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LiHo(PO₃)₄Emna Ben Zarkouna,^{a*} Ahmed Driss^a and Mokhtar Férid^b

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{P}-\text{O}) = 0.004$ Å; R factor = 0.025; wR factor = 0.071; data-to-parameter ratio = 12.8.

Lithium holmium(III) polyphosphate(V), LiHo(PO₃)₄, belongs to the type I of polyphosphates with general formula $ALn(\text{PO}_3)_4$, where A is a monovalent cation and Ln is a trivalent rare earth cation. In the crystal structure, the polyphosphate chains spread along the b -axis direction, with a repeat period of four tetrahedra and 2_1 internal symmetry. The Li and Ho atoms are both located on twofold rotation axes and are surrounded by four and eight O atoms, leading to a distorted tetrahedral and dodecahedral coordination, respectively. The HoO₈ polyhedra are isolated from each other, the closest Ho...Ho distance being 5.570 (1) Å.

Related literature

For isotopic LiLn(PO₃)₄ structures, see: Ben Zarkouna & Driss (2004) for $Ln = \text{Yb}$; Ben Zarkouna *et al.* (2005) for $Ln = \text{Er}$; Ben Zarkouna *et al.* (2007) for $Ln = \text{Tb}$. For related structures, see: Amami *et al.* (2004) (NaHo(PO₃)₄); Palkina *et al.* (1976) (β -KHo(PO₃)₄); Tranqui *et al.* (1972) (HoP₅O₁₄). For general background, see: Brown & Altermatt (1985); Durif (1995); Liu *et al.* (1999); Palkina *et al.* (1981); International Tables for X-Ray Crystallography (1968).

Experimental

Crystal data

LiHo(PO ₃) ₄	$V = 886.5$ (4) Å ³
$M_r = 487.75$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 16.280$ (3) Å	$\mu = 9.72$ mm ⁻¹
$b = 7.039$ (2) Å	$T = 293$ (2) K
$c = 9.561$ (2) Å	$0.31 \times 0.14 \times 0.07$ mm
$\beta = 125.99$ (2)°	

Data collection

Enraf–Nonius CAD-4 diffractometer	$T_{\min} = 0.095$, $T_{\max} = 0.378$ (expected range = 0.128–0.507)
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	1500 measured reflections
	1078 independent reflections

1076 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$

2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$	84 parameters
$wR(F^2) = 0.071$	$\Delta\rho_{\text{max}} = 2.75$ e Å ⁻³
$S = 1.12$	$\Delta\rho_{\text{min}} = -3.18$ e Å ⁻³
1078 reflections	

Table 1

Selected bond lengths (Å).

Li—O ⁱ	1.962 (9)	P1—O6	1.499 (3)
Li—O6	1.999 (9)	P1—O4	1.589 (4)
Ho—O3	2.287 (3)	P1—O5 ⁱⁱⁱ	1.594 (3)
Ho—O1 ⁱ	2.348 (4)	P2—O2	1.486 (3)
Ho—O2 ⁱⁱ	2.411 (3)	P2—O3	1.488 (3)
Ho—O6	2.516 (3)	P2—O5	1.588 (3)
P1—O1	1.488 (4)	P2—O4	1.601 (4)

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

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS*; Macíček & Yordanov, 1992); data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2216).

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supporting information

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LiHo(PO₃)₄**Emna Ben Zarkouna, Ahmed Driss and Mokhtar Férid****S1. Comment**

The present paper is an extension of our earlier work on polyphosphates of general formula LiLn(PO₃)₄ [Ln = Yb (Ben Zarkouna & Driss, 2004), Er (Ben Zarkouna *et al.*, 2005) and Tb (Ben Zarkouna *et al.*, 2007)]. This family is now expanded to include the lithium holmium polyphosphate, LiHo(PO₃)₄, which might be of particular interest in the area of luminescent materials, because an avalanche up-conversion emission was observed previously for Ho³⁺-containing compounds (Liu *et al.*, 1999).

The LiLn(PO₃)₄ polyphosphates are isostructural and belong to form I according to the classification of Palkina *et al.* (1981). In this type of arrangement, helical ribbons, ∞ (PO₃)_n, formed by corner-sharing of PO₄ tetrahedra, spread parallel to the *b* axis. The period of the chains corresponds to four tetrahedra but, owing to the presence of 2₁ screw axes, only two of them are crystallographically independent. The P—O bonds involving terminal O atoms are the shortest within a PO₄ tetrahedron, because of the dπ-pπ orbital overlap (Durif, 1995). In LiHo(PO₃)₄, the mean P—O bond lengths for terminal and bridging O atoms, are of 1.490 and 1.593 Å, respectively. The O—P—O angles are within the range 101.2 (2)–119.6 (2)°, the smallest and the largest ones are those involving the longest and the shortest P—O bonds, respectively. The P—O—P bridges exhibit angles of 131.6 (2) and 134.8 (2)°, larger than the O—P—O angles. The Li and Ho atoms are arranged alternately on twofold rotation axes at roughly similar spacings [3.486 (1) and 3.553 (1) Å] in comparison with the quite different spacings between K and Ho atoms [3.721 (2) and 8.589 (2) Å] in β-KHo(PO₃)₄ (Palkina *et al.*, 1976). The Ho atom is surrounded by eight terminal oxygen atoms forming a distorted dodecahedron, with an average Ho—O distance of 2.390 Å, while the Li atom is located inside an irregular tetrahedron with a mean Li—O distance of 1.980 Å. All these bond lengths are conform with those mentioned in the literature (International Tables for X-Ray Crystallography, 1968; Durif, 1995; Amami *et al.*, 2004).

By sharing edges, the HoO₈ and LiO₄ polyhedra are joined to produce infinite linear chains running along the *b* axis (Fig. 1), in contrast to crystal structure of NaHo(PO₃)₄ (form II) (Amami *et al.*, 2004) where zigzag chains of face-sharing HoO₈ and NaO₈ polyhedra are observed. As shown in Fig. 2, each chain shares corners of its polyhedra with four adjacent polyphosphate chains.

It is noteworthy that no O atom is common to two Ho atoms, and the closest Ho···Ho distance of 5.570 (1) Å in LiHo(PO₃)₄ is comparable with that found in HoP₅O₁₄ (Tranqui *et al.*, 1972). Bond-valence-sum values (Brown & Altermatt, 1985) are 0.998, 3.054, 4.936 and 4.967 valence units for Li, Ho, P1 and P2, respectively, in good agreement with the expected formal charges.

S2. Experimental

The title compound was prepared in single crystalline form using the flux method. At room temperature, 3 g of Li₂CO₃ and 0.5 g of Ho₂O₃ were slowly added to 10 ml of H₃PO₄ (85%_{w/w}) in a glassy carbon crucible. The resulting mixture was then progressively heated to 573 K and kept at this temperature for 8 days. After cooling to room temperature and

removal of the excess phosphoric flux with boiling water, pale yellow crystals of $\text{LiHo}(\text{PO}_3)_4$ were separated.

S3. Refinement

The highest peak is located 0.87 Å from Ho and the deepest hole is located 1.00 Å from the same atom.

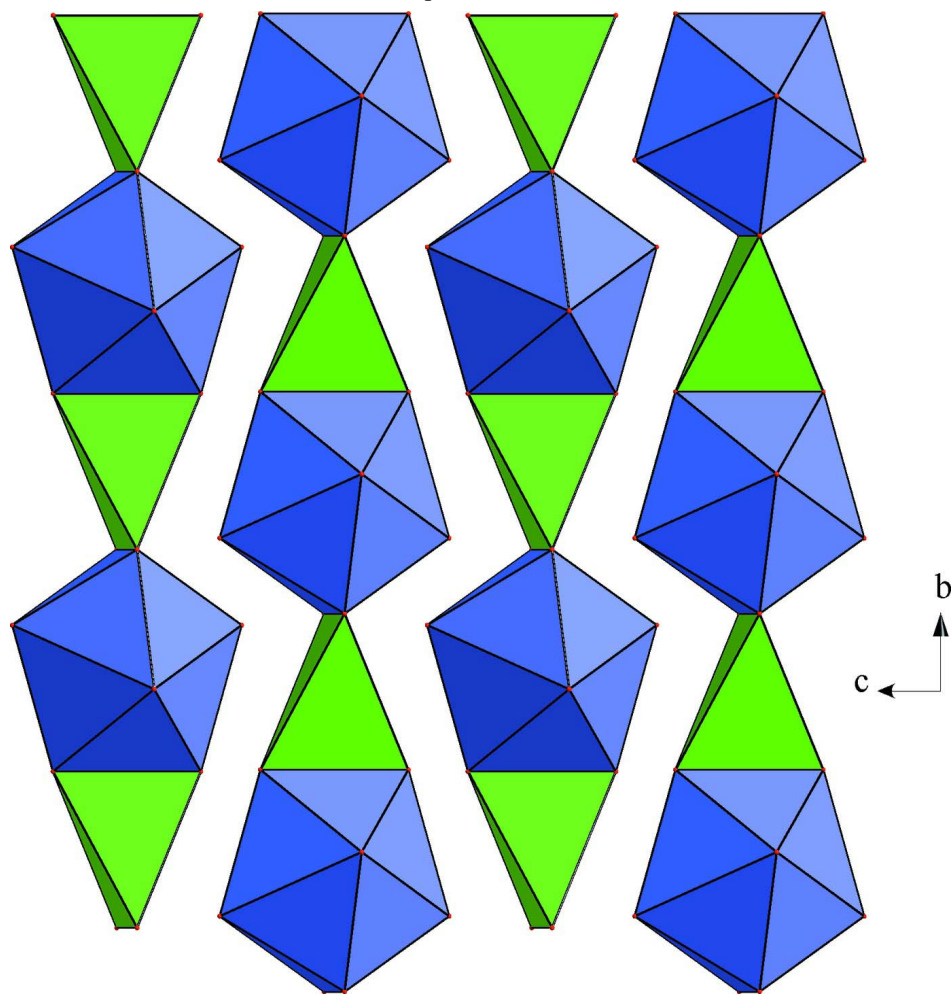
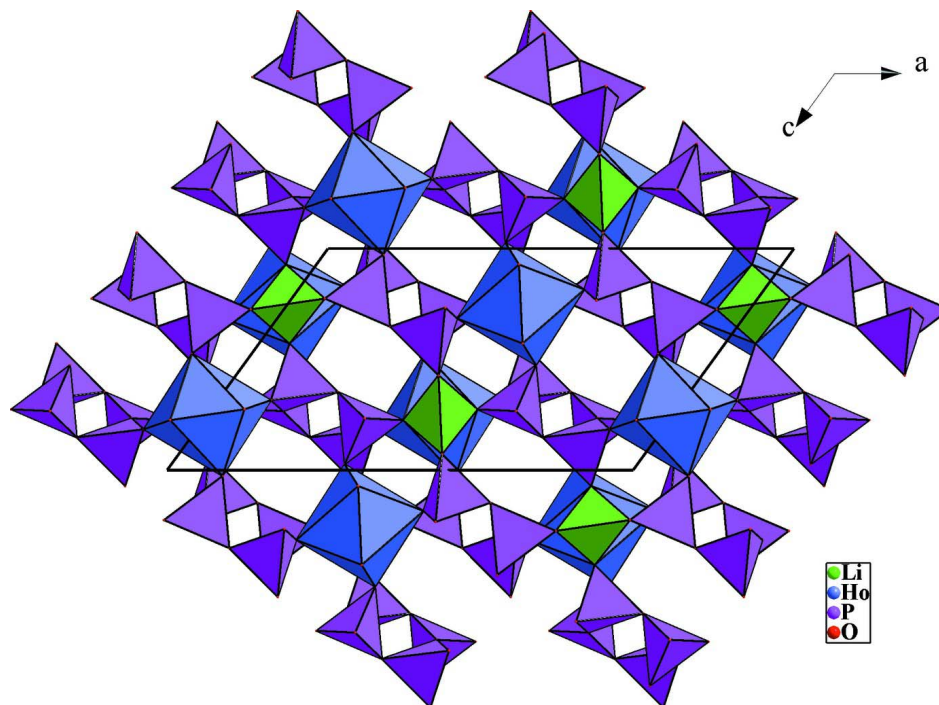


Figure 1

Alternating arrangement of HoO_8 and LiO_4 polyhedra projected along the a axis. PO_4 tetrahedra are omitted for clarity.

**Figure 2**

Projection of the $\text{LiHo}(\text{PO}_3)_4$ structure along the b axis.

Lithium holmium(III) polyphosphate(V)

Crystal data

$\text{LiHo}(\text{PO}_3)_4$

$M_r = 487.75$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 16.280\ (3)\ \text{\AA}$

$b = 7.039\ (2)\ \text{\AA}$

$c = 9.561\ (2)\ \text{\AA}$

$\beta = 125.99\ (2)^\circ$

$V = 886.5\ (4)\ \text{\AA}^3$

$Z = 4$

$F(000) = 904$

$D_x = 3.654\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71069\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 10.1\text{--}14.7^\circ$

$\mu = 9.72\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Plate, pale yellow

$0.31 \times 0.14 \times 0.07\ \text{mm}$

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega/2\theta$ scans

Absorption correction: ψ scan
(North *et al.*, 1968)

$T_{\min} = 0.095$, $T_{\max} = 0.378$

1500 measured reflections

1078 independent reflections

1076 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 28.0^\circ$, $\theta_{\min} = 3.1^\circ$

$h = -21 \rightarrow 17$

$k = -2 \rightarrow 9$

$l = 0 \rightarrow 12$

2 standard reflections every 120 min

intensity decay: none

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.071$
 $S = 1.12$
 1078 reflections
 84 parameters
 0 restraints
 Primary atom site location: heavy method

Secondary atom site location: difference Fourier map
 $w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 12.7265P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 2.75 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -3.18 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0014 (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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Li	0.0000	0.708 (2)	0.2500	0.015 (3)
Ho	0.0000	0.20312 (4)	0.2500	0.0073 (1)
P1	0.13774 (8)	0.5517 (2)	0.6157 (1)	0.0067 (2)
P2	0.14654 (8)	0.1504 (2)	0.6961 (1)	0.0068 (2)
O1	0.1137 (3)	0.7154 (5)	0.6843 (5)	0.0118 (7)
O2	0.0711 (3)	0.0845 (5)	0.7255 (5)	0.0116 (6)
O3	0.1280 (3)	0.1150 (5)	0.5262 (4)	0.0121 (7)
O4	0.1568 (3)	0.3740 (5)	0.7337 (4)	0.0107 (6)
O5	0.2552 (2)	0.0776 (5)	0.8526 (4)	0.0105 (6)
O6	0.0652 (2)	0.5022 (5)	0.4280 (4)	0.0104 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Li	0.018 (6)	0.011 (6)	0.020 (7)	0.000	0.012 (6)	0.000
Ho	0.0063 (2)	0.0076 (2)	0.0071 (2)	0.000	0.0034 (1)	0.000
P1	0.0052 (5)	0.0069 (5)	0.0072 (5)	-0.0002 (4)	0.0031 (4)	-0.0001 (4)
P2	0.0051 (5)	0.0072 (5)	0.0073 (5)	-0.0001 (4)	0.0032 (4)	0.0009 (4)
O1	0.012 (2)	0.009 (2)	0.016 (2)	0.001 (1)	0.009 (1)	-0.002 (1)
O2	0.008 (1)	0.012 (2)	0.016 (2)	0.001 (1)	0.008 (1)	0.002 (1)
O3	0.012 (2)	0.014 (2)	0.008 (1)	0.002 (1)	0.004 (1)	-0.000 (1)
O4	0.015 (2)	0.007 (1)	0.009 (1)	0.001 (1)	0.007 (1)	0.002 (1)
O5	0.005 (1)	0.016 (2)	0.010 (1)	0.002 (1)	0.005 (1)	0.002 (1)
O6	0.007 (1)	0.014 (2)	0.006 (1)	-0.001 (1)	0.001 (1)	-0.000 (1)

Geometric parameters (Å, °)

Li—O2 ⁱ	1.962 (9)	Ho—O6	2.516 (3)
Li—O2 ⁱⁱ	1.962 (9)	Ho—O6 ⁱⁱⁱ	2.516 (3)
Li—O6 ⁱⁱⁱ	1.999 (9)	P1—O1	1.488 (4)
Li—O6	1.999 (9)	P1—O6	1.499 (3)
Ho—O3 ⁱⁱⁱ	2.287 (3)	P1—O4	1.589 (4)
Ho—O3	2.287 (3)	P1—O5 ^{vi}	1.594 (3)
Ho—O1 ⁱⁱ	2.348 (4)	P2—O2	1.486 (3)
Ho—O1 ⁱ	2.348 (4)	P2—O3	1.488 (3)
Ho—O2 ^{iv}	2.411 (3)	P2—O5	1.588 (3)
Ho—O2 ^v	2.411 (3)	P2—O4	1.601 (4)
O2 ⁱ —Li—O2 ⁱⁱ	83.7 (5)	O6—P1—O5 ^{vi}	105.0 (2)
O2 ⁱ —Li—O6 ⁱⁱⁱ	119.57 (14)	O4—P1—O5 ^{vi}	102.7 (2)
O2 ⁱⁱ —Li—O6 ⁱⁱⁱ	125.85 (14)	O2—P2—O3	119.6 (2)
O2 ⁱ —Li—O6	125.85 (14)	O2—P2—O5	107.9 (2)
O2 ⁱⁱ —Li—O6	119.57 (14)	O3—P2—O5	111.9 (2)
O6 ⁱⁱⁱ —Li—O6	87.2 (5)	O2—P2—O4	104.6 (2)
O1—P1—O6	118.8 (2)	O3—P2—O4	109.7 (2)
O1—P1—O4	106.8 (2)	O5—P2—O4	101.2 (2)
O6—P1—O4	110.8 (2)	P1—O4—P2	131.6 (2)
O1—P1—O5 ^{vi}	111.7 (2)	P2—O5—P1 ^{vii}	134.8 (2)

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