Terbium(III) hydrogendiphosphate(V) tetrahydrate

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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

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

Data collection

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

Refinement

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

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 (19)
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*.

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

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supplementary materials

Terbium(III) hydrogendiphosphate(V) tetrahydrate

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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 frame-work. 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)°.

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.

Refinement

The H atoms were localized from a difference Fourier map. Their coordinates were refined independently with O—H dis-tances 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)°.
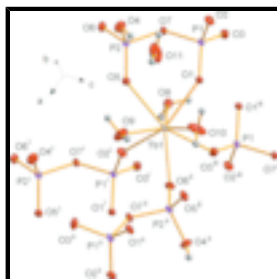
Figures

Fig. 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) $1 - x, 1 - y, 2 - z$]
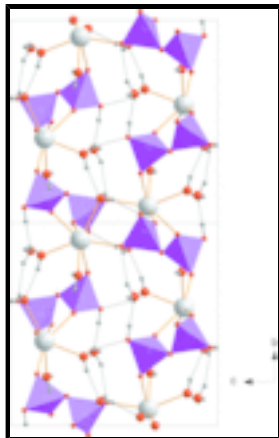
supplementary materials

Fig. 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.

Terbium(III) hydrogendiphosphate(V) tetrahydrate

Crystal data

$TbHP_2O_7 \cdot 4H_2O$	$F_{000} = 768$
$M_r = 405.9$	$D_x = 3.037$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71069$ Å
Hall symbol: -P 2yn	Cell parameters from 972 reflections
$a = 6.6006$ (6) Å	$\theta = 2.5–26.5°$
$b = 11.4744$ (9) Å	$\mu = 8.38$ mm^{-1}
$c = 11.7252$ (13) Å	$T = 295$ K
$\beta = 92.150$ (8)°	Prism, colorless
$V = 887.42$ (15) Å^3	$0.14 \times 0.06 \times 0.03$ mm
$Z = 4$	

Data collection

Oxford Diffraction CCD diffractometer	1850 independent reflections
Radiation source: X-ray tube	1628 reflections with $I > 3\sigma(I)$
Monochromator: graphite	$R_{int} = 0.019$
Detector resolution: 8.3438 pixels mm^{-1}	$\theta_{max} = 26.6°$
$T = 295$ K	$\theta_{min} = 2.5°$
ω scans	$h = -8 \rightarrow 7$
Absorption correction: analytical [CrysAlis RED (Oxford Diffraction, 2005), using a multifaceted crystal model based on expressions derived by Clark & Reid (1995)]	$k = -14 \rightarrow 14$
$T_{min} = 0.329$, $T_{max} = 0.635$	$l = -14 \rightarrow 14$
8671 measured reflections	

Refinement

Refinement on F^2	H atoms treated by a mixture of

independent and constrained refinement

$R[F^2 > 2\sigma(F^2)] = 0.011$

Weighting scheme based on measured s.u.'s $w = 1/[\sigma^2(I) + 0.0004I^2]$

$wR(F^2) = 0.034$

$(\Delta/\sigma)_{max} = 0.009$

$S = 1.21$

$\Delta\rho_{max} = 0.29$ e Å^{-3}

1850 reflections

$\Delta\rho_{min} = -0.21$ e Å^{-3}

155 parameters

Extinction correction: B-C type 1 Lorentzian isotropic [Becker, P. J. & Coppens, P. (1974). Acta Cryst. A30, 129–147]

10 restraints

Extinction coefficient: 2.9 (8)

9 constraints

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, °)

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)
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)

O3ⁱⁱ—Tb1—O9	146.04 (7)	O5—P2—O7	108.46 (10)
O3ⁱⁱ—Tb1—O10	86.44 (8)	O6—P2—O7	105.28 (10)
O5—Tb1—O6ⁱⁱⁱ	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, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
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O8—H82⋯O3ⁱ	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⋯O8ⁱⁱⁱ	0.828 (18)	1.95 (2)	2.750 (3)	164 (3)
O10—H101⋯O5ⁱⁱⁱ	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: (ii) $-x+1, -y+1, -z+2$; (i) $x+1, y, z$; (iv) $-x+1, -y+1, -z+1$; (iii) $-x+3/2, y-1/2, -z+3/2$; (v) $-x+1/2, y-1/2, -z+3/2$.
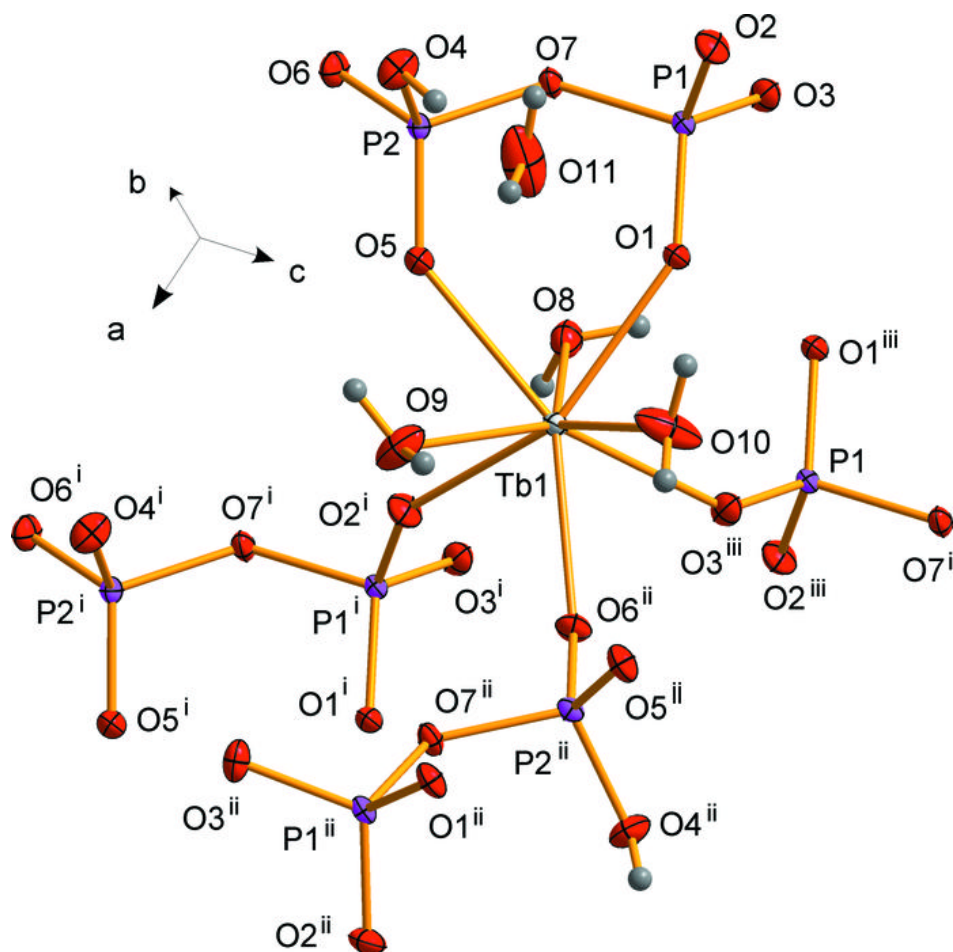
Fig. 1

Fig. 2