Synthesis and X-ray crystal structures of two new alkaline-earth metal borates: $SrBO_2(OH)$ and $Ba_3B_6O_9(OH)_6$

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Using hydrothermal techniques, two new compounds—strontium borate $SrBO_2(OH)$ and barium polyborate $Ba_3B_6O_9(OH)_6$—have been prepared. The structures of the title compounds were solved by single-crystal X-ray diffraction analysis. In the structure of $SrBO_2(OH)$, the Sr^{2+} ion is surrounded by eight oxygen atoms and the borate ion is identified as an individual $[BO_2(OH)]^{2-}$ group. The structure of $Ba_3B_6O_9(OH)_6$ can be regarded as constructed from anionic borate chains, the negative charges of which are compensated for by the Ba^{2+} cations residing between the adjacent chains. The unusual feature of this compound can also be described in terms of infinite chains of B_3O_3 six-membered rings sharing B atoms, which are all tetrahedrally coordinated by oxygen atoms. The materials have also been characterized by infrared and energy dispersive spectroscopies, thermal analysis, and second harmonic generation powder measurement.

Introduction

The synthesis and structural studies of borates have attracted considerable interest in these past ten years because the extremely wide variability of borate crystal chemistry allows the creation of very different structure types.[1] The study of borates is of interest both academically and commercially. In the late 1980s, β-$Ba_2B_2O_4$ (BBO) was reported to exhibit efficient bulk second-order nonlinear optical (NLO) effects,[2] which can be exploited in the manufacture of second harmonic generation (SHG), electro-optical and photorefractive devices. Furthermore, following the advent of $K[B_5O_6(OH)_4]\cdot2H_2O$ (KB5),[3] LiB_3O_5 (LBO)[4] and $Sr_2Be_2B_2O_7$ (SBBO),[5] the synthesis of borate compounds continues to be an important research subject because these materials have enormous potential as NLO materials,[6] as the hosts of laser and luminescent materials, and as thermoelectronic cathodal materials for microgenerators.[7]

Nevertheless, it is notable that a borate crystals are generally grown by high temperature methods, exemplified by the high temperature flux and melt techniques.[2–5] In addition, there are some reports on the growth of borates by the sol–gel technique.[8] It is only during the last two decades that our knowledge about the behavior of boron in hydrothermal solutions and its interaction with various metal cations has increased substantially, and borates synthesized by using hydrothermal techniques have occasionally appeared in the literature.[9,10]

In general, alkaline-earth metal borates exhibit framework structures made up of BO_4 tetrahedra and BO_3 triangles. Only a few compounds show isolated islands, and layered structural features and chain arrangements are absent. The structures of strontium and barium borates have been addressed in the past, among the few strontium borates are SrB_2O_4, consisting of slightly puckered anionic layers with the composition $(B_2O_4)_n^{2n-}$,[11] SrB_4O_7, with a three-dimensional network structure,[12] $Sr_2B_2O_5$, composed of SrO_7 and SrO_6 polyhedra and isolated B_2O_5 groups,[13] and $SrB_6O_{10}\cdot4H_2O$, with infinite sheets of composition $n[B_6O_9(OH)_2]^{2-}$.[14] Previously reported barium borates include BaB_2O_4, containing isolated borate anions $(B_3O_6)^{3-}$,[15] BaB_4O_7[16] and BaB_8O_{13},[17] with a framework structure, $Ba[B(OH)_4]_2\cdot H_2O$[18] and $Ba[B(OH)_4]_2$,[19] containing discrete tetrahedral $B(OH)_4$ groups, and $Ba_2[B_5O_8(OH)_2](OH)$,[20] $Ba[B_5O_8(OH)](OH)\cdot H_2O$ and $Ba_5[B_{20}O_{33}(OH)_4]\cdot H_2O$ with sheet

structures.[21] No barium borate chain structure has yet been discovered prior to this work. In this paper, we report the synthesis and X-ray crystal structures of two new hydrothermally-synthesized compounds—strontium borate $SrBO_2(OH)$ (1) and barium borate $Ba_3B_6O_9(OH)_6$ (2), containing polyborate chains.

Experimental

Synthesis

1 and 2 were synthesized by employing a hydrothermal technique in the presence of ethylenediamine and methylamine. All reagents were of analytical grade. The syntheses were carried out in 20 mL Teflon-lined stainless steel vessels under autogenous pressure with a filling capacity of ~50%. The sole resulting crystals for both 1 and 2 were collected by filtration, washed with distilled water and dried in air at ambient temperature.

$SrBO_2(OH)$ (1). A typical reaction mixture of $Sr(NO_3)_2$ (2.12 g), H_3BO_3 (0.62 g), $H_2NCH_2CH_2NH_2$ (1.78 g) and H_2O (12.00 g) in the molar ratio 1 : 1 : 3 : 67 was stirred until homogeneous, then heated at 180 °C for about 5 days to give colorless columnar crystals of $SrBO_2(OH)$. The initial pH of the reaction system was approximately 13, and the yield of the product was about 75%, based on the amount of the source material H_3BO_3 used.

$Ba_3B_6O_9(OH)_6$ (2). A typical reaction mixture of $Ba(COO)_2$ (1.30 g), H_3BO_3 (0.46 g), $H_2NCH_2CH_2NH_2$ (1.78 g), CH_3NH_2 (1.35 g) and H_2O (12.00 g) in the molar ratio 1 : 0.75 : 3 : 4 : 67 was stirred until homogeneous, heated at 180 °C for about 3 days to give colorless columnar crystals of $Ba_3B_6O_9(OH)_6$. The initial pH of the reaction system was approximately 13. Based on the amount of H_3BO_3 used, the product yield for this reaction system was about 80%.

General characterization

The IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer with KBr discs in the 400–4000 cm^{-1} region. The differential thermal (DT) and thermogravimetric analyses (TGA) were performed on a Netzsch STA 449C analyzer under

Table 1 Crystallographic data for SrBO$_2$(OH) (**1**) and Ba$_3$B$_6$O$_9$(OH)$_6$ (**2**)

	1	**2**
Empirical formula	SrBO$_2$(OH)	Ba$_3$B$_6$O$_9$(OH)$_6$
Formula weight	147.44	722.93
T/K	293(2)	293(2)
Crystal system	Orthorhombic	Monoclinic
Space group	$Pnma$	$P2/c$
a/Å	6.991(2)	6.9868(2)
b/Å	5.707(2)	7.1366(2)
c/Å	6.952(3)	11.9209(4)
β/°		90.955(2)
V/Å^3	277.34(18)	594.32(3)
Z	4	2
μ/mm^{-1}	19.189	9.921
D_c/Mg m^{-3}	3.531	4.040
Reflections collected	589	4776
Independent reflections	220 [R(int) = 0.0546]	1728 [R(int) = 0.0234]
Final $R1$, $wR2$ indices [$I > 2\sigma(I)$]	0.0349, 0.0896	0.0207, 0.0515
$R1$, $wR2$ (all data)	0.0366, 0.0909	0.0245, 0.0525

a flow of dry air at a heating rate of 10 K min^{-1}. The qualitative electron probe microanalysis was carried out with a Hitachi TEM H8100 IV microscope equipped with an energy dispersive spectral (EDS) analyzer. The X-ray powder diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer using Cu-Kα radiation (λ = 1.5418 Å) with a graphite mono-chromator. The recording speed was 8° min^{-1} over the 2θ range 10–40° at room temperature. Powder second harmonic generation tests were carried out on the sample by means of the method of Kurtz and Perry.[22]

X-Ray crystallography

A columnar crystal of the strontium borate SrBO$_2$(OH) with approximate dimensions 0.20 × 0.20 × 0.08 mm and a 0.40 × 0.40 × 0.20 mm columnar crystal of the barium borate Ba$_3$B$_6$O$_9$-(OH)$_6$ were selected and mounted on a Siemens SMART1000 X-ray diffractometer with a CCD area detector. The data were collected using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K. The structures were solved by direct methods (SHELXTL version 5.10) and refined by full-matrix least-squares on F^2 using SHELXTL version 5.10, together with absorption correction by an empirical method. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the BO$_4$ units in **2** were placed geometrically (d = 0.90 Å) and allowed to ride on the atoms to which they were attached with fixed isotropic thermal parameters. The experimental crystallographic data for SrBO$_2$(OH) and Ba$_3$B$_6$O$_9$(OH)$_6$ are listed in Table 1.

CCDC reference numbers 174294 and 174295.

See http://www.rsc.org/suppdata/dt/b1/b110468c/ for crystallographic data in CIF or other electronic format.

Results and discussion

Hydrothermal synthesis and related methods are useful techniques for the preparation of metastable crystalline materials.[23] However, the process is relatively complex. Many factors, such as initial reactants, starting concentration, pH, crystallization temperature and pressure, can affect the reactions. The role of ethylenediamine and methylamine in the crystallization systems for compounds **1** and **2** is not very clear yet, but these species seem to be critical for the growth of the crystals in the synthesis, although they are not incorporated in the final structures. We have tried a variety of recipes (reactant ratios) and reaction conditions (pH, temperature and reaction time) in the absence of the amine molecules and found that no crystals of the title compounds appear in the reaction products. The reagent ratios given in the Experimental section are optimal for obtaining highly crystalline single phases.

Energy dispersive spectroscopy (EDS) shows the existence of Sr and Ba as major components in compounds **1** and **2**, respectively, and infrared spectroscopy confirms the presence of triangular BO$_3$ or tetrahedral BO$_4$ and OH groups in the crystal structures. Two strong bands occur in the IR spectrum of the as-synthesized compound **1** at about 1030 and 1315 cm^{-1},[24] in accordance with the existence of BO$_3$ groups in the crystal structure. The bands due to OH stretching vibrations are seen at around 3440 cm^{-1}. The IR spectrum of compound **2** exhibits broad bands at 854 cm^{-1} due to vibrations of BO$_4$ groups.[25] The broad strong bands at 3440 cm^{-1} can also be assigned to OH stretching vibrations.

Thermogravimetric analysis shows a weight loss of about 6.0% in the range 100–300 °C in air for **1**. This weight loss, attributed to the removal of the hydroxyl groups in the SrBO$_2$(OH) structure (calculated value 6.1%) accompanies a distinct endothermic effect at around 171 °C, as shown by the DTA curve. For the Ba$_3$B$_6$O$_9$(OH)$_6$, the weight loss corresponding to the removal of the hydroxyl groups (calculated value 7.5%) is observed to be about 7.0% in the range 100–600 °C in air, with endothermic effects at about 140 and 350 °C from the DTA curve.

The two powder samples were tested for nonlinear optical activity by a powder second-harmonic generation test which gave two null responses, indicating the existence of centrosymmetry and, unfortunately, the unsuitability of **1** and **2** for nonlinear optics.

Crystal structures

The space groups of **1** and **2** are $Pnma$ and $P2/c$, respectively, both of which contain a centre of symmetry, in accordance with the SHG test results. The absence of SHG effects for **1** and **2** also indicates that the crystals selected for structural analysis represent the respective bulk products obtained from the reaction systems. For both compounds **1** and **2**, the peak positions of the experimental powder X-ray diffraction patterns correspond well with those of the patterns simulated on the basis of the single crystal structures, confirming that the two compounds are essentially single phases. The coordination environments for the Sr, Ba and B atoms in compounds **1** and **2** are shown in Fig. 1 and 2, whilst selected bond lengths and angles are presented in Tables 2 and 3, respectively.

Single-crystal X-ray diffraction analysis reveals that the unit cell of compound **1** contains crystallographically independent individual [BO$_2$(OH)]$^{2-}$ groups (Fig. 3). Such an individual borate group was also reported for Na$_2$[BO$_2$(OH)], in which all atoms lie at special positions on the mirror planes at y = 1/4 and 3/4.[26] However, all atoms except for O(1) in **1** lie on the symmetry planes at y = 1/4. As is the case for Na$_2$[BO$_2$(OH)], in **1**, three oxygens [O(1), O(1A) and O(2)] are bonded to each B to

Table 2 Selected bond lengths (Å) and angles (°) for SrBO$_2$(OH) (**1**)^a

Sr–O(1)	2.612(5)	Sr–O(2C)	2.807(7)
Sr–O(1A)	2.557(4)	Sr–O(2D)	2.862(7)
Sr–O(1B)	2.575(5)		
B–O(1)	1.354(7)	B–O(2)	1.428(13)
O(1)–B–O(2)	117.9(5)	O(1E)–B–O(1)	124.1(9)

^{a} Symmetry transformations used to generate equivalent atoms: (A) $-x + 2, -y + 1, -z + 1$; (B) $-x + 3/2, y - 1/2, z - 1/2$; (C) $x, y, z - 1$; (D) $x - 1/2, y, -z + 3/2$; (E) $x, -y + 1/2, z$.
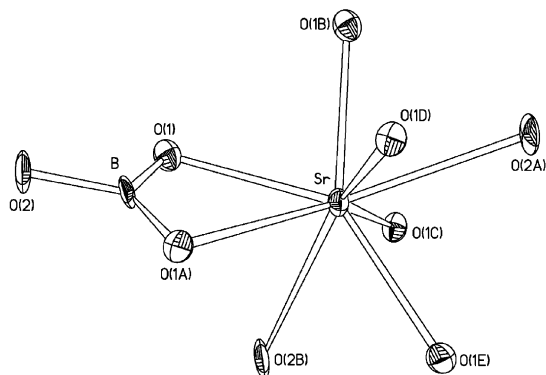
Fig. 1 Arrangement of Sr polyhedra in SrBO$_2$(OH) (**1**). Atom labelled "A", "B", "C", and so on refer to symmetry-generated atoms.
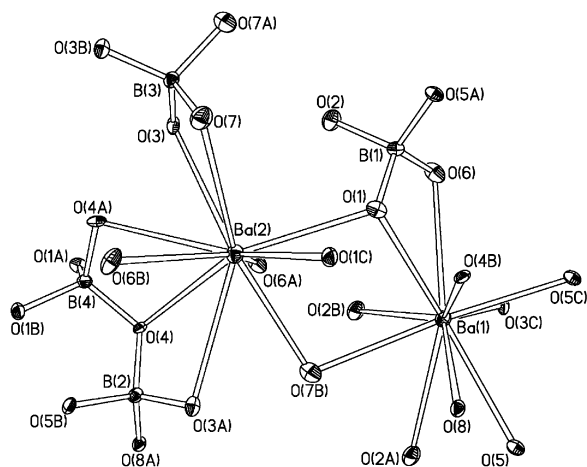
Fig. 2 Arrangement of Ba(1) and Ba(2) polyhedra in Ba$_3$B$_6$O$_9$(OH)$_6$ (**2**). Atom labelled "A", "B", and "C", refer to symmetry-generated atoms.
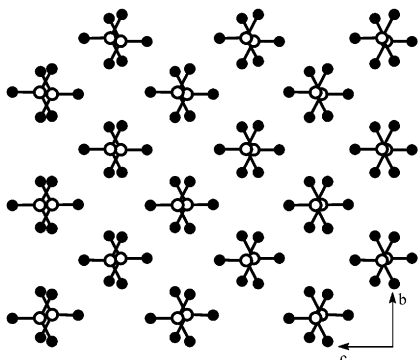
Fig. 3 Arrangement of the individual borate anions [BO$_2$(OH)]$^{2-}$ in SrBO$_2$(OH) (**1**) parallel to (1 0 0). For clarity, the H atoms are not shown. Open circles: B atoms; solid circles: O atoms.

Table 3 Selected bond lengths (Å) for Ba$_3$B$_6$O$_9$(OH)$_6$ (**2**)^a

|			
Ba(1)–O(1)	2.786(3)	Ba(1)–O(7E)	2.819(3)
Ba(1)–O(2A)	2.834(3)	Ba(1)–O(8)	2.8002(11)
Ba(1)–O(2B)	3.034(3)	Ba(2)–O(1)	2.831(3)
Ba(1)–O(3A)	2.786(3)	Ba(2)–O(3)	3.303(3)
Ba(1)–O(4C)	2.798(2)	Ba(2)–O(4)	3.021(2)
Ba(1)–O(5)	2.859(2)	Ba(2)–O(6A)	2.746(3)
Ba(1)–O(5D)	2.752(2)	Ba(2)–O(7)	2.845(3)
Ba(1)–O(6)	2.984(3)		
B(1)–O(1)	1.444(5)	B(2)–O(5G)	1.491(4)
B(1)–O(2)	1.523(5)	B(2)–O(8H)	1.482(4)
B(1)–O(5F)	1.451(4)	B(3)–O(3)	1.444(4)
B(1)–O(6)	1.492(5)	B(3)–O(7)	1.518(4)
B(2)–O(3E)	1.483(4)	B(4)–O(4)	1.472(4)
B(2)–O(4)	1.474(4)	B(4)–O(1H)	1.478(4)

^{a} Symmetry transformations used to generate equivalent atoms: (A) $-x, -y + 1, -z$; (B) $x + 1, y, z$; (C) $x, y + 1, z$; (D) $-x + 1, -y + 2, -z$; (E) $-x, y, -z + 1/2$; (F) $x - 1, y, z$; (G) $-x + 1, y - 1, -z + 1/2$; (H) $x, y - 1, z$.

form BO$_3$ triangles. The average value of the three O–B–O angles around B is 120.03°, which compares with the usual average ring angle of an O–B–O trigon, 120.0°. Due to the symmetry of the space group, the BO$_3$ groups are exactly planar and lie nearly parallel to the bc plane; each BO$_3$ group is surrounded by six nearest BO$_3$ neighbors with B–B distances of 3.52, 4.38 and 4.99 Å. There is a distinct difference between the structures of compound **1** and Na$_2$[BO$_2$(OH)]. For **1**, the layers containing the BO$_3$ triangles in the bc plane are stacked in such a way that the BO$_3$ triangles in adjacent layers are in a staggered form when the structure is viewed along the a axis. That is, a B–O bond in a particular BO$_3$ triangle bisects an O–B–O angle of the corresponding BO$_3$ groups in adjacent layers above and below the given BO$_3$ group (Fig. 3). In comparison, the BO$_3$ groups in Na$_2$[BO$_2$(OH)] are stacked in an eclipsed form. That is, the B–O bonds of one BO$_3$ group in a given layer are "lined-up" with those of the adjacent layers. The three B–O distances in the structure of **1** are 1.354(7), 1.354(7) and 1.428(13) Å, with an average distance of 1.379 Å (Table 2), in good agreement with the usual trigonal B–O distance.[27] In each BO$_3$ triangle, one of the B–O bond lengths is markedly different from the other two, since O(1) and O(1A) are only coordinated to B while O(2) may also be linked to an H atom. The bond between the B and O(1) or O(1A) atoms is stronger than that between the B and O(2) atoms, such that the bond length B–O(2) is longer than the other two B–O bond lengths. It should be noted that the H-bond interaction in **1** is not defined due to the presence of heavy Sr atoms. In Na$_2$[BO$_2$(OH)], the three B–O bond distances are 1.351, 1.354 and 1.439 Å. Similarly, the longest one is the B–OH bond.

The eightfold-coordinated Sr atom presents regular Sr–O bond distances between 2.557(4) and 2.862(7) Å (mean, 2.645 Å) (Table 2). Comparable values have been encountered in other Sr oxide structures.[11–14,28] The B triangles are connected by common edges or corners to SrO$_8$ polyhedra (Fig. 1). Each Sr shares only one edge of its coordination polyhedron with a neighboring BO$_3$ triangle, while all other O atoms of this particular SrO$_8$ polyhedron are corner-shared with other BO$_3$ units.

The structure of compound **2** contains anionic infinite chains extending along the a direction, with a composition of [B$_6$O$_9$(OH)$_6$]$_n^{6n-}$ built up from non-planar six-membered B$_3$O$_3$ rings, which are found to join together by sharing B atoms (Fig. 4). In each B$_3$O$_3$ ring, all the three B atoms are bonded to four oxygen atoms. The B–O bond distances range from 1.444(4) to 1.523(5) Å (average, 1.479 Å) (Table 3), comparable with the normal average tetrahedral B–O distance observed previously.[29]

The negative charges of the polyborate chains are compensated for by the Ba^{2+} cations residing between adjacent chains,
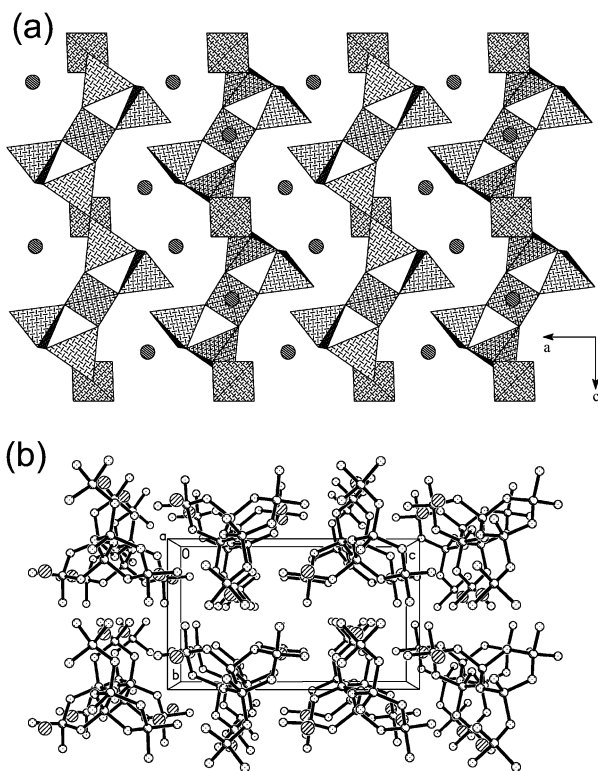
Fig. 4 (a) Polyhedral representation of the chain structure along the *b* axis for $Ba_3B_6O_9(OH)_6$ (**2**). (b) View of the structure along the *a* axis for **2**. Hashed circles: Ba atoms; partly hashed circles: B atoms; dotted circles: O atoms.

and these cations are believed to be responsible for holding the chain structures together, mainly through electrostatic interactions with the chains (Fig. 4). In this monoclinic barium borate, there are two crystallographically independent Ba atoms coordinated to ten oxygen atoms from distorted tetrahedral BO_4 groups, with an average Ba–O distance of 2.845 and 2.895 Å, respectively. These values are in accordance with those found in the literature, where irregular coordination polyhedra about Ba atoms are often described.[15–21,30] Furthermore, there are two bridging O atoms between Ba1 and Ba2. One is O(7B) and the other [O(1)] is from the distorted tetrahedral B(1)O$_4$ group. Ba(1)O$_{10}$ and B(1)O$_4$ share one edge with each other and so do Ba(2) and B(2), Ba(2) and B(3), and Ba(2) and B(4). In addition, there are short O ⋯ O distances ranging from 2.857(4) to 3.086(4) Å between the terminal oxygens O(2), O(6) and O(7), assigned as hydroxo ligands, and the oxygens in adjacent chains. Together with the Ba cations, the hydroxyl groups are located between adjacent chains and they may also play a role in holding the chains together through H-bonds.

Compound **2** is the only chain borate containing solely BO_4 tetrahedra, whereas, in previously discovered chain borates, such as $Na_2B_4O_7 \cdot 4H_2O$,[31] $Na_3[B_5O_9] \cdot H_2O$,[9] LiB_3O_5,[32] LaB_3O_6,[33] $Tl_2[B_4O_6(OH)_2] \cdot 2H_2O$[34] and $Pb_6B_{11}O_{18}(OH)_9$,[35] the chains are unexceptionally composed of BO_4 and BO_3 units together. Although the natural mineral kernite, $Na_2B_4O_7 \cdot 4H_2O$, is also composed of B_3O_3 rings sharing B atoms to form infinite chains, the rings of this mineral each contain one B–O triangle and two B–O tetrahedra. Furthermore, the chains in kernite are less folded than those in compound **2**. The structural differences between kernite and **2** may be attributed to the difference between the cations, that is, the Na^+ and Ba^{2+} species.

The rationality of the two structures was examined by valence bond theory.[36] The bond valence, *S*, was also calculated according to the Brown and Altermatt parameters. The valence bond sum of each cation in the two compounds, based on strength analysis, except for Ba(1) which remains slightly upbonded ($\Sigma s = 2.25$ for tenfold coordination) probably due to

the complexity of the partial occupancy of the Ba site, is in good agreement with the formal oxidation states, indicating that the structures are reasonable.

Conclusions

Two new borate compounds have been prepared in the presence of amines by employing hydrothermal techniques. The structure of $SrBO_2(OH)$ contains individual $[BO_2(OH)]^{2-}$ groups, which were also observed in the previously reported $Na_2BO_2(OH)$. However, the $[BO_2(OH)]^{2-}$ groups in $SrBO_2(OH)$ are stacked in a staggered form, whereas those in $Na_2BO_2(OH)$ are in an eclipsed form. $Ba_3B_6O_9(OH)_6$ consists of infinite chains of composition of $[B_6O_9(OH)_6]_n^{6n-}$ and Ba^{2+} cations residing between the negatively-charged chains. This compound is the first reported chain borate in which the boron atoms are all tetrahedrally coordinated by oxygen atoms. The successful synthesis of these two compounds may help in the search for new ways of synthesizing borate crystals with interesting structural features.

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