

Sodium terbium(III) polyphosphate

Abdelghani Oudahmane,^a Mohamed Daoud,^a
Boumediene Tanouti,^a Daniel Avignant^{b*} and Daniel
Zamboni^b

^aUniversité Cadi Ayyad, Laboratoire de Physico-Chimie des Matériaux et Environnement, Faculté des Sciences Semlalia, Département de Chimie, BP 2390, 40000, Marrakech, Morocco, and ^bUniversité Blaise Pascal, Laboratoire des Matériaux Inorganiques, UMR CNRS 6002, 24 Avenue des Landais, 63177 Aubière, France

Correspondence e-mail: daniel.avignant@univ-bpclermont.fr

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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{P}-\text{O}) = 0.001$ Å; R factor = 0.022; wR factor = 0.055; data-to-parameter ratio = 42.8.

Single crystals of the title compound, $\text{NaTb}(\text{PO}_3)_4$, were obtained by solid-state reaction. This compound belongs to type II of long-chain polyphosphates with the general formula $A^{\text{I}}B^{\text{III}}(\text{PO}_3)_4$. It is isotypic with the $\text{NaNd}(\text{PO}_3)_4$ and $\text{NaEr}(\text{PO}_3)_4$ homologues. The crystal structure is built up of infinite crenelated chains of corner-sharing PO_4 tetrahedra with a repeating unit of four tetrahedra. These chains, extending parallel to [100], are linked by isolated TbO_8 square antiprisms, forming a three-dimensional framework. The Na^+ ions are located in channels running along [010] and are surrounded by six oxygen atoms in a distorted octahedral environment within a cut-off distance <2.9 Å.

Related literature

All $\text{NaN}(\text{PO}_3)_4$ polyphosphates reported up to now, where N is a trivalent rare earth element, belong to type II of long-chain polyphosphates $A^{\text{I}}B^{\text{III}}(\text{PO}_3)_4$. For corresponding isotypic crystal structures, see: El Masloumi *et al.* (2005) and Zhu *et al.* (2006) for $N = \text{La}$; Zhu *et al.* (2008) for Ce and Eu; Horchani-Naifer *et al.* (2009) for Pr; Koizumi *et al.* (1976) for Nd; Amami *et al.* (2005) for Gd; El Masloumi *et al.* (2008) for Y; Amami *et al.* (2004) for Ho; Maksimova *et al.* (1988) for Er. For other isotypic polyphosphates with general composition $A^{\text{I}}B^{\text{III}}(\text{PO}_3)_4$, see: Linde *et al.* (1983) for $AB = \text{KCe}$; Naili *et al.* (2006) for AgGd ; Belam *et al.* (2007) and Jaoudi *et al.* (2003); for NaBi. For a review on the crystal chemistry of polyphosphates, see: Durif (1995).

Experimental

Crystal data

$\text{NaTb}(\text{PO}_3)_4$
 $M_r = 497.79$
Monoclinic, $P2_1/n$

$a = 7.1712$ (1) Å
 $b = 13.0512$ (2) Å
 $c = 9.7547$ (1) Å

$\beta = 90.604$ (1)°
 $V = 912.92$ (2) Å³
 $Z = 4$
Mo $K\alpha$ radiation

$\mu = 8.56$ mm⁻¹
 $T = 296$ K
 $0.41 \times 0.12 \times 0.10$ mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2008)
 $T_{\text{min}} = 0.127$, $T_{\text{max}} = 0.478$

26640 measured reflections
6971 independent reflections
6445 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.055$
 $S = 1.10$
6971 reflections

163 parameters
 $\Delta\rho_{\text{max}} = 2.12$ e Å⁻³
 $\Delta\rho_{\text{min}} = -2.03$ e Å⁻³

Table 1

Selected bond lengths (Å).

P1—O10	1.4896 (14)	P3—O11	1.4827 (13)
P1—O6	1.4918 (13)	P3—O1 ⁱⁱⁱ	1.4868 (13)
P1—O8 ⁱ	1.5857 (13)	P3—O7 ^{iv}	1.5897 (13)
P1—O5	1.5876 (12)	P3—O5	1.5915 (13)
P2—O3 ⁱⁱ	1.4792 (13)	P4—O9 ⁱⁱ	1.4853 (13)
P2—O4	1.4858 (13)	P4—O12 ^v	1.4867 (13)
P2—O8	1.5768 (13)	P4—O2	1.5952 (13)
P2—O2	1.5937 (13)	P4—O7	1.5997 (13)

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

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2313).

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Sodium terbium(III) polyphosphate

A. Oudahmane, M. Daoud, B. Tanouti, D. Avignant and D. Zambon

Comment

It is now well established that long-chain polyphosphates with general formula $A^I B^{III}(\text{PO}_3)_4$ can be divided in seven structural types (Jaoudi *et al.*, 2003). All long-chain polyphosphates of formula $\text{NaLnP}_4\text{O}_{12}$ (Ln = rare earth element) reported up to now (El Masloumi *et al.* 2005; Zhu *et al.* 2006; Zhu *et al.* 2008; Horchani-Naifer *et al.* 2009; Koizumi *et al.* 1976; Amami *et al.* 2005; El Masloumi *et al.* 2008; Amami *et al.* 2004; Maksimova *et al.* 1988) belong to the structural type II which has been first described on basis of the $\text{KCe}(\text{PO}_3)_4$ structure (Linde *et al.*, 1983). A few other $A^I B^{III}$ cationic combinations such as AgGd (Naïli *et al.* 2006) and NaBi (Jaoudi *et al.* 2003; Belam *et al.* 2007) also lead to polyphosphates which belong to the structural type II. The structure of the title compound also fits in this isotopic series. The underlying structure has many times been described as built up of $(\text{PO}_3)_\infty$ chains running along the [100] direction and further linked by isolated LnO_8 polyhedra. The resulting three dimensional framework delimits tunnels where the Na^+ ions are located. Instead of using this description, we will focus on the connectivity between the $(\text{PO}_3)_\infty$ chains and the TbO_8 square antiprisms for our account. Each TbO_8 square antiprism is linked to four $(\text{PO}_3)_\infty$ chains by corner-sharing involving the non-bridging oxygen atoms of the PO_4 groups that exhibit the shorter P—O distances within the chain. Their P—O distances range from 1.4792 (13) Å to 1.4918 (13) Å. The chains are crenelated with a repeating unit of four corner-sharing tetrahedra, as displayed in Fig. 1. The repeating unit is built up of PO_4 tetrahedra corresponding to the four crystallographically independent phosphorus atoms labelled from P1 to P4. If the origin of the chain is taken at the O2 position for instance, then the P2 and P4 tetrahedra are the end-groupings of the repeating unit while P1 and P3 tetrahedra are involved in the internal diphosphate group. Each $(\text{PO}_3)_\infty$ chain is linked to four rows of isolated TbO_8 square antiprisms parallel to the direction of the chain (Fig. 2). With the aforementioned origin convention both terminal $\text{P}(2)\text{O}_4$ and $\text{P}(4)\text{O}_4$ tetrahedra are connected in a bidentate fashion on one side of the square face of the archimedean antiprisms of the first row while the internal $\text{P}(1)\text{O}_4$ — $\text{P}(3)\text{O}_4$ diphosphate group is also connected in a bidentate fashion on one side of the square face of the antiprisms of the second row (Fig. 3a and 3 b). Therefore the two rows of TbO_8 polyhedra are translated with a half-period of the $(\text{PO}_3)_\infty$ chain relative to one another (Fig. 3c). Thus the tetrahedra involved in the internal P_2O_7 groups share their non-bridging oxygen atoms with two TbO_8 polyhedra belonging to each of the first and second rows, respectively. Then the $(\text{PO}_3)_\infty$ chain is connected to the third and fourth rows in a similar way but the role played by the couples $\text{P}(1)\text{O}_4$ — $\text{P}(3)\text{O}_4$ and $\text{P}(2)\text{O}_4$ — $\text{P}(4)\text{O}_4$ are inverted, this last becoming the internal diphosphate group.

For a general review on the crystal chemistry of polyphosphates, see: Durif (1995).

Experimental

Crystals of the title compound were synthesized by reacting Tb_4O_7 with $(\text{NH}_4)\text{H}_2\text{PO}_4$ and Na_2CO_3 in a platinum crucible. A mixture of these reagents in the molar ratio 5 : 85 : 10 was used for the synthesis. The mixture has first been heated at 473 K for 12 h, then at 573 K for 12 h and finally at 773 K for 24 h. The muffle furnace was then cooled down first to

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723 K at the rate of 2 K h^{-1} and then to room temperature at the rate of 15 K h^{-1} . Single crystals were extracted from the batch by washing with hot water.

Refinement

The highest residual peak in the final difference Fourier map was located 0.61 \AA from atom Tb and the deepest hole was located 0.45 \AA from atom Tb.

Figures

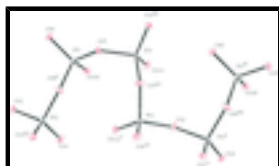


Fig. 1. ORTEP view of the repeating unit of the $(\text{PO}_3)_\infty$ chains. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) $-x+1, -y, -z+2$; (ii) $x+1/2, -y+1/2, z-1/2$; (iii) $x+1/2, -y+1/2, z+1/2$; (iv) $-x+2, -y, -z+2$; (v) $x+1, y, z$.

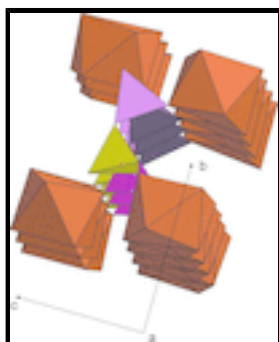


Fig. 2. View of four rows of TbO_8 polyhedra connected through one $(\text{PO}_3)_\infty$ chain.

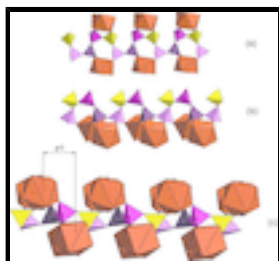


Fig. 3. Details of the connections between the $(\text{PO}_3)_\infty$ chains and the TbO_8 polyhedra: a) view showing the two kind of bidentate attachments. b) view showing the bidentate attachments and the PO_4 groups shared between two TbO_8 square antiprisms belonging to two adjacent rows. c) view showing the shift ($p/2$) of one chain relative to the other.

Sodium terbium polytetrphosphate

Crystal data

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

$M_r = 497.79$

Monoclinic, $P2_1/n$

Hall symbol: $-P 2_1n$

$a = 7.1712 (1) \text{ \AA}$

$b = 13.0512 (2) \text{ \AA}$

$c = 9.7547 (1) \text{ \AA}$

$\beta = 90.604 (1)^\circ$

$V = 912.92 (2) \text{ \AA}^3$

$F(000) = 928$

$D_x = 3.622 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 27177 reflections

$\theta = 3.5\text{--}43.9^\circ$

$\mu = 8.56 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Needle, colourless

$0.41 \times 0.12 \times 0.10 \text{ mm}$

$Z = 4$

Data collection

Bruker APEXII CCD diffractometer	6971 independent reflections
Radiation source: fine-focus sealed tube graphite	6445 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3333 pixels mm^{-1}	$R_{\text{int}} = 0.025$
ω and φ scans	$\theta_{\text{max}} = 43.8^\circ$, $\theta_{\text{min}} = 3.5^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2008)	$h = -13 \rightarrow 8$
$T_{\text{min}} = 0.127$, $T_{\text{max}} = 0.478$	$k = -25 \rightarrow 17$
26640 measured reflections	$l = -19 \rightarrow 18$

Refinement

Refinement on F^2	0 constraints
Least-squares matrix: full	Primary atom site location: structure-invariant direct methods
$R[F^2 > 2\sigma(F^2)] = 0.022$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.055$	$w = 1/[\sigma^2(F_o^2) + (0.0212P)^2 + 1.888P]$
$S = 1.10$	where $P = (F_o^2 + 2F_c^2)/3$
6971 reflections	$(\Delta/\sigma)_{\text{max}} = 0.003$
163 parameters	$\Delta\rho_{\text{max}} = 2.12 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -2.03 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Na	-0.00068 (15)	0.22179 (9)	1.06373 (11)	0.02105 (19)
Tb	0.512736 (10)	0.219027 (5)	0.976594 (7)	0.00611 (2)
P1	0.24948 (6)	0.10137 (3)	1.24460 (4)	0.00585 (6)
P2	0.87630 (6)	0.11488 (3)	0.76336 (4)	0.00525 (5)
P3	0.64720 (6)	0.12784 (3)	1.30443 (4)	0.00514 (5)

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P4	1.26813 (6)	0.09081 (3)	0.69983 (4)	0.00584 (6)
O1	0.22211 (18)	0.28938 (9)	0.89407 (14)	0.01015 (19)
O2	1.08668 (17)	0.08115 (10)	0.79214 (13)	0.00956 (18)
O3	0.36683 (19)	0.31058 (10)	1.14928 (13)	0.01003 (18)
O4	0.79883 (18)	0.14688 (10)	0.89738 (13)	0.00974 (18)
O5	0.42970 (17)	0.12511 (10)	1.33504 (13)	0.00876 (17)
O6	0.09345 (18)	0.16584 (10)	1.29625 (14)	0.01081 (19)
O7	1.28234 (19)	-0.02144 (9)	0.63492 (13)	0.01000 (19)
O8	0.7833 (2)	0.01335 (10)	0.70784 (14)	0.01089 (19)
O9	0.73740 (19)	0.33790 (10)	1.08306 (14)	0.01139 (19)
O10	0.28652 (19)	0.10837 (10)	1.09492 (13)	0.01001 (18)
O11	0.67772 (19)	0.13293 (10)	1.15449 (13)	0.01040 (19)
O12	0.42899 (18)	0.11069 (11)	0.79349 (15)	0.0125 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na	0.0165 (4)	0.0309 (5)	0.0157 (4)	0.0077 (3)	-0.0022 (3)	0.0012 (3)
Tb	0.00563 (3)	0.00740 (3)	0.00529 (3)	0.00035 (2)	0.00018 (2)	-0.00028 (2)
P1	0.00480 (13)	0.00573 (13)	0.00703 (14)	-0.00036 (10)	0.00008 (10)	-0.00060 (11)
P2	0.00561 (13)	0.00468 (12)	0.00548 (13)	0.00011 (10)	0.00126 (10)	0.00071 (10)
P3	0.00532 (13)	0.00475 (12)	0.00534 (13)	-0.00013 (10)	-0.00051 (10)	-0.00029 (10)
P4	0.00542 (13)	0.00510 (13)	0.00700 (14)	0.00056 (10)	0.00050 (10)	0.00007 (11)
O1	0.0087 (4)	0.0083 (4)	0.0134 (5)	0.0018 (3)	-0.0021 (4)	0.0039 (4)
O2	0.0055 (4)	0.0131 (5)	0.0101 (4)	0.0020 (3)	0.0015 (3)	0.0033 (4)
O3	0.0113 (5)	0.0089 (4)	0.0100 (4)	-0.0008 (4)	0.0020 (3)	-0.0047 (4)
O4	0.0090 (4)	0.0131 (5)	0.0071 (4)	0.0025 (4)	0.0029 (3)	-0.0016 (4)
O5	0.0052 (4)	0.0133 (5)	0.0077 (4)	-0.0013 (3)	-0.0003 (3)	-0.0016 (4)
O6	0.0076 (4)	0.0113 (5)	0.0135 (5)	0.0027 (4)	0.0004 (3)	-0.0030 (4)
O7	0.0151 (5)	0.0058 (4)	0.0090 (4)	0.0031 (4)	-0.0026 (4)	-0.0009 (3)
O8	0.0137 (5)	0.0067 (4)	0.0123 (5)	-0.0031 (4)	-0.0005 (4)	-0.0007 (4)
O9	0.0130 (5)	0.0094 (4)	0.0118 (5)	-0.0029 (4)	0.0043 (4)	-0.0046 (4)
O10	0.0121 (5)	0.0105 (4)	0.0074 (4)	-0.0018 (4)	-0.0006 (3)	-0.0001 (3)
O11	0.0106 (5)	0.0140 (5)	0.0066 (4)	0.0017 (4)	0.0009 (3)	0.0027 (4)
O12	0.0070 (4)	0.0156 (5)	0.0149 (5)	-0.0001 (4)	-0.0020 (4)	-0.0064 (4)

Geometric parameters (\AA , $^\circ$)

Na—O4 ⁱ	2.3680 (17)	P2—O4	1.4858 (13)
Na—O9 ⁱ	2.4223 (17)	P2—O8	1.5768 (13)
Na—O6	2.4700 (17)	P2—O2	1.5937 (13)
Na—O1	2.4750 (18)	P2—Na ^{vi}	3.3550 (12)
Na—O10	2.5520 (17)	P3—O11	1.4827 (13)
Na—O11 ⁱ	2.7369 (18)	P3—O1 ^{vii}	1.4868 (13)
Na—P1	2.9554 (11)	P3—O7 ^{viii}	1.5897 (13)
Na—O3	2.9897 (17)	P3—O5	1.5915 (13)
Na—P4 ⁱⁱ	3.2464 (11)	P3—Na ^{vii}	3.3808 (12)

Na—P2 ⁱ	3.3550 (12)	P4—O9 ^{iv}	1.4853 (13)
Na—P3 ⁱⁱⁱ	3.3808 (12)	P4—O12 ^{vi}	1.4867 (13)
Tb—O3	2.3232 (12)	P4—O2	1.5952 (13)
Tb—O12	2.3511 (13)	P4—O7	1.5997 (13)
Tb—O11	2.3729 (12)	P4—Na ^{ix}	3.2464 (12)
Tb—O6 ^{iv}	2.3894 (13)	O1—P3 ⁱⁱⁱ	1.4868 (12)
Tb—O4	2.3930 (12)	O3—P2 ^x	1.4792 (13)
Tb—O1	2.4082 (12)	O4—Na ^{vi}	2.3680 (17)
Tb—O9	2.4589 (13)	O6—Tb ^x	2.3894 (13)
Tb—O10	2.4676 (13)	O7—P3 ^{viii}	1.5897 (13)
P1—O10	1.4896 (14)	O8—P1 ^v	1.5857 (13)
P1—O6	1.4918 (13)	O9—P4 ^x	1.4853 (13)
P1—O8 ^v	1.5857 (13)	O9—Na ^{vi}	2.4223 (17)
P1—O5	1.5876 (12)	O11—Na ^{vi}	2.7369 (18)
P2—O3 ^{iv}	1.4792 (13)	O12—P4 ⁱ	1.4867 (13)
O4 ⁱ —Na—O9 ⁱ	81.14 (5)	O1—Tb—O10	78.97 (4)
O4 ⁱ —Na—O6	131.70 (7)	O9—Tb—O10	127.07 (4)
O9 ⁱ —Na—O6	108.55 (6)	O3—Tb—Na ^{vi}	105.53 (4)
O4 ⁱ —Na—O1	94.62 (6)	O12—Tb—Na ^{vi}	115.25 (4)
O9 ⁱ —Na—O1	109.61 (6)	O11—Tb—Na ^{vi}	49.79 (4)
O6—Na—O1	123.18 (6)	O6 ^{iv} —Tb—Na ^{vi}	85.72 (4)
O4 ⁱ —Na—O10	109.00 (6)	O4—Tb—Na ^{vi}	40.92 (4)
O9 ⁱ —Na—O10	168.27 (7)	O1—Tb—Na ^{vi}	155.88 (4)
O6—Na—O10	60.44 (5)	O9—Tb—Na ^{vi}	42.38 (4)
O1—Na—O10	76.15 (5)	O10—Tb—Na ^{vi}	122.57 (4)
O4 ⁱ —Na—O11 ⁱ	62.55 (5)	O3—Tb—Na	52.13 (4)
O9 ⁱ —Na—O11 ⁱ	65.37 (5)	O12—Tb—Na	86.28 (4)
O6—Na—O11 ⁱ	78.51 (5)	O11—Tb—Na	108.59 (4)
O1—Na—O11 ⁱ	156.84 (6)	O6 ^{iv} —Tb—Na	113.76 (4)
O10—Na—O11 ⁱ	113.41 (6)	O4—Tb—Na	156.20 (4)
O4 ⁱ —Na—P1	123.36 (5)	O1—Tb—Na	39.78 (4)
O9 ⁱ —Na—P1	138.81 (6)	O9—Tb—Na	122.23 (4)
O6—Na—P1	30.27 (3)	O10—Tb—Na	41.86 (4)
O1—Na—P1	101.34 (5)	Na ^{vi} —Tb—Na	153.28 (3)
O10—Na—P1	30.27 (3)	O3—Tb—Na ^{iv}	127.53 (4)
O11 ⁱ —Na—P1	95.15 (4)	O12—Tb—Na ^{iv}	50.51 (4)
O4 ⁱ —Na—O3	151.45 (6)	O11—Tb—Na ^{iv}	144.46 (4)
O9 ⁱ —Na—O3	114.70 (6)	O6 ^{iv} —Tb—Na ^{iv}	33.06 (4)
O6—Na—O3	68.08 (5)	O4—Tb—Na ^{iv}	76.60 (3)
O1—Na—O3	58.34 (5)	O1—Tb—Na ^{iv}	65.71 (4)
O10—Na—O3	58.91 (4)	O9—Tb—Na ^{iv}	107.72 (4)

supplementary materials

O11 ⁱ —Na—O3	144.81 (5)	O10—Tb—Na ^{iv}	124.12 (3)
P1—Na—O3	60.77 (3)	Na ^{vi} —Tb—Na ^{iv}	104.11 (3)
O4 ⁱ —Na—P4 ⁱⁱ	106.40 (5)	Na—Tb—Na ^{iv}	101.88 (2)
O9 ⁱ —Na—P4 ⁱⁱ	25.46 (3)	O10—P1—O6	116.01 (8)
O6—Na—P4 ⁱⁱ	89.03 (4)	O10—P1—O8 ^v	111.91 (7)
O1—Na—P4 ⁱⁱ	109.94 (5)	O6—P1—O8 ^v	108.64 (8)
O10—Na—P4 ⁱⁱ	143.44 (5)	O10—P1—O5	112.35 (7)
O11 ⁱ —Na—P4 ⁱⁱ	75.60 (4)	O6—P1—O5	108.14 (7)
P1—Na—P4 ⁱⁱ	117.77 (4)	O8 ^v —P1—O5	98.28 (7)
O3—Na—P4 ⁱⁱ	92.66 (4)	O10—P1—Na	59.71 (6)
O4 ⁱ —Na—P2 ⁱ	22.72 (3)	O6—P1—Na	56.56 (6)
O9 ⁱ —Na—P2 ⁱ	97.54 (5)	O8 ^v —P1—Na	125.86 (6)
O6—Na—P2 ⁱ	138.23 (5)	O5—P1—Na	135.51 (6)
O1—Na—P2 ⁱ	74.33 (4)	O3 ^{iv} —P2—O4	117.55 (8)
O10—Na—P2 ⁱ	93.86 (4)	O3 ^{iv} —P2—O8	106.17 (8)
O11 ⁱ —Na—P2 ⁱ	83.77 (4)	O4—P2—O8	112.19 (8)
P1—Na—P2 ⁱ	116.91 (4)	O3 ^{iv} —P2—O2	110.49 (7)
O3—Na—P2 ⁱ	128.89 (4)	O4—P2—O2	106.54 (7)
P4 ⁱⁱ —Na—P2 ⁱ	122.67 (3)	O8—P2—O2	102.98 (7)
O4 ⁱ —Na—P3 ⁱⁱⁱ	85.41 (4)	O3 ^{iv} —P2—Na ^{vi}	113.14 (6)
O9 ⁱ —Na—P3 ⁱⁱⁱ	86.83 (4)	O8—P2—Na ^{vi}	139.10 (6)
O6—Na—P3 ⁱⁱⁱ	140.69 (5)	O2—P2—Na ^{vi}	73.82 (5)
O1—Na—P3 ⁱⁱⁱ	23.52 (3)	O11—P3—O1 ^{vii}	119.43 (8)
O10—Na—P3 ⁱⁱⁱ	99.60 (5)	O11—P3—O7 ^{viii}	110.89 (7)
O11 ⁱ —Na—P3 ⁱⁱⁱ	139.46 (4)	O1 ^{vii} —P3—O7 ^{viii}	107.72 (7)
P1—Na—P3 ⁱⁱⁱ	124.20 (4)	O11—P3—O5	109.95 (7)
O3—Na—P3 ⁱⁱⁱ	72.62 (4)	O1 ^{vii} —P3—O5	104.75 (7)
P4 ⁱⁱ —Na—P3 ⁱⁱⁱ	91.96 (3)	O7 ^{viii} —P3—O5	102.65 (7)
P2 ⁱ —Na—P3 ⁱⁱⁱ	70.71 (2)	O11—P3—Na ^{vii}	139.71 (6)
O4 ⁱ —Na—Tb ⁱ	41.45 (3)	O7 ^{viii} —P3—Na ^{vii}	109.24 (5)
O9 ⁱ —Na—Tb ⁱ	43.17 (4)	O5—P3—Na ^{vii}	63.70 (5)
O6—Na—Tb ⁱ	118.09 (5)	O9 ^{iv} —P4—O12 ^{vi}	118.03 (9)
O1—Na—Tb ⁱ	118.61 (5)	O9 ^{iv} —P4—O2	111.53 (7)
O10—Na—Tb ⁱ	143.63 (5)	O12 ^{vi} —P4—O2	107.41 (8)
O11 ⁱ —Na—Tb ⁱ	41.46 (3)	O9 ^{iv} —P4—O7	106.24 (7)
P1—Na—Tb ⁱ	136.04 (4)	O12 ^{vi} —P4—O7	110.53 (7)
O3—Na—Tb ⁱ	157.45 (4)	O2—P4—O7	101.93 (7)
P4 ⁱⁱ —Na—Tb ⁱ	66.69 (2)	O12 ^{vi} —P4—Na ^{ix}	73.95 (7)
P2 ⁱ —Na—Tb ⁱ	62.75 (2)	O2—P4—Na ^{ix}	135.52 (6)
P3 ⁱⁱⁱ —Na—Tb ⁱ	98.09 (3)	O7—P4—Na ^{ix}	119.55 (6)
O3—Tb—O12	138.31 (5)	P3 ⁱⁱⁱ —O1—Tb	141.24 (8)

O3—Tb—O11	86.46 (5)	P3 ⁱⁱⁱ —O1—Na	114.86 (8)
O12—Tb—O11	113.09 (5)	Tb—O1—Na	101.72 (5)
O3—Tb—O6 ^{iv}	108.96 (5)	P2—O2—P4	130.93 (8)
O12—Tb—O6 ^{iv}	83.15 (5)	P2 ^x —O3—Tb	150.04 (8)
O11—Tb—O6 ^{iv}	135.52 (5)	P2 ^x —O3—Na	119.88 (7)
O3—Tb—O4	146.18 (5)	Tb—O3—Na	90.04 (4)
O12—Tb—O4	74.40 (5)	P2—O4—Na ^{vi}	119.28 (8)
O11—Tb—O4	68.11 (4)	P2—O4—Tb	136.43 (8)
O6 ^{iv} —Tb—O4	78.14 (5)	Na ^{vi} —O4—Tb	97.62 (5)
O3—Tb—O1	69.60 (5)	P1—O5—P3	133.93 (8)
O12—Tb—O1	76.24 (5)	P1—O6—Tb ^x	142.34 (8)
O11—Tb—O1	148.01 (5)	P1—O6—Na	93.17 (7)
O6 ^{iv} —Tb—O1	74.31 (5)	Tb ^x —O6—Na	115.10 (6)
O4—Tb—O1	141.63 (5)	P3 ^{viii} —O7—P4	132.38 (8)
O3—Tb—O9	70.57 (4)	P2—O8—P1 ^v	139.15 (9)
O12—Tb—O9	149.47 (5)	P4 ^x —O9—Na ^{vi}	110.04 (8)
O11—Tb—O9	70.76 (5)	P4 ^x —O9—Tb	144.13 (8)
O6 ^{iv} —Tb—O9	75.61 (5)	Na ^{vi} —O9—Tb	94.45 (5)
O4—Tb—O9	79.89 (4)	P1—O10—Tb	128.26 (7)
O1—Tb—O9	117.48 (5)	P1—O10—Na	90.02 (7)
O3—Tb—O10	70.03 (5)	Tb—O10—Na	97.96 (5)
O12—Tb—O10	80.76 (5)	P3—O11—Tb	131.68 (8)
O11—Tb—O10	72.90 (4)	P3—O11—Na ^{vi}	118.15 (8)
O6 ^{iv} —Tb—O10	151.40 (4)	Tb—O11—Na ^{vi}	88.75 (5)
O4—Tb—O10	119.40 (5)	P4 ⁱ —O12—Tb	139.65 (8)

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

Fig. 1

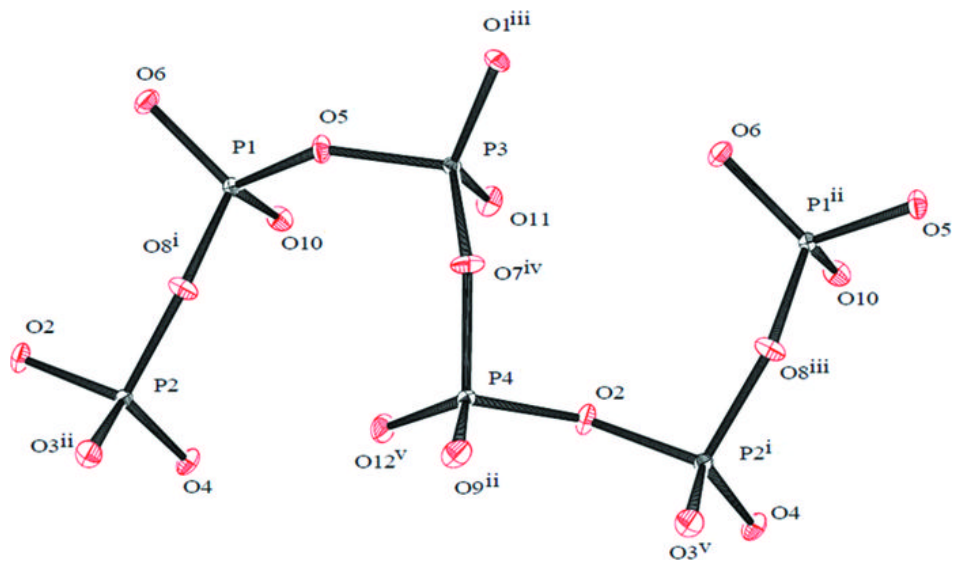


Fig. 2

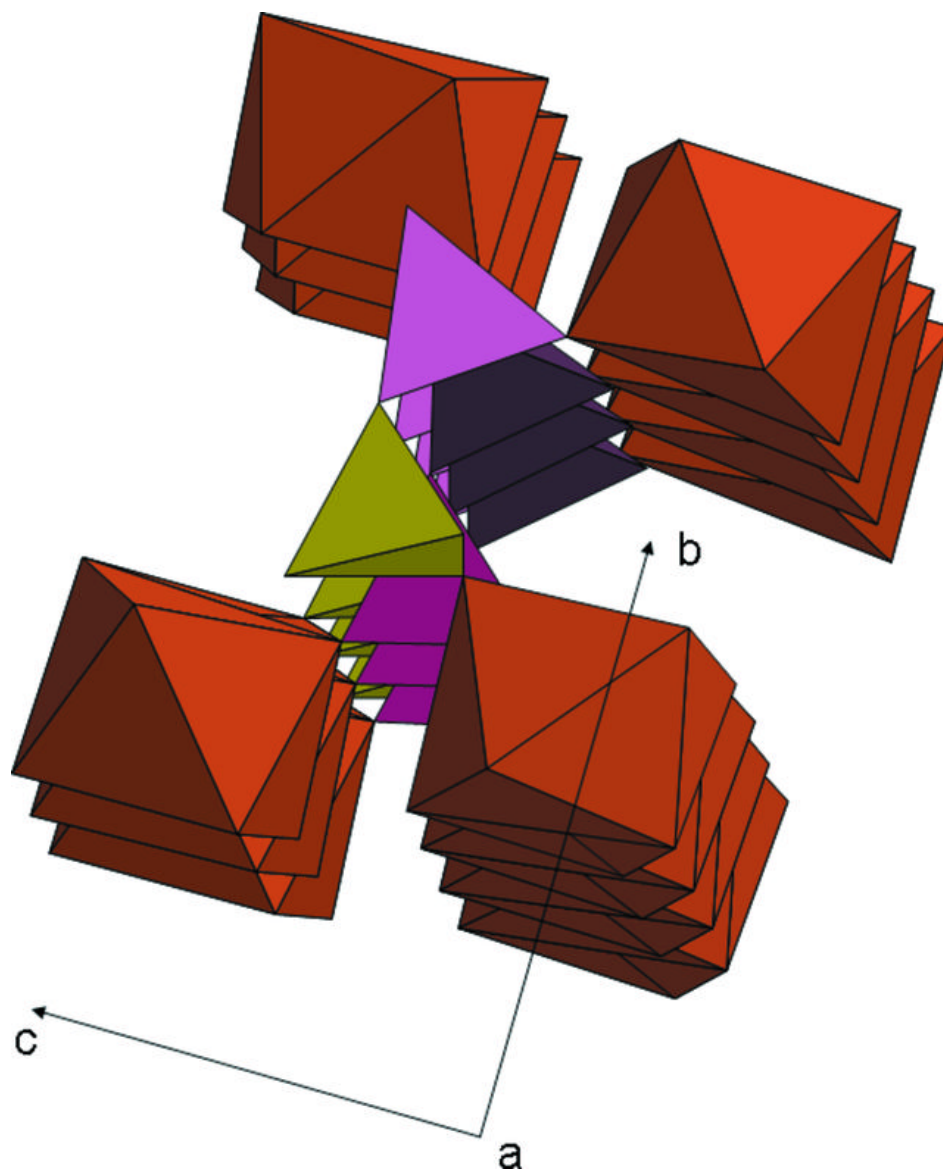


Fig. 3

