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Bismuth octaborate, $Bi_2B_8O_{15}$

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In the title compound, $Bi_2B_8O_{15}$, the Bi atom is coordinated to five or six O atoms. The B atoms exhibit two kinds of hybridization, sp^2 and sp^3, seen in the BO_3 triangles and BO_4 tetrahedra, respectively. Three BO_3 triangles are connected to form a B_3O_6 planar ring. All atoms in the structure are connected together to form an infinite three-dimensional network.

Comment

The growing field of non-linear optical (NLO) research and applications still requires new materials for developing new laser sources and extending applications. Much effort has been devoted to developing the borate series. Among them, β-BaB_2O_4 (BBO), LiB_3O_5 (LBO), $YCa_4(BO_3)_3O$ (YCOB) and BiB_3O_6 (BIBO) have been studied as promising NLO crystals (Becker, 1998). The B atom usually coordinates with either three or four O atoms, forming BO_3 or BO_4 groups, where the electronic orbitals are hybridized to a planar sp^2 or a three-dimensional sp^3 configuration. The structural unit can comprise several different B_mO_n groups through different combinations, such as the B_3O_6 group in BBO, the B_3O_7 group in LBO, and a combination of BO_3 and BO_4 groups as in BIBO (Xue & Zhang, 1997). Levin & McDaniel (1962) investigated the binary system Bi_2O_3–B_2O_3 and described $Bi_2B_8O_{15}$ for the first time. Based on their study, the authors have grown a low-temperature form of $Bi_2B_8O_{15}$ single crystals. To our best knowledge, $Bi_2B_8O_{15}$ has not been grown as a single crystal in the past.

The crystal structure of $Bi_2B_8O_{15}$ is shown in Fig. 2. The three-dimensional framework is composed of the following principal components: (*a*) Bi atoms of fivefold and sixfold coordination, (*b*) BO_3 triangles, (*c*) B_3O_6 planar rings and (*d*) BO_4 tetrahedra. The BiO_5 and BiO_6 polyhedra are linked to B_3O_6 rings *via* BO_3 triangles or BO_4 tetrahedra. The ratio of BO_3 triangles to BO_4 tetrahedra is 3:1. The lone-pair electrons are supposedly located near the Bi cation (Hellwig *et al.*, 1999).

The crystal consists of nearly planar B_3O_6 rings bonded through Bi cations, as shown in Fig. 1. The average B—O distances in the B_3O_6 six-membered rings is 1.39 Å. The B2—O3 bond length [1.44 (3) Å] is significantly longer than the others, including B3—O3 [1.36 (3) Å] and B1—O2 [1.34 (3) Å]. The average B—O—B angle is 120.8° with the angles B1—O2—B3 [119.3 (16)°] and B3—O3—B2 [121.0 (17)°] showing the the largest deviation. The Bi atom has a distorted octahedral coordination, with average Bi—O distance of 2.396 Å.

The anionic group theory (Chen & Wu, 1989) revealed that the B_3O_6 groups in BBO play an important role in its excellent NLO responses. Accordingly, the NLO-active clusters in $Bi_2B_8O_{15}$ should be B_3O_6 rings. The additional presence of distorted BiO_6 and BiO_5 polyhedra and lone-pair electrons of Bi may enhance the NLO effect (Zhang & Wang, 1996). The structural features indicated above show that $Bi_2B_8O_{15}$ is a potential NLO crystal and, in fact, the authors observed a strong second harmonic generation (SHG) effect by irradiation with IR light.

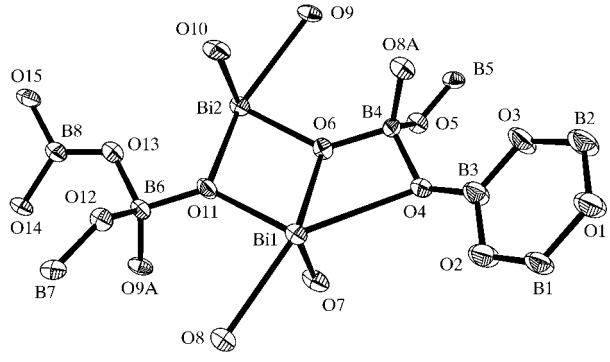

Figure 1
The molecular structure of $Bi_2B_8O_{15}$ showing 50% probability displacement ellipsoids.

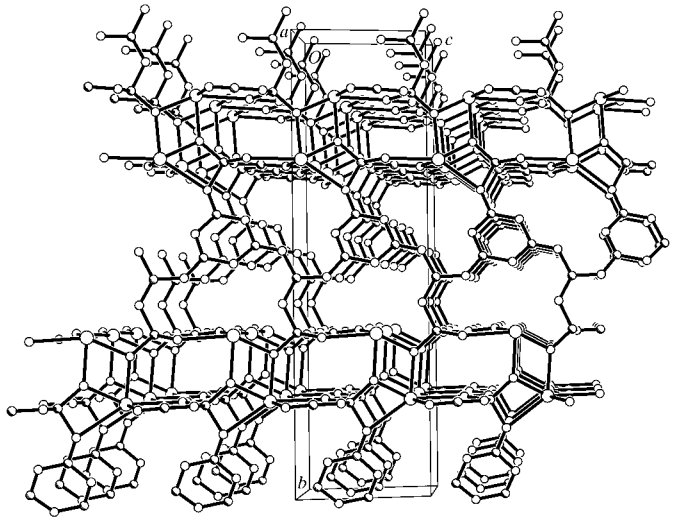

Figure 2
Packing diagram showing the parallel (010) layers of sixfold coordinated Bi atoms alternating with borate layers and B_3O_6 rings.

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Experimental

Since the crystal melted congruently, the top-seeded solution method was used. $Bi_2B_8O_{15}$ contains two modifications. The low-temperature form was obtained by rapidly cooling the crystal after its growth ended.

Crystal data

$Bi_2B_8O_{15}$	D_x = 4.152 Mg m^{-3}
M_r = 744.44	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 40 reflections
a = 4.3142 (7) Å	θ = 5.5–15.9°
b = 22.141 (4) Å	μ = 29.60 mm^{-1}
c = 6.4675 (10) Å	T = 293 (2) K
β = 105.441 (11)°	Prism, colourless
V = 595.49 (16) Å^3	0.10 × 0.10 × 0.09 mm
Z = 2	

Data collection

Bruker $P4$ diffractometer	R_{int} = 0.072
$\theta/2\theta$ scans	θ_{max} = 35.0°
Absorption correction: ψ scan (*XSCANS*; Siemens, 1996)	$h = -6 \rightarrow 1$
T_{min} = 0.05, T_{max} = 0.07	$k = -35 \rightarrow 1$
3607 measured reflections	$l = -10 \rightarrow 10$
2751 independent reflections	3 standard reflections every 97 reflections
2655 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1457P)^2 + 1.4317P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.070	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.171	$\Delta\rho_{max}$ = 11.45 e Å^{-3}
S = 1.07	$\Delta\rho_{min}$ = −6.20 e Å^{-3}
2751 reflections	Absolute structure: Flack (1983)
227 parameters	Flack parameter = 0.19 (6)

The structure was refined as a racemic twin with components 0.81 (6) and 0.19 (6). 856 Friedel pairs were used. Because the anisotropic atomic displacement parameters (ADP) of the light atoms are very large in this kind of structure, the *SHELXTL* commands *DELU*, *ISOR* and *SIMU* (Bruker, 1997) were used for all atoms in the refinement to restrain their ADPs in the direction of the bond to be equal within an s.u. of 0.01; atoms closer than 1.7 Å were restrained with an s.u. of 0.04 to have the same ADP components and to approximate isotropic behaviour with an s.u. of 0.1. The high R factor and large residual electron density is probably due to the poor crystal quality (R_{int} = 0.072). $\Delta\rho_{max}$ was located at the position x = 0.2966, y = 0.2605, z = 0.115, at a distance of 0.66 Å from the Bi1 atom.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1016). Services for accessing these data are described at the back of the journal.

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