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$LiTb(PO_3)_4$

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The lithium terbium polyphosphate $LiTb(PO_3)_4$ was prepared by the flux method using a large excess of H_3PO_4. It was structurally characterized by single-crystal X-ray diffraction and found to be isotypic with $LiYb(PO_3)_4$. The basic structural units are endless spiral chains, $(PO_3)_n$, along the *b*-axis direction. The Li^+ and Tb^{3+} cations alternate on twofold axes and are four- and eight-coordinated, respectively. The results of an optical study of this material are also given and discussed.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(P–O) = 0.003 Å
R factor = 0.020
wR factor = 0.054
Data-to-parameter ratio = 11.6

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

Comment

The level of activity directed to the chemistry of lanthanide phosphates has steadily increased during the past three decades owing to their remarkable optical properties and high luminescence efficiency (Bimberg *et al.*, 1975; Hashimoto *et al.*, 1991; Obaton *et al.*, 2000). In particular, in our laboratories much attention has been focused on the preparation and characterization of double phosphates combining monovalent and lanthanide cations in order to determine their structural, optical and electrical features (Férid, 2006; Ben Zarkouna *et al.*, 2006). In this context, we report here the chemical preparation and structural and optical investigation of the lithium terbium polyphosphate, $LiTb(PO_3)_4$.

The title compound is found to be isotypic with $LiYb(PO_3)_4$ (Ben Zarkouna & Driss, 2004). The basic structural units are endless chains, $(PO_3)_n$, spiraling around the 2_1 screw axes, in the *b*-axis direction, with a period of four tetrahedra (Fig. 1). These chains have a 2_1 internal symmetry, so they are built up by only two crystallographically independent PO_4 tetrahedra. The bond lengths and angles within the phosphate chains are

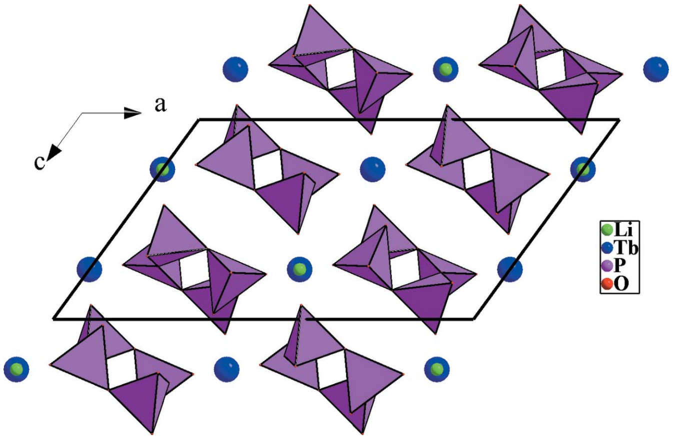

Figure 1
The structural arrangement of $LiTb(PO_3)_4$ viewed along the [010] direction.

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typical of those observed in polyphosphates (Rzaigui, 1983) and, as expected, the longest P—O distances are found for the bridging P—O bonds, while the shortest are the ones involving the terminal O atoms. As in $KDyP_4O_{12}$ (Horchani *et al.*, 2002), the alkali and lanthanide cations are located on twofold axes in the $z = \frac{1}{4}$ and $\frac{3}{4}$ planes. However, in $LiTb(PO_3)_4$, the Li^+ and Tb^{3+} cations alternate at almost equal spacings [3.51 (1) and 3.54 (1) Å], compared with the quite different spacings of K^+ and Dy^{3+} [3.743 (2) and 8.597 (2) Å] in $KDyP_4O_{12}$. The coordination environments of Li^+ and Tb^{3+}, in the present structure, are formed by four and eight terminal O atoms, respectively, in the shape of a distorted tetrahedron for Li^+, and an irregular dodecahedron for Tb^{3+}; the mean Li—O and Tb—O distances are 1.980 (7) and 2.412 (3) Å, respectively. It can be noted that the TbO_8 dodecahedra are isolated from each other since they have no common O atom. The shortest Tb···Tb distance has a value of 5.598 (1) Å, somewhat greater than that of the corresponding Yb···Yb distance [5.545 (1) Å] in $LiYb(PO_3)_4$ (Ben Zarkouna & Driss, 2004).

Under an UV excitation of 254 nm, $LiTb(PO_3)_4$ exhibits green emission corresponding to the ${}^5D_4 \rightarrow {}^7F_j$ (j = 3,4,5,6) electronic transitions of the Tb^{3+} ions; the dominant green emission is around 545 nm and originates from the ${}^5D_4 \rightarrow {}^7F_5$ transition. No blue emission from the ${}^5D_3$ level is observed. This is typical of luminescent materials with a high concentration of Tb^{3+}, and it is due to the well known effect of cross-relaxation, which results from a resonant energy transfer between the ${}^5D_3 \rightarrow {}^5D_4$ and ${}^7F_6 \rightarrow {}^7F_{0,1}$ transitions of Tb^{3+} ions (Berdowski *et al.*, 1985).

Experimental

A mixture of Li_2CO_3 (2 g), Tb_4O_7 (0.4 g) and H_3PO_4 (85%, 16 ml) was slowly heated, in a vitreous carbon crucible, up to 620 K and held at this temperature for 10 d. After cooling to room temperature and removal of the excess phosphoric flux by boiling water, colourless crystals of $LiTb(PO_3)_4$ were gathered. Optical properties of $LiTb(PO_3)_4$ were investigated at room temperature by means of a Jobin Yvon THR 1500 monochromator and a 254 nm Hg lamp as excitation source. The optical signal was detected by a Hamamatsu R928 photomultiplier.

Crystal data

$LiTb(PO_3)_4$
$M_r = 481.74$
Monoclinic, $C2/c$
$a = 16.358$ (2) Å
$b = 7.050$ (2) Å
$c = 9.629$ (2) Å
$\beta = 126.15$ (1)°
$V = 896.7$ (4) Å^3

$Z = 4$
$D_x = 3.569$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 8.67$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.28 × 0.16 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.236$, $T_{\max} = 0.646$ (expected range = 0.182–0.500)
1324 measured reflections

974 independent reflections
951 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 26.9°$
2 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.054$
$S = 1.08$
974 reflections
84 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 5.8217P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.38$ e Å^{-3}
$\Delta\rho_{\min} = -1.15$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0025 (2)

Table 1
Selected geometric parameters (Å, °).

Li—O2$^{\rm i}$	1.974 (8)	P1—O6	1.502 (3)
Li—O6	1.987 (7)	P1—O4	1.591 (3)
Tb—O3	2.312 (3)	P1—O5$^{\rm iii}$	1.596 (3)
Tb—O1$^{\rm i}$	2.374 (3)	P2—O2	1.488 (3)
Tb—O2$^{\rm ii}$	2.432 (3)	P2—O3	1.490 (3)
Tb—O6	2.530 (3)	P2—O5	1.586 (3)
P1—O1	1.488 (3)	P2—O4	1.606 (3)
O1—P1—O6	118.7 (2)	O2—P2—O5	107.9 (1)
O1—P1—O4	106.7 (2)	O3—P2—O5	111.9 (2)
O6—P1—O4	111.1 (1)	O2—P2—O4	104.8 (1)
O1—P1—O5$^{\rm iii}$	111.5 (2)	O3—P2—O4	109.8 (1)
O6—P1—O5$^{\rm iii}$	105.0 (1)	O5—P2—O4	101.0 (2)
O4—P1—O5$^{\rm iii}$	102.8 (1)	P1—O4—P2	131.5 (2)
O2—P2—O3	119.6 (2)	P2—O5—P1$^{\rm iv}$	134.6 (2)

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

The highest peak is located 0.90 Å from the Tb atom and the deepest hole is located 1.18 Å also from the Tb atom.

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); 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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