Acta Cryst. (1983). C**39**, 23–24

Structures of $ErPO_4$, $TmPO_4$, and $YbPO_4$

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(*Received* 17 *May* 1982; *accepted* 5 *August* 1982)

Abstract. $M_r = 262{\cdot}2$, 263·9, and 268·0, respectively, tetragonal, $I4_1/amd$, zircon structure, $a = 6{\cdot}860$ (1), 6·839 (1) and 6·816 (2), $c = 6{\cdot}003$ (1), 5·986 (1), and 5·966 (2) Å, $V = 282{\cdot}5$, 280·0, and 277·2 Å^3, $Z = 4$, $D_x = 6{\cdot}164$, 6·259, and 6·421 Mg m^{-3}, Mo $K\alpha$(λ = 0·71073 Å), 292 K, R_1 and $R_2 = 0{\cdot}035$, 0·016, and 0·035 for 411, 332, and 335 reflections, respectively; $F(000) = 460$, 464, and 468. The lanthanoid metal atom in each compound is coordinated to eight O atoms that form two orthogonal interpenetrating tetrahedra. Each has distinct bond distances.

Introduction. The structural investigations of $ErPO_4$, $TmPO_4$, and $YbPO_4$ reported here are part of an extensive research program dealing with the practicability of employing the lanthanoid orthophosphates as fundamental hosts for the isolation of nuclear wastes. The potential for accommodating chemically diverse cations such as thorium, uranium, α-active transuranic isotopes, and fission products such as Sr and Cs, which are produced during the operation of a nuclear reactor, in the lattice of the predominantly trivalent $LnPO_4$ systems has been discussed elsewhere (Beall, Boatner, Mullica & Milligan, 1981). These compounds have the zircon structure (Schwarz, 1963).

Experimental. Single crystals of $ErPO_4$, $TmPO_4$, and $YbPO_4$ were grown by means of the flux technique (Feigelson, 1964). The appropriate lanthanoid oxide (*i.e.* Er_2O_3, Tm_2O_3, or Yb_2O_3) and $PbHPO_4$ were placed in a Pt crucible that was closed with a tightly fitting lid. $PbHPO_4$ decomposes at high temperature to form $Pb_2P_2O_7$ which then serves as the flux matrix. Lead pyrophosphate reacts with the lanthanoid oxide to form the appropriate lanthanoid orthophosphate, and, after soaking the mixture for approximately 16 h at 1633 K, the crucible was slowly cooled to 1173 K at a rate of 1 K h^{-1}. The Pt crucible was then allowed to cool directly to room temperature at which time the $Pb_2P_2O_7$ flux was dissolved in boiling HNO_3 in order to free the orthophosphate crystals. A more complete description of the crystal-growth process has been given elsewhere (Rappaz, Boatner & Abraham, 1980).

Single crystals of $ErPO_4$, $TmPO_4$, and $YbPO_4$ selected on the basis of their optical quality; cell dimensions from 25 centered reflections in the range $1{\cdot}5 < \theta < 25°$ for $ErPO_4$, $TmPO_4$, and $YbPO_4$, CAD-4 diffractometer; two monitored reflections in each data set examined every 2 h of data collection, examination of each set revealed only random variations (1·3, 1·3, and 1·7%, respectively); Lorentz, polarization and absorption corrections applied; standard deviations of the structure factors computed as $\sigma(|F_o|) = 0{\cdot}5(\mathrm{VLp})^{1/2}[(\mathrm{Pk} + \mathrm{Bg} + p^2I_{\mathrm{rel}}{}^2)/I_{\mathrm{rel}}]^{1/2}$, where VLp is the standard Lorentz–polarization term, Pk is the peak intensity, Bg is the sum of the background counts taken on both sides of the peak, p is the ignorance factor (0·02 in this work) and I_{rel} is Pk – Bg, all data with $I_{\mathrm{rel}} > 3\sigma(I_{\mathrm{rel}})$ used in the solution and refinement of the structure.

An origin at the center ($2/m$) was chosen for the structural refinement; full-matrix least-squares refinements (Larson, 1967), anisotropic thermal parameters, secondary-extinction corrections, reliability values $R_1 = \sum \Delta F/\sum |F_o|$ and $R_2 = [\sum w(\Delta F)^2/\sum w(F_o)^2]^{1/2}$ where $w = \sigma^{-2}(|F_o|)$ and $\Delta F = ||F_o| - |F_c||$; 'goodness of fit' values ($\sum_2$) 1·35, 0·95, and 1·47, respectively; atomic scattering factors and anomalous-dispersion correction terms for all atoms from Ibers & Hamilton (1974). Table 1 presents the fractional atomic parameters with e.s.d.'s in parentheses and the equivalent values of the isotropic temperature factors.*

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* Lists of structure factors, anisotropic thermal parameters and interatomic distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38104 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/83/010023-02$01.50

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature parameters* ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{eq}*
$ErPO_4$				
Er	0	7500	1250	53
P	0	2500	3750	52
O	0	4249 (6)	2165 (8)	74
$TmPO_4$				
Tm	0	7500	1250	57
P	0	2500	3750	64
O	0	4253 (5)	2155 (5)	61
$YbPO_4$				
Yb	0	7500	1250	57
P	0	2500	3750	73
O	0	4274 (9)	2141 (10)	86

* $U_{eq} = \frac{1}{3}\,\text{trace}\,\tilde{\mathbf{U}}$.

Table 2. *Bond and contact lengths* (Å) *and angles* (°)

	$ErPO_4$	$TmPO_4$	$YbPO_4$
M—O	2·297 (4)	2·286 (3)	2·262 (6)
—O^{i}	2·376 (5)	2·364 (3)	2·357 (6)
Average	2·336	2·325	2·309
P—O	1·531 (4)	1·532 (3)	1·544 (6)
O—O^{ii}	2·400 (9)	2·397 (7)	2·419 (12)
O—$O^{iii,iv}$	2·550 (8)	2·554 (6)	2·571 (10)
O—P—O^{ii}	103·2 (5)	102·9 (3)	103·2 (7)
O—P—$O^{iii,iv}$	112·8 (5)	112·9 (3)	112·7 (7)

Symmetry code: (i) $0, 1-y, -z$; (ii) $0, \frac{1}{2}-y, z$; (iii) $-\frac{1}{4}+y, \frac{1}{4}, \frac{3}{4}-z$; (iv) $\frac{1}{4}-y, \frac{1}{4}, \frac{3}{4}-z$.

Discussion. A representative stereoscopic drawing of the molecular packing in the unit cell for tetragonal $ErPO_4$, $TmPO_4$, and $YbPO_4$ is shown in Fig. 1, with 50% equiprobability ellipsoids represented. Erbium, thulium, and ytterbium phosphate best fit the space-group model *I*4$_1$/*amd*. The lanthanoid metal atom is coordinated to eight O atoms forming two unique orthogonal interpenetrating tetrahedra, each of which has unique metal—oxygen bond lengths (see Table 2). The perpendicular-viewed tetrahedron of the bisphenoidal set which is associated with the phosphate group has the shorter discrete M—O distance. The polyhedral structure formed from the O—O contact distances (see Table 2) is a distorted dodecahedron (D_{2d}).

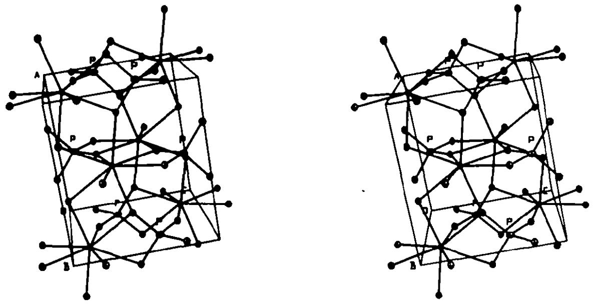

Fig. 1. A representative stereoview of the polyhedron in the tetragonal $LnPO_4$ system.

The bond distances given in Table 2 are in good agreement with listed experimental bond distances found in the *Bond Index of the Determination of Inorganic Crystal Structures* (1969–1980). The listed bond and contact lengths found in Table 2 are also internally consistent with the structural model.

The authors thank The Robert A. Welch Foundation in part for financial support (Grant No. AA-668). Further, the authors acknowledge appreciation for the experimental facilities of the Oak Ridge National Laboratory operated by Union Carbide Corporation for the US Department of Energy under contract W-7405-eng-26.

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