & Devine (2000); Moine & Bizarri (2006). For general background, see: Porai-Koshits & Aslanov (1972).

Experimental

Crystal data

YP$_5$O$_{14}$
M_r = 467.76
Orthorhombic, $Pnma$
a = 8.7128 (2) Å
b = 12.7218 (4) Å
c = 8.9377 (3) Å
V = 990.68 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 6.79 mm^{-1}
T = 296 K
$0.22 \times 0.15 \times 0.11$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008a)
T_{min} = 0.330, T_{max} = 0.460
5338 measured reflections
1194 independent reflections
1136 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.110
S = 1.22
1194 reflections
97 parameters
$\Delta\rho_{max}$ = 1.60 e Å^{-3}
$\Delta\rho_{min}$ = −1.11 e Å^{-3}

Table 1
Selected bond lengths (Å).

Y1—O6	2.278 (3)	P1—O5	1.553 (3)
Y1—O6^i	2.278 (3)	P1—O7	1.567 (3)
Y1—O4^i	2.341 (3)	P2—O3^{iii}	1.460 (5)
Y1—O4	2.341 (3)	P2—O1	1.479 (5)
Y1—O8^i	2.391 (4)	P2—O2	1.623 (4)
Y1—O8	2.391 (4)	P2—O2^i	1.623 (4)
Y1—O1	2.455 (5)	P3—O4	1.467 (3)
Y1—O3	2.518 (5)	P3—O6^{iv}	1.468 (3)
P1—O8^{ii}	1.455 (4)	P3—O7^v	1.607 (3)
P1—O2	1.549 (4)	P3—O5^{vi}	1.611 (3)

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008b); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008b); molecular graphics: *CaRIne* (Boudias & Monceau, 1998); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008b).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2221).

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supporting information

An orthorhombic polymorph of the ultraphosphate YP_5O_{14}

Aïcha Mbarek, Abdelghani Oudahmane, Malika El-Ghozzi and Daniel Avignant

S1. Comment

Rare earths ultraphosphates exhibit a growing attention because of their potential applications as optical materials, including lasers, phosphors, matrices for the energy up-conversion and more recently for plasma display panels (PDP) as they exhibit an absorption band overlapping the emission spectrum of a Xe—Ne plasma in the VUV region (Rao & Devine, 2000; Moine & Bizarri, 2006). The non-optically active matrix of YP_5O_{14} can be used as host material for such applications and hence needs to be structurally well-characterized. This article deals with the crystal structure refinement of the orthorhombic polymorph that is isotypic with HoP_5O_{14} (Durif, 1972) and ErP_5O_{14} (Katrusiak & Kaczmarek, 1995; Dimitrova *et al.* 2004).

Two PO_4 tetrahedra are Q^2 type bridging tetrahedra with typical two shorter and two longer P—O bonds (Durif, 1995). The third PO_4 tetrahedron is a branching Q^3 type tetrahedron and exhibits also characteristic bond lengths ranging from 1.455 (4) to 1.567 (3) Å. These PO_4 groups form infinite ribbons with composition $(P_5O_{14})^{3-}$ which can be considered as built of two infinite $(PO_3)_n$ chains running along the *a* axis and connected by alternating up and down capping PO_4 tetrahedra (Figs. 1, 2). The repetition unit in these ribbons is $P_{10}O_{28}$.

The coordination polyhedron around the Y^{3+} cation is a distorted bicapped trigonal prism according to criteria defined by Porai-Koshits & Aslanov (1972) with ($\delta_1 = 0°$, $\delta_2 = 18.28°$, $\delta_3 = \delta_4 = 42.87°$; theoretical values $\delta_1 = 0°$, $\delta_2 = 21.7°$, $\delta_3 = \delta_4 = 48.2°$). The YO_8 polyhedra are isolated from each other. They are linked by corner-sharing to six Q^2 type PO_4 tetrahedra and to two Q^3 type tetrahedra leading to the three-dimensional framework.

S2. Experimental

Crystals of the title compounds were synthesized by reacting Y_2O_3 with $(NH_4)_2HPO_4$ in a graphite crucible. A mixture of these reagents in the molar ratio 1:9 was used for the synthesis. The mixture was first heated at 473 K for 12 h. Then the temperature was raised up to 673 K and was held for 2 days before cooling to room temperature at a rate of 10 K/h. Single-crystals were extracted from the batch by washing with hot water. Besides crystals of the title compound, crystals of the monoclinic polymorph were also obtained (Mbarek *et al.*, 2009).

S3. Refinement

The highest residual peak in the final difference Fourier maps was located 0.26 Å from atom Y1 and the deepest hole was located 0.44 Å from atom P2.
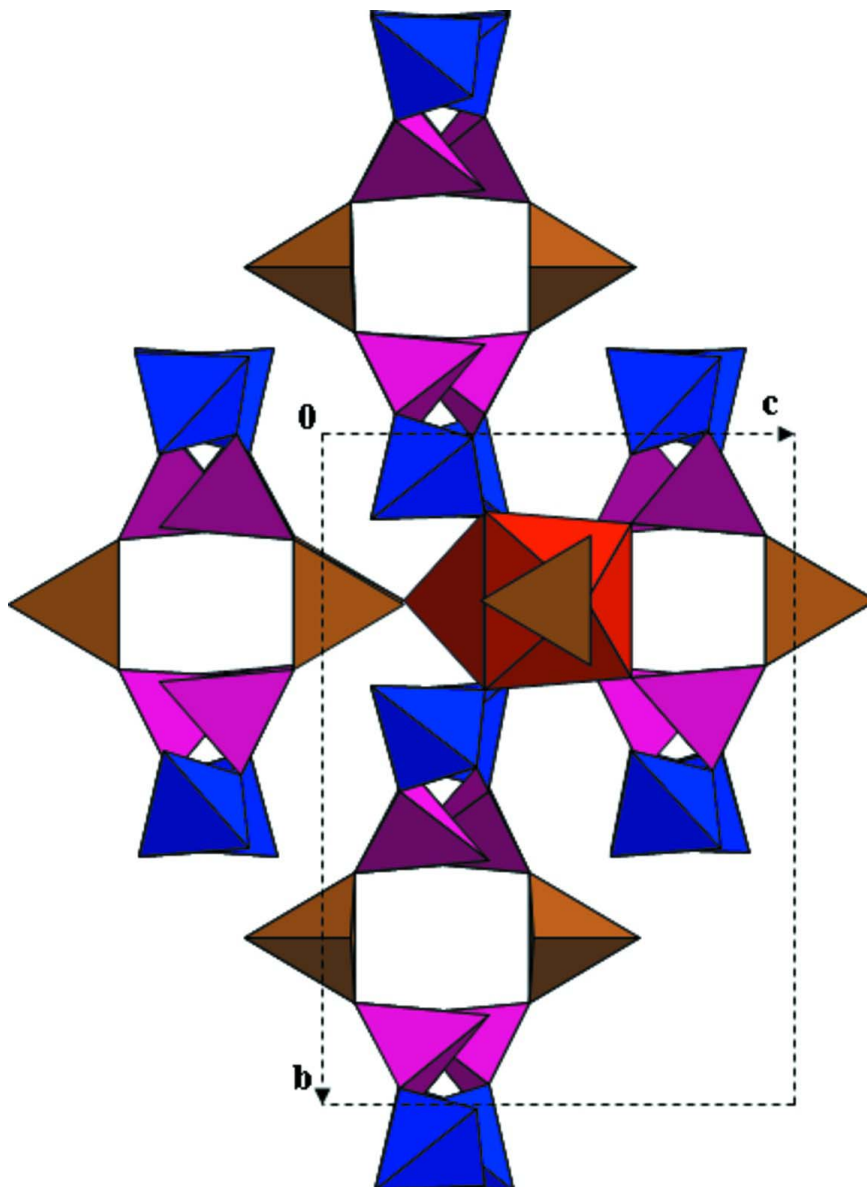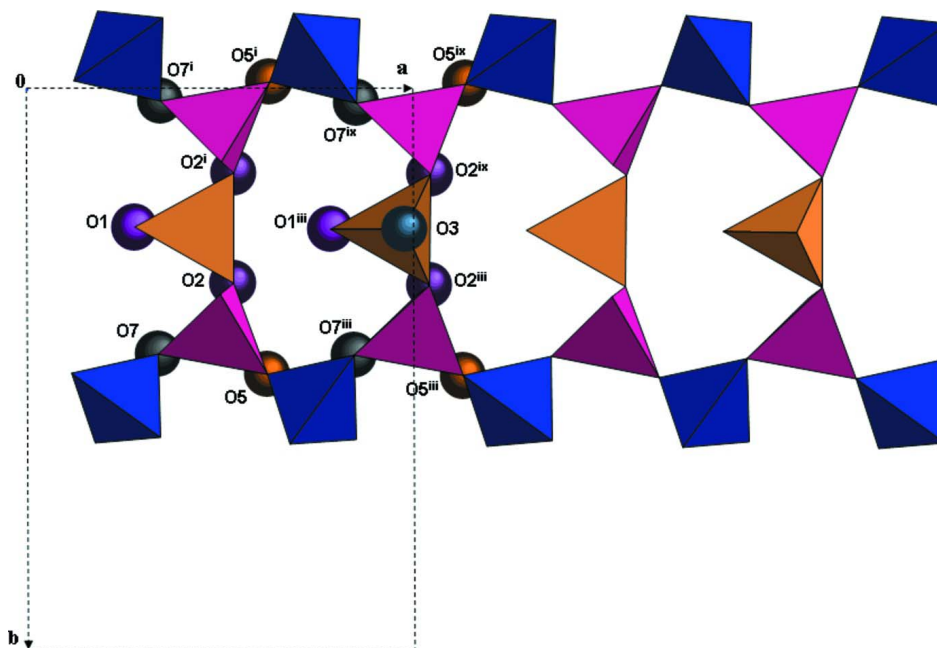
Figure 1
Projection along [100] of the structure of YP_5O_{14} showing the isolated $_\infty(P_5O_{14})^{3-}$ ribbons.

Figure 2
Details of the $_\infty(P_5O_{14})^{3-}$ ribbon in a projection along [001], symmetry codes: (i) x, -y+1/2, z; (iii) x+1/2, y, -z+1/2; (ix) x+1/2, 1/2-y+1/2, 1/2-z.

yttrium pentaphosphate(V)

Crystal data

YP_5O_{14}	$F(000) = 904$
$M_r = 467.76$	$D_x = 3.136$ Mg m^{-3}
Orthorhombic, *Pnma*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ac 2n	Cell parameters from 3391 reflections
$a = 8.7128$ (2) Å	$\theta = 3.6–27.5°$
$b = 12.7218$ (4) Å	$\mu = 6.79$ mm^{-1}
$c = 8.9377$ (3) Å	$T = 296$ K
$V = 990.68$ (5) Å^3	Platelet, colourless
$Z = 4$	$0.22 \times 0.15 \times 0.11$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	5338 measured reflections
	1194 independent reflections
Radiation source: fine-focus sealed tube	1136 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.019$
Detector resolution: 8.3333 pixels mm^{-1}	$\theta_{max} = 27.6°$, $\theta_{min} = 2.8°$
φ and ω scans	$h = -7 \rightarrow 11$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008a)	$k = -16 \rightarrow 16$
	$l = -11 \rightarrow 7$
$T_{min} = 0.330$, $T_{max} = 0.460$	

Refinement

Refinement on F^2	$wR(F^2) = 0.110$
Least-squares matrix: full	$S = 1.22$
$R[F^2 > 2\sigma(F^2)] = 0.030$	1194 reflections

97 parameters

0 restraints

0 constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 6.1916P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 1.60$ e Å^{-3}

$\Delta\rho_{min} = -1.11$ e Å^{-3}

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 (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Y1	0.01824 (6)	0.2500	0.05695 (6)	0.0042 (2)
P1	0.49261 (13)	0.41750 (10)	−0.20198 (13)	0.0101 (3)
P2	0.4300 (2)	0.2500	0.00645 (18)	0.0117 (4)
P3	−0.24466 (12)	0.43269 (9)	0.22692 (13)	0.0104 (3)
O1	0.2739 (6)	0.2500	−0.0586 (5)	0.0164 (10)
O2	0.5265 (4)	0.3470 (3)	−0.0646 (4)	0.0148 (7)
O3	−0.0382 (6)	0.2500	0.3332 (6)	0.0193 (11)
O4	−0.1756 (4)	0.3732 (3)	0.1035 (4)	0.0166 (7)
O5	0.6146 (4)	0.5051 (3)	−0.1804 (4)	0.0146 (7)
O6	0.1567 (4)	0.3836 (3)	0.1598 (4)	0.0172 (7)
O7	0.3374 (4)	0.4704 (3)	−0.1552 (4)	0.0150 (7)
O8	−0.0066 (4)	0.3649 (3)	−0.1534 (4)	0.0191 (8)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Y1	0.0044 (3)	0.0036 (3)	0.0045 (3)	0.000	−0.00084 (18)	0.000
P1	0.0105 (6)	0.0099 (6)	0.0101 (5)	−0.0001 (4)	0.0002 (4)	0.0000 (4)
P2	0.0129 (8)	0.0116 (8)	0.0107 (8)	0.000	0.0003 (6)	0.000
P3	0.0089 (5)	0.0100 (5)	0.0123 (5)	−0.0004 (4)	0.0002 (4)	−0.0001 (4)
O1	0.012 (2)	0.020 (2)	0.016 (2)	0.000	0.0002 (18)	0.000
O2	0.0141 (16)	0.0138 (17)	0.0165 (17)	−0.0023 (13)	−0.0028 (12)	0.0050 (13)
O3	0.020 (3)	0.022 (3)	0.015 (2)	0.000	0.001 (2)	0.000
O4	0.0158 (16)	0.0187 (17)	0.0154 (15)	0.0041 (14)	0.0008 (13)	−0.0021 (13)
O5	0.0139 (16)	0.0146 (15)	0.0153 (15)	−0.0052 (13)	0.0019 (13)	0.0009 (13)
O6	0.0153 (17)	0.0166 (16)	0.0196 (16)	−0.0025 (13)	−0.0035 (14)	−0.0032 (13)
O7	0.0125 (15)	0.0154 (15)	0.0172 (16)	0.0037 (13)	0.0021 (13)	0.0038 (13)
O8	0.0207 (19)	0.0215 (19)	0.0150 (16)	0.0009 (14)	0.0014 (13)	0.0058 (16)

Geometric parameters (Å, º)

Y1—O6	2.278 (3)	P1—O5	1.553 (3)
Y1—O6^i	2.278 (3)	P1—O7	1.567 (3)
Y1—O4^i	2.341 (3)	P2—O3^{iii}	1.460 (5)
Y1—O4	2.341 (3)	P2—O1	1.479 (5)
Y1—O8^i	2.391 (4)	P2—O2	1.623 (4)
Y1—O8	2.391 (4)	P2—O2^i	1.623 (4)
Y1—O1	2.455 (5)	P3—O4	1.467 (3)
Y1—O3	2.518 (5)	P3—O6^{iv}	1.468 (3)
P1—O8^{ii}	1.455 (4)	P3—O7^v	1.607 (3)
P1—O2	1.549 (4)	P3—O5^{vi}	1.611 (3)
O6—Y1—O6^i	96.52 (18)	O1—Y1—O3	126.14 (16)
O6—Y1—O4^i	144.08 (12)	O8^{ii}—P1—O2	115.9 (2)
O6^i—Y1—O4^i	79.10 (13)	O8^{ii}—P1—O5	115.9 (2)
O6—Y1—O4	79.10 (13)	O2—P1—O5	100.76 (19)
O6^i—Y1—O4	144.08 (12)	O8^{ii}—P1—O7	116.0 (2)
O4^i—Y1—O4	84.04 (18)	O2—P1—O7	101.63 (19)
O6—Y1—O8^i	145.21 (13)	O5—P1—O7	104.42 (19)
O6^i—Y1—O8^i	84.77 (13)	O3^{iii}—P2—O1	124.1 (3)
O4^i—Y1—O8^i	70.44 (12)	O3^{iii}—P2—O2	106.61 (19)
O4—Y1—O8^i	118.93 (12)	O1—P2—O2	108.82 (17)
O6—Y1—O8	84.77 (13)	O3^{iii}—P2—O2^i	106.61 (19)
O6^i—Y1—O8	145.21 (13)	O1—P2—O2^i	108.82 (17)
O4^i—Y1—O8	118.93 (12)	O2—P2—O2^i	99.0 (3)
O4—Y1—O8	70.44 (12)	O4—P3—O6^{iv}	122.6 (2)
O8^i—Y1—O8	75.38 (19)	O4—P3—O7^v	107.59 (18)
O6—Y1—O1	71.89 (11)	O6^{iv}—P3—O7^v	107.87 (19)
O6^i—Y1—O1	71.89 (11)	O4—P3—O5^{vi}	110.6 (2)
O4^i—Y1—O1	136.82 (9)	O6^{iv}—P3—O5^{vi}	105.42 (19)
O4—Y1—O1	136.82 (9)	O7^v—P3—O5^{vi}	100.51 (18)
O8^i—Y1—O1	75.61 (12)	P2—O1—Y1	132.0 (3)
O8—Y1—O1	75.61 (12)	P1—O2—P2	130.7 (2)
O6—Y1—O3	73.01 (12)	P2^{iv}—O3—Y1	179.7 (3)
O6^i—Y1—O3	73.01 (12)	P3—O4—Y1	140.8 (2)
O4^i—Y1—O3	71.63 (12)	P1—O5—P3^{vii}	140.4 (2)
O4—Y1—O3	71.63 (12)	P3^{iii}—O6—Y1	155.0 (2)
O8^i—Y1—O3	138.88 (10)	P1—O7—P3^v	131.1 (2)
O8—Y1—O3	138.88 (10)	P1^{viii}—O8—Y1	168.4 (3)

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