

Monoclinic modification of polymorphic
 TbB_3O_6 Alexandra Goriounova, Peter
Held,* Petra Becker and Ladislav
BohatýInstitut für Kristallographie, Universität zu Köln,
Zùlpicher Straße 49b, D-50674 Köln, GermanyCorrespondence e-mail:
peter.held@uni-koeln.de

Terbium triborate, TbB_3O_6 , is confirmed to adopt at least two different structural modifications. Its monoclinic modification represents the terminal member of the isostructural series of REB_3O_6 with $\text{RE} = \text{La-Tb}$, and crystallizes in space group $I2/a$. The structure consists of chains of $[\text{B}_6\text{O}_{12}]_n^{6-}$ building units, that run parallel to the c axis, and tenfold coordinated Tb^{3+} which link the borate chains to give a three-dimensional framework.

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Key indicators

Single-crystal X-ray study
 $T = 293 \text{ K}$
Mean $\sigma(\text{O-B}) = 0.005 \text{ \AA}$
 R factor = 0.036
 wR factor = 0.082
Data-to-parameter ratio = 33.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

Among the binary rare earth oxoborates of the general composition REB_3O_6 only the compounds LaB_3O_6 (Ysker & Hoffmann, 1970; Abdullaev *et al.*, 1981), NdB_3O_6 (Pakhomov *et al.*, 1972), SmB_3O_6 and GdB_3O_6 (Abdullaev *et al.*, 1975) are fully structurally characterized. They form an isostructural series and crystallize in the monoclinic space group $I2/a$. For REB_3O_6 with $\text{RE} = \text{Dy-Lu}$, only a somewhat doubtful indication of their existence can be found in the literature (Tananaev *et al.*, 1975). In earlier works on cell parameters of TbB_3O_6 (Bambauer *et al.*, 1969; Weidelt, 1970), the compound is described as crystallizing with monoclinic symmetry, similar

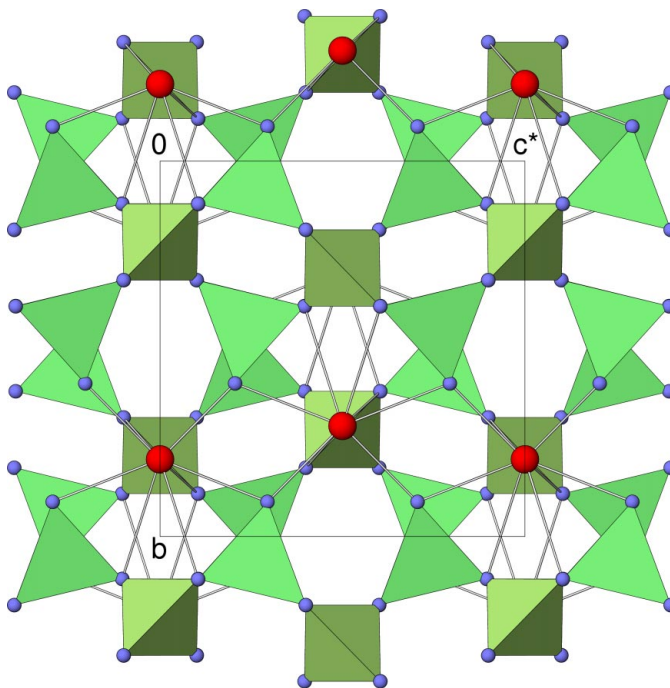


Figure 1

Projection of the structure of the title compound along $[100]$. Tb atoms are shown as red spheres, O atoms as small blue spheres; $[\text{BO}_4]$ groups (olive) and $[\text{BO}_3]$ (green) are represented as polyhedra.

to REB_3O_6 with $RE = La-Gd$, while a later structural analysis on single crystals of TbB_3O_6 reveals an orthorhombic symmetry ($Pbnm$ or $Pbn2_1$) of the compound (Pakhomov *et al.*, 1971). Very recently the crystal structure of orthorhombic TbB_3O_6 has been solved by Nikelski & Schleid (2003); the results of our own structure determination of the orthorhombic structure of TbB_3O_6 are in good agreement with the data of these authors. Orthorhombic TbB_3O_6 crystallizes in space group $Pnma$ (No. 62); $a = 15.9770(7)$ Å, $b = 7.4136(3)$ Å, $c = 12.2905(6)$ Å and $Z = 16$.

During our systematic investigations of the crystal chemistry and crystal-growth conditions of binary rare earth borates, methods of synthesis from ternary systems were established that led to single crystals of REB_3O_6 with $RE = La-Tb$. Depending on the composition of the ternary system used, orthorhombic as well as monoclinic crystals of TbB_3O_6 were grown. The crystal structure of the monoclinic modification of TbB_3O_6 is presented here for the first time. Monoclinic TbB_3O_6 is isostructural with REB_3O_6 with $RE = La, Nd, Sm$ and Gd , and crystallizes in space group $I2/a$ (No. 15). The structure consists of infinite chains of $[B_6O_{12}]_n^{6-}$ running along the c axis. Tenfold coordinated Tb atoms link the borate chains to give a three-dimensional framework. The complex borate polyanion ($4D2T:D < DTTD > D$; Becker, 2001) is composed of $[BO_4]$ tetrahedra that are linked *via* two $[BO_3]$ triangles to the adjacent $[BO_4]$ tetrahedra on both sides. Each $[BO_3]$ is connected to two $[BO_4]$, and the bridging O atoms belong also to the coordination polyhedron of one Tb. Each of the non-bridging O atoms of the $[BO_3]$ groups coordinates to two Tb atoms. The irregular $[TbO_{10}]$ coordination polyhedra are connected *via* edges to form infinite chains along the c axis.

The mean B—O distances of 1.370 Å for $[BO_3]$ and 1.465 Å for $[BO_4]$ fit well into the range of B—O distances found for many other borate structures [see, for comparison, Zobetz (1982) and Zobetz (1990)]. However, the $[BO_3]$ triangles are substantially distorted, with a B—O distance of non-bridging atoms O2 that is significantly shorter than the B—O distances of bridging atoms O1 and O3 (see Table 1).

According to the results of structural investigations of TbB_3O_6 , the compound seems to play the role of a transient point within the series of REB_3O_6 with $RE = La-Lu$. TbB_3O_6 shows a structural flexibility that allows it to be on one hand the terminal member of the isostructural monoclinic series of REB_3O_6 with $RE = La-Tb$, but probably also the starting point of an assumed orthorhombic series for the smaller lanthanides Dy—Lu, that still has to be synthesized.

This structural variability of TbB_3O_6 is further corroborated by a structural phase transition at about 143 K that was recently discovered in our group.

Experimental

Crystals of monoclinic TbB_3O_6 were grown in the ternary system $Tb_2O_3-B_2O_3-PbO$. A homogenized powder mixture of Tb_4O_7 (99.9%, Alfa Aesar), H_3BO_3 (99.8%, Merck) and PbO (99%, Riedel de Haën), in a mol% ratio of 1.1:87.9:11.0, was heated in a covered platinum crucible to 1213 K and subsequently cooled at a rate of

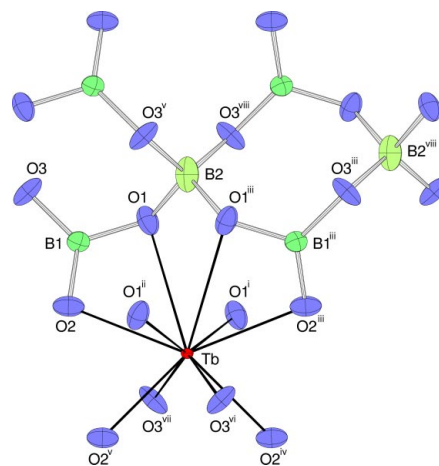


Figure 2
ORTEP projection (Burnett & Johnson, 1996) of the title compound, with the atom-numbering scheme (projection along $[100]$). Atoms are drawn as 50% probability ellipsoids.

about 3.4 K h^{-1} to 943 K. Transparent single crystals of the title compound were separated from the lead borate flux using hot dilute HCl.

Crystal data

TbB_3O_6	$D_x = 4.910$ Mg m^{-3}
$M_r = 287.35$	Mo $K\alpha$ radiation
Monoclinic, $I2/a$	Cell parameters from 25 reflections
$a = 6.2147(4)$ Å	$\theta = 12.3-19.1^\circ$
$b = 8.0225(5)$ Å	$\mu = 18.13$ mm $^{-1}$
$c = 7.8111(7)$ Å	$T = 293(2)$ K
$\beta = 93.44(1)^\circ$	Parallelepiped, colourless
$V = 388.74(5)$ Å 3	$0.15 \times 0.13 \times 0.11$ mm
$Z = 4$	

Data collection

Nonius MACH3 diffractometer	$R_{int} = 0.094$
$\omega/2\theta$ scans	$\theta_{max} = 44.9^\circ$
Absorption correction: ψ scan	$h = -12 \rightarrow 12$
<i>MolEN</i> (Fair, 1990)	$k = -15 \rightarrow 15$
$T_{min} = 0.082$, $T_{max} = 0.136$	$l = -15 \rightarrow 15$
5729 measured reflections	3 standard reflections
1602 independent reflections	frequency: 60 min
1321 reflections with $I > 2\sigma(I)$	intensity decay: 4.5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2 + 2.4096P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.082$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.07$	$\Delta\rho_{max} = 2.91$ e Å $^{-3}$
1602 reflections	$\Delta\rho_{min} = -2.45$ e Å $^{-3}$
48 parameters	Extinction correction: <i>SHELXL97</i>
	Extinction coefficient: 0.0023 (4)

Table 1
Selected geometric parameters (Å).

Tb1—O2 ⁱ	2.323 (3)	B1—O1	1.414 (5)
Tb1—O3 ⁱⁱⁱ	2.460 (3)	B1—O2	1.311 (6)
Tb1—O2	2.477 (3)	B1—O3	1.385 (5)
Tb1—O1 ⁱⁱⁱ	2.485 (3)	B2—O3 ^{iv}	1.440 (5)
Tb1—O1	2.823 (4)	B2—O1	1.489 (6)

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

The highest peak and deepest hole are located 0.61 and 0.97 Å, respectively, from Tb1.

Data collection: *MACH3* (Enraf–Nonius, 1993); cell refinement: *MACH3*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2002) and *ORTEP* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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