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Terbium(III) hydrogendiphosphate(V) tetrahydrate

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Key indicators: single-crystal X-ray study; T = 295 K; mean σ(P–O) = 0.002 Å; R factor = 0.012; wR factor = 0.034; data-to-parameter ratio = 11.9.

The Tb atom of the title compound, $TbHP_2O_7{\cdot}4H_2O$, is coordinated by the O atoms of three symmetrically independent water molecules and by five O atoms belonging to $HP_2O_7^-$ groups. The TbO_8 polyhedra are interconnected by the diphospate anions, forming a three-dimensional network which is additionally stabilized by O—H···O hydrogen bonding between water molecules and O atoms of the $HP_2O_7^-$ anions. Uncoordinated water molecules are situated in channels and are connected *via* hydrogen bonds with the framework.

Related literature

Isostructural compounds of the type $REHP_2O_7{\cdot}4H_2O$ were reported for RE = Sm by Chehimi-Moumen *et al.* (2002), for RE = Gd by Hraiech *et al.* (2005) and for RE = Eu by Anna-Rabah *et al.* (2006).

Experimental

Crystal data

$TbHP_2O_7{\cdot}4H_2O$
M_r = 405.9
Monoclinic, $P2_1/n$
a = 6.6006 (6) Å
b = 11.4744 (9) Å
c = 11.7252 (13) Å
β = 92.150 (8)°
V = 887.42 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 8.38 mm^{-1}
T = 295 K
0.14 × 0.06 × 0.03 mm

Data collection

Oxford Diffraction Xcalibur 2 diffractometer with Sapphire 2 CCD area-detector
Absorption correction: analytical [*CrysAlis RED* (Oxford Diffraction, 2005), using a multi-faceted crystal model based on expressions derived by Clark & Reid (1995)]
T_{min} = 0.329, T_{max} = 0.635
8671 measured reflections
1850 independent reflections
1628 reflections with $I > 3\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.011
$wR(F^2)$ = 0.034
S = 1.21
1850 reflections
155 parameters
10 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected bond lengths (Å).

Tb1—O1	2.3145 (17)	P1—O1	1.5129 (18)
Tb1—O2^{i}	2.2877 (17)	P1—O2	1.5063 (18)
Tb1—O3^{ii}	2.3514 (18)	P1—O3	1.5169 (19)
Tb1—O5	2.3718 (18)	P1—O7	1.6201 (18)
Tb1—O6^{iii}	2.3842 (17)	P2—O4	1.562 (2)
Tb1—O8	2.605 (2)	P2—O5	1.4957 (19)
Tb1—O9	2.433 (2)	P2—O6	1.4891 (18)
Tb1—O10	2.421 (2)	P2—O7	1.6116 (18)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H41···O11	0.813 (13)	1.736 (14)	2.546 (3)	174 (3)
O8—H81···O1^{ii}	0.82 (2)	1.98 (3)	2.762 (3)	159 (3)
O8—H82···O3^{i}	0.822 (18)	2.231 (14)	2.972 (3)	150 (3)
O9—H91···O4^{iv}	0.83 (3)	2.06 (3)	2.851 (3)	161 (3)
O9—H92···O8^{iii}	0.828 (18)	1.95 (2)	2.750 (3)	164 (3)
O10—H101···O5^{iii}	0.82 (2)	2.16 (3)	2.880 (3)	147 (3)
O10—H102···O7^{v}	0.812 (16)	2.28 (2)	2.991 (3)	147 (3)
O11—H111···O3^{v}	0.80 (2)	2.18 (2)	2.941 (3)	157 (3)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *JANA2000* (Petříček *et al.*, 2007); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *JANA2000*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2172).

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supporting information

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S1. Comment

Acidic rare earth diphosphates of general formula $REHP_2O_7{\cdot}nH_2O$ exhibit interesting luminescent and optical properties (Hraiech *et al.*, 2005 and references herein). The title compound is isostructural with other compounds of formula type $REHP_2O_7{\cdot}4H_2O$, RE = Sm (Chehimi-Moumen *et al.*, 2002), Gd (Hraiech *et al.*, 2005), and Eu (Anna-Rabah *et al.*, 2006).

The structure of $TbHP_2O_7{\cdot}4H_2O$ is made up of TbO_8 polyhedra and HP_2O_7 groups that form a three-dimensional framework. In channels running along *a* (Fig. 2) free water molecules are located which are connected *via* hydrogen bonds with the framework (see hydrogen-bonding Table).

The P_2O_7 group is protonated, with the H atom located at O4 (Fig. 1), as also indicated by elongation of the corresponding P—O distance. The bridging angle P1—O7—P2 between the two PO_4 tetrahedra is 130.73 (11)°.

S2. Experimental

An aqueous solution of $TbCl_3{\cdot}6H_2O$ (0.1*M*) was added dropwise to anhydrous $Na_4P_2O_7$ dissolved in destilled water (0.1*M*). The pH of the mixture was controlled with diluted hydrochloric acid to be slightly acidic, and the solution was stirred for two h at room temperature. Prismatic-shaped colourless crystals with a maximal size of 0.3 mm formed after a few days on slow evaporation.

S3. Refinement

The H atoms were localized from a difference Fourier map. Their coordinates were refined independently with O—H distances restrained to 0.82 (1) Å. The isotropic temperature parameters of the H atoms were refined with $1.2U_{eq}$ of the parent atom. The H111—O11—H112 angle of the free water molecule was restrained to 109.47 (10)°.

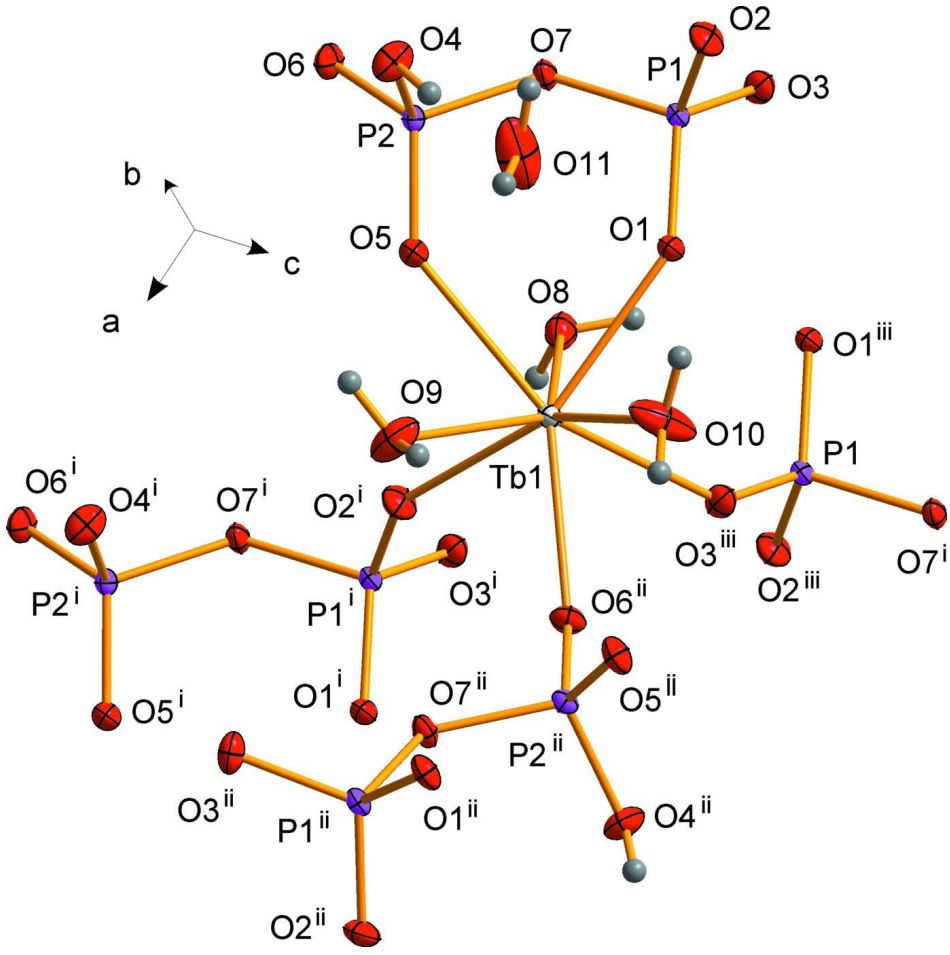

Figure 1

Part of the structure of $HTbP_2O_7{\cdot}4H_2O$ drawn with displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) 1.5 - *x*, -1/2 + *y*, 1.5 - *z*; (iii) 1 - *x*, 1 - *y*, 2 - *z*]

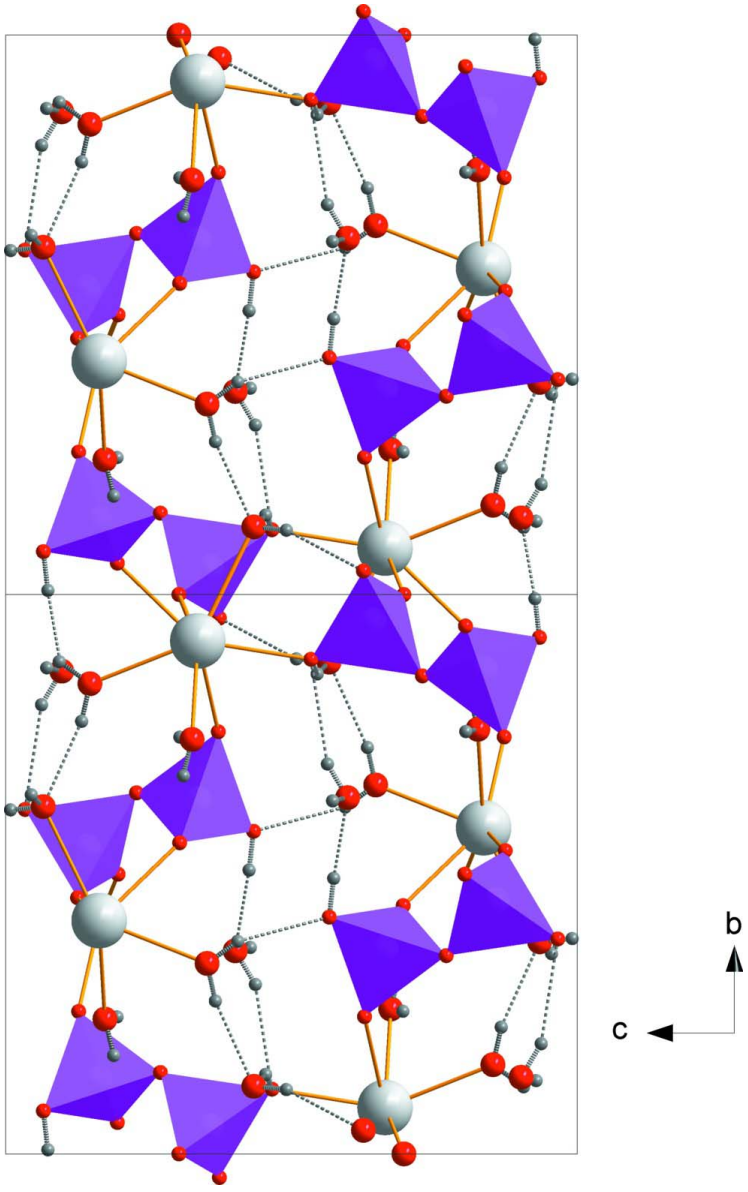

Figure 2

The packing of $TbHP_2O_7{\cdot}4H_2O$ viewed along **a**. Hydrogen bonds are represented by dashed lines. Colour code: Pink (P_2O_7 polyhedra), red spheres (O), grey spheres (Tb), dark grey spheres (H). All atoms are displayed with arbitrary radii. For clarity, O atoms belonging to PO_4 tetrahedra have a smaller size than O atoms of water molecules. O atoms that would obscure H atoms important for understanding the hydrogen bonding scheme are plotted semitransparently.

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Crystal data

$TbHP_2O_7{\cdot}4H_2O$
$M_r = 405.9$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 6.6006\ (6)$ Å
$b = 11.4744\ (9)$ Å
$c = 11.7252\ (13)$ Å
$\beta = 92.150\ (8)°$
$V = 887.42\ (15)$ Å^3
$Z = 4$
$F(000) = 768$
$D_x = 3.037$ Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71069 Å
Cell parameters from 972 reflections
θ = 2.5–26.5°
μ = 8.38 mm^{-1}
T = 295 K
Prism, colorless
0.14 × 0.06 × 0.03 mm

Data collection

Oxford Diffraction CCD diffractometer
Radiation source: X-ray tube
Graphite monochromator
Detector resolution: 8.3438 pixels mm^{-1}
ω scans
Absorption correction: analytical [*CrysAlis RED* (Oxford Diffraction, 2005), using a multifaceted crystal model based on expressions derived by Clark & Reid (1995)]
T_{min} = 0.329, T_{max} = 0.635
8671 measured reflections
1850 independent reflections
1628 reflections with $I > 3\sigma(I)$
R_{int} = 0.019
θ_{max} = 26.6°, θ_{min} = 2.5°
h = −8→7
k = −14→14
l = −14→14

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.011
$wR(F^2)$ = 0.034
S = 1.21
1850 reflections
155 parameters
10 restraints
9 constraints
H atoms treated by a mixture of independent and constrained refinement
Weighting scheme based on measured s.u.'s $w = 1/[\sigma^2(I) + 0.0004I^2]$
$(\Delta/\sigma)_{max}$ = 0.009
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Extinction correction: B-C type 1 Lorentzian isotropic [Becker, P. J. & Coppens, P. (1974). Acta Cryst. A30, 129–147]
Extinction coefficient: 2.9 (8)

Special details

Refinement. The refinement was carried out against all reflections. The conventional *R*-factor is always based on *F*. The goodness of fit as well as the weighted *R*-factor are based on *F* and F^2 for refinement carried out on *F* and F^2, respectively. The threshold expression is used only for calculating *R*-factors *etc*. and it is not relevant to the choice of reflections for refinement.
The program used for refinement, Jana2000, uses the weighting scheme based on the experimental expectations, see _refine_ls_weighting_details, that does not force *S* to be one. Therefore the values of *S* may be larger then the ones from the *SHELX* program.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Tb1	0.755557 (17)	0.417027 (10)	0.836213 (10)	0.00831 (5)
P1	0.25551 (9)	0.54805 (6)	0.85787 (5)	0.00834 (18)
P2	0.47954 (9)	0.63300 (5)	0.66266 (5)	0.00860 (18)
O1	0.4213 (3)	0.45787 (15)	0.87403 (15)	0.0122 (5)
O2	0.0629 (3)	0.50007 (16)	0.80317 (16)	0.0157 (5)
O3	0.2158 (3)	0.61576 (15)	0.96588 (15)	0.0149 (5)
O4	0.3423 (3)	0.57670 (15)	0.56618 (17)	0.0169 (6)
O5	0.6553 (3)	0.55618 (15)	0.69557 (16)	0.0137 (5)
O6	0.5259 (2)	0.75465 (15)	0.62791 (15)	0.0135 (5)
O7	0.3378 (3)	0.64547 (14)	0.77094 (14)	0.0112 (5)
O8	0.7671 (3)	0.62083 (18)	0.93419 (17)	0.0177 (6)
O9	0.8201 (4)	0.34050 (17)	0.64753 (17)	0.0252 (7)

O10	0.5535 (3)	0.24098 (19)	0.8262 (2)	0.0333 (7)
O11	0.2577 (4)	0.36300 (19)	0.5980 (2)	0.0394 (9)
H81	0.697 (4)	0.614 (3)	0.9904 (18)	0.0212*
H111	0.294 (4)	0.3021 (18)	0.572 (3)	0.0472*
H82	0.881 (2)	0.643 (3)	0.955 (2)	0.0212*
H112	0.141 (2)	0.375 (3)	0.577 (3)	0.0472*
H101	0.593 (5)	0.1757 (15)	0.810 (3)	0.04*
H91	0.776 (5)	0.380 (3)	0.593 (2)	0.0303*
H92	0.777 (4)	0.2742 (13)	0.633 (3)	0.0303*
H41	0.323 (4)	0.5072 (10)	0.574 (3)	0.0203*
H102	0.434 (2)	0.243 (3)	0.807 (3)	0.04*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tb1	0.00694 (8)	0.00827 (8)	0.00975 (8)	0.00064 (4)	0.00087 (5)	0.00041 (4)
P1	0.0067 (3)	0.0093 (3)	0.0092 (3)	0.0008 (2)	0.0021 (2)	0.0011 (2)
P2	0.0082 (3)	0.0085 (3)	0.0092 (3)	−0.0007 (2)	0.0009 (2)	0.0011 (2)
O1	0.0097 (9)	0.0127 (8)	0.0146 (9)	0.0029 (7)	0.0037 (7)	0.0037 (7)
O2	0.0095 (9)	0.0182 (9)	0.0192 (10)	−0.0040 (7)	−0.0004 (8)	0.0001 (7)
O3	0.0201 (10)	0.0137 (8)	0.0110 (10)	0.0048 (8)	0.0034 (7)	−0.0010 (7)
O4	0.0225 (11)	0.0120 (9)	0.0157 (10)	−0.0038 (8)	−0.0041 (8)	−0.0012 (7)
O5	0.0113 (9)	0.0156 (9)	0.0143 (10)	0.0031 (7)	0.0031 (8)	0.0039 (7)
O6	0.0141 (9)	0.0107 (8)	0.0159 (9)	−0.0034 (7)	0.0016 (7)	0.0022 (7)
O7	0.0115 (9)	0.0091 (8)	0.0133 (9)	0.0003 (7)	0.0055 (7)	0.0018 (7)
O8	0.0163 (11)	0.0208 (10)	0.0160 (11)	−0.0033 (9)	0.0013 (8)	0.0035 (8)
O9	0.0432 (13)	0.0160 (10)	0.0159 (11)	0.0057 (10)	−0.0061 (9)	−0.0017 (8)
O10	0.0138 (10)	0.0163 (10)	0.0697 (17)	−0.0019 (9)	−0.0005 (11)	−0.0122 (11)
O11	0.0541 (17)	0.0120 (11)	0.0542 (16)	−0.0102 (10)	0.0317 (14)	−0.0094 (10)

Geometric parameters (Å, º)

Tb1—O1	2.3145 (17)	P1—O1	1.5129 (18)
Tb1—O2^{i}	2.2877 (17)	P1—O2	1.5063 (18)
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Tb1—O6^{iii}	2.3842 (17)	P2—O4	1.562 (2)
Tb1—O8	2.605 (2)	P2—O5	1.4957 (19)
Tb1—O9	2.433 (2)	P2—O6	1.4891 (18)
Tb1—O10	2.421 (2)	P2—O7	1.6116 (18)
O1—Tb1—O2^{i}	143.70 (6)	O6^{iii}—Tb1—O8	128.03 (6)
O1—Tb1—O3^{ii}	83.41 (6)	O6^{iii}—Tb1—O9	75.70 (7)
O1—Tb1—O5	75.74 (6)	O6^{iii}—Tb1—O10	71.65 (6)
O1—Tb1—O6^{iii}	134.37 (6)	O8—Tb1—O9	136.20 (6)
O1—Tb1—O8	75.29 (6)	O8—Tb1—O10	141.01 (7)
O1—Tb1—O9	116.61 (7)	O9—Tb1—O10	76.69 (8)
O1—Tb1—O10	69.56 (7)	O1—P1—O2	113.46 (10)

O2^{i}—Tb1—O3^{ii}	101.23 (6)	O1—P1—O3	113.12 (10)
O2^{i}—Tb1—O5	80.10 (6)	O1—P1—O7	107.03 (10)
O2^{i}—Tb1—O6^{iii}	79.67 (6)	O2—P1—O3	111.92 (11)
O2^{i}—Tb1—O8	71.90 (6)	O2—P1—O7	106.35 (10)
O2^{i}—Tb1—O9	79.03 (7)	O3—P1—O7	104.14 (10)
O2^{i}—Tb1—O10	146.08 (7)	O4—P2—O5	111.48 (10)
O3^{ii}—Tb1—O5	143.50 (6)	O4—P2—O6	107.99 (10)
O3^{ii}—Tb1—O6^{iii}	71.04 (6)	O4—P2—O7	105.60 (10)
O3^{ii}—Tb1—O8	73.05 (6)	O5—P2—O6	117.25 (10)
O3^{ii}—Tb1—O9	146.04 (7)	O5—P2—O7	108.46 (10)
O3^{ii}—Tb1—O10	86.44 (8)	O6—P2—O7	105.28 (10)
O5—Tb1—O6^{iii}	143.13 (6)	H81—O8—H82	109 (3)
O5—Tb1—O8	72.85 (6)	H91—O9—H92	104 (3)
O5—Tb1—O9	70.39 (6)	H101—O10—H102	106 (3)
O5—Tb1—O10	112.90 (7)	H111—O11—H112	109 (3)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H41···O11	0.813 (13)	1.736 (14)	2.546 (3)	174 (3)
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O10—H102···O7^{v}	0.812 (16)	2.28 (2)	2.991 (3)	147 (3)
O11—H111···O3^{v}	0.80 (2)	2.18 (2)	2.941 (3)	157 (3)

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