Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

The type IV polymorph of $KDy(PO_3)_4$

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Received 8 March 2007
Accepted 3 April 2007

Single crystals of potassium dysprosium polyphosphate, $KDy(PO_3)_4$, were prepared by the flux method. The title compound crystallizes in structure type IV of $KLn(PO_3)_4$ (Ln = lanthanide) compounds. Two helical polyphosphate chains cross the unit cell along [101] with a repeat unit of eight tetrahedra, creating channels where the Dy and K atoms are situated. They have coordination numbers of 8 and 9, respectively.

Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(P–O) = 0.004 Å
R factor = 0.027
wR factor = 0.059
Data-to-parameter ratio = 13.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Phosphates of general formula $M^{I}Ln(PO_3)_4$ (M = alkaline metal or silver; Ln = lanthanide) have been the subject of several investigations due to their interesting optical properties (Hong & Chinn, 1976; Hashimoto *et al.*, 1991; Horchani *et al.*, 2003). Because most of these phosphates show polymorphism, they have been classified into seven structural types denoted by Roman numerals I to VII (Palkina *et al.*, 1981; Bagieu-Beucher & Guitel, 1988).

Although representatives of potassium lanthanide polyphosphates, $KLn(PO_3)_4$, are known to crystallize in types III, IV, V and VII (Durif, 1995), for $KDy(PO_3)_4$ only the existence of type III was originally reported by Palkina *et al.* (1976). In a later study, the synthesis and the crystal structure of another polymorph with a cyclotetraphosphate anion were described by Horchani *et al.* (2002). Here, we report the preparation and crystal structure refinement of a third $KDy(PO_3)_4$ polymorph, crystallizing in structure type IV (space group $P2_1/n$).

Two helical polyphosphate chains cross the unit cell of the title compound along [101], with a repeat unit of eight tetrahedra, creating channels where the K and Dy atoms are located (Fig. 1). The P—O distances within the polyphosphate

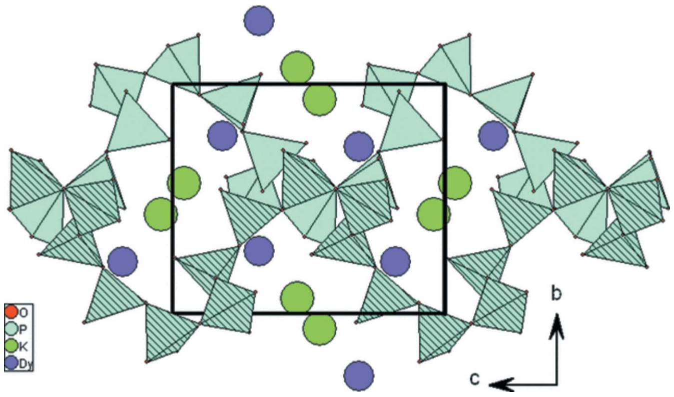

Figure 1
The structural arrangement of $KDy(PO_3)_4$, viewed along [100]. The polyphosphate chains are displayed in the polyhedral representation, with one chain gshown as hatched polyhedra.

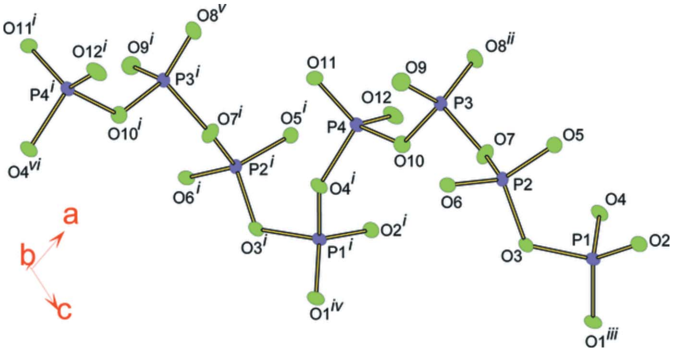

Figure 2
The repeat unit of the polyphosphate chain in $KDy(PO_3)_4$, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $x - \frac{1}{2}, -y - \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z - \frac{1}{2}$; (iii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + 1, -y - 1, -z$; (v) $x + 1, -y - 1, -z - 1$; (vi) $x - 1, y, z - 1$.]

chains range from 1.476 (3) to 1.492 (3) Å for the terminal P—O bonds and from 1.588 (3) to 1.608 Å for the bridging P—O bonds (Table 1 and Fig. 2) and are comparable with those of other condensed phosphates (Durif, 1995; Averbuch-Pouchot & Bagieu-Beucher, 1987; Chehimi-Moumen & Férid, 2007; Férid, 2006; Ben Zarkouna *et al.*, 2007).

Dy has coordination number 8 and is coordinated by terminal O atoms of four different polyphosphate chains in the form of a distorted dodecahedron, with Dy—O distances ranging from 2.301 (3) to 2.438 (3) Å (Table 1). The DyO_8 dodecahedra are isolated from each other, with the shortest Dy···Dy separation being 6.396 (8) Å.

K is ninefold coordinated by terminal O atoms of four different polyphosphate chains, with K—O distances ranging from 2.953 (3) to 3.370 (3) Å (Table 1).

Experimental

Single crystals of $KDy(PO_3)_4$ were synthesized by the flux method. K_2CO_3 (3 g) and Dy_2O_3 (0.3 g) were dissolved in H_3PO_4 (85%; 20 ml). The resulting mixture was heated to 473 K for 1 d and then kept at 673 K for 12 d. Excess phosphoric acid was leached out with hot water. Colourless crystals of (I) with a pseudo-cubic habit were obtained.

Crystal data

$KDy(PO_3)_4$
$M_r = 517.48$
Monoclinic, $P2_1/n$
$a = 10.2822$ (4) Å
$b = 8.9006$ (3) Å
$c = 10.9848$ (4) Å
$\beta = 106.284$ (2)°
$V = 964.97$ (6) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 8.90$ mm^{-1}
$T = 298$ (2) K
0.14 × 0.14 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.288$, $T_{\max} = 0.291$
3857 measured reflections
2270 independent reflections
2054 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.059$
$S = 1.11$
2270 reflections
163 parameters
$\Delta\rho_{\max} = 1.98$ e Å^{-3}
$\Delta\rho_{\min} = -1.03$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Dy—O5	2.301 (3)	P1—O1^{viii}	1.485 (3)
Dy—O9^{i}	2.329 (3)	P1—O2	1.492 (3)
Dy—O12^{ii}	2.349 (3)	P1—O3	1.607 (3)
Dy—O8^{ii}	2.372 (3)	P1—O4	1.608 (3)
Dy—O11^{iii}	2.380 (3)	P2—O5	1.481 (3)
Dy—O1^{iv}	2.384 (3)	P2—O6	1.485 (3)
Dy—O6^{i}	2.404 (3)	P2—O7	1.603 (3)
Dy—O2	2.438 (3)	P2—O3	1.605 (3)
K—O2^{v}	2.953 (3)	P3—O8^{iii}	1.482 (3)
K—O1	3.031 (3)	P3—O9	1.482 (3)
K—O9^{vi}	3.052 (3)	P3—O7	1.588 (3)
K—O11^{ii}	3.075 (3)	P3—O10	1.605 (3)
K—O12	3.123 (4)	P4—O11	1.476 (3)
K—O10	3.177 (3)	P4—O12	1.477 (3)
K—O8	3.287 (4)	P4—O4^{ix}	1.601 (3)
K—O4	3.308 (3)	P4—O10	1.605 (3)
K—O6^{vii}	3.370 (3)		

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y - \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z - \frac{1}{2}$; (iv) $x, y + 1, z$; (v) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (vi) $-x + \frac{3}{2}, y - \frac{1}{2}, -z - \frac{1}{2}$; (vii) $x, y - 1, z$; (viii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ix) $x - \frac{1}{2}, -y - \frac{1}{2}, z - \frac{1}{2}$.

The highest peak in the final difference Fourier map is 1.05 Å away from atom O6 and the deepest hole is 0.73 Å away from Dy.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

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