



Synthesis, structure and properties of a new noncentrosymmetric aluminoborate



Qin Meng^a, Guo-Ming Wang^{b,*}, Bai-Feng Yang^a, Huan He^a, Guo-Yu Yang^{a,c,**}

^a MOE Key Laboratory of Cluster Science, School of Chemistry, Beijing Institute of Technology, Beijing 100081, China

^b Teachers College, College of Chemistry and Environment of Qingdao University, Shandong 266071, China

^c State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

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ABSTRACT

A new noncentrosymmetric aluminoborate (H₂TETA)[Al(B₅O₁₀)] (**1**), has been solvothermally synthesized by using triethylenetetramine (TETA) as the structure-directing agent. Single-crystal X-ray diffraction analysis reveals that the compound crystallizes in the orthorhombic space group *Pna*2₁ with unit cell parameters $a = 12.9696(9)$ Å, $b = 17.0035(8)$ Å, $c = 7.3660(5)$ Å, $V = 1624.41(18)$ Å³ and $Z = 4$. Its structure consists of AlO₄ tetrahedra and B₅O₁₀ clusters and possesses 8-, 11- and 14-ring channels with sra topology. Second-harmonic generation (SHG) measurements on the powder samples reveal that **1** exhibits moderate SHG signals approximately 1.5 times that of KH₂PO₄ (KDP).

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Crystalline borate materials are of great interest due to their diverse structural chemistry and promising applications in mineralogy, luminescence and nonlinear optical (NLO) materials [1]. From the perspective of structure, the flexibility of boron to adopt both BO₃ and BO₄ coordination modes, together with the propensity of such groups to polymerize into a wide range of polyanions, offers greater opportunities in making new borates with structural and compositional complexity [2]. A particular driving force in this area is to synthesize new solids with acentric structures and NLO properties [3]. Compared to only 15% of inorganic crystals crystallizing in acentric space groups, more than 35% of known borates are featured with acentric structures [4], which may provide an ideal candidate for pursuing borate NLO materials. β-BaB₂O₄ (BBO), LiB₃O₅ (LBO) and Sr₂Be₂B₂O₇ (SBBO), for example, represent typical B-containing materials with excellent NLO activities [5]. Recently, attempts to introduce heteroatoms into borate backbones have also resulted in some intriguing systems, such as borophosphates, borogermanates, galloborates and zincborates, etc. [6–9]. In the specific field of aluminoborates, the compositional Al element has more flexible coordination modes (AlO₄: tetrahedral, AlO₅: square–pyramidal or trigonal–bipyramidal, and AlO₆: octahedral), and a series of new materials with novel topologies and useful properties have been successfully synthesized through different synthetic approaches [10]. Notable examples include porous frameworks of PKU-1 and PKU-2 with extra-large

pores of 18- and 24-ring channels [11], multimetal-centered borate clusters PKU-8 and QD-6 [12], as well as a very few cases with helical channels [13].

One important reason for our interest in this area is to design and synthesize new aluminoborates with acentric structural features and NLO properties. It has been demonstrated that the simultaneous introduction of Al components into pure borate frameworks may greatly increase the likelihood of producing acentric structures, especially when the acentric B–O clusters were combined with the chiral Al center, *i.e.* four-coordinated AlO₄ groups. On the basis of the above consideration, we successfully obtained a new organically templated aluminoborate, (H₂TETA)[Al(B₅O₁₀)] (**1**), which is constructed from AlO₄ and B₅O₁₀ groups and exhibits a noncentrosymmetric three-dimensional architecture.

Compound **1** was synthesized by the solvothermal reaction of Al(*i*-PrO)₃, H₃BO₃, triethylenetetramine and pyridine at 180 °C for 7 days [14]. Note that **1** appeared to be only achieved in the absence of water; otherwise, a known polyborate [C₆N₄H₂₀]_{0.5}·[B₅O₆(OH)₄] [15] would be obtained when pyridine and water were used as the solvent under similar conditions. The structure of **1** was characterized by single-crystal X-ray diffraction, elemental analysis, IR and thermogravimetric analysis. The purity of the crystalline solid was verified by the powder XRD (Fig. 1).

Single crystal X-ray analysis [16] reveals that **1** crystallizes in the orthorhombic space group *Pna*2₁, and the asymmetric unit contains one independent Al atom, one unique B₅O₁₀ unit and one diprotonated H₂TETA cation. As depicted in Fig. 2, the unique Al atom adopts tetrahedral geometry with Al–O bond lengths varying from 1.711(4) to 1.743(6) Å and O–Al–O bond angles changing from 108.5(2) to

* Corresponding author. Tel./fax: +86 10 68918572.

** Correspondence to: G.-Y. Yang, MOE Key Laboratory of Cluster Science, School of Chemistry, Beijing Institute of Technology, Beijing 100081, China. Tel./fax: + 86 1068918572.

E-mail addresses: gmwang_pub@163.com (G.-M. Wang), ygy@bit.edu.cn, ygy@fjirsm.ac.cn (G.-Y. Yang).

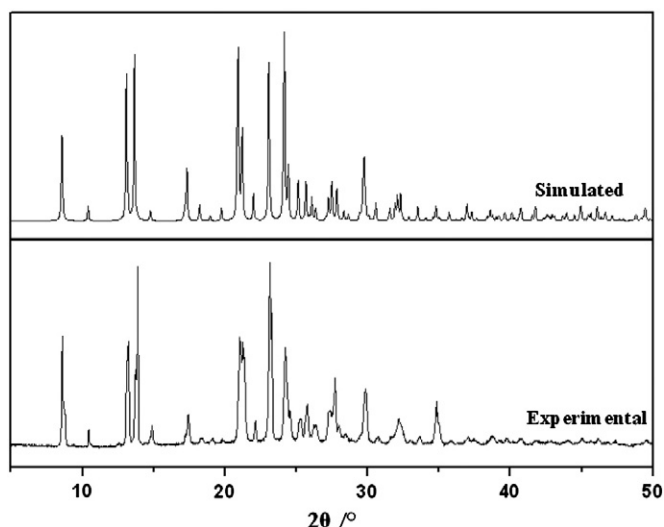


Fig. 1. Experimental and simulated powder X-ray diffraction patterns of **1**.

112.8(3)°. The B_5O_{10} cluster is made up of one BO_4 tetrahedron and four BO_3 triangles, in which two planar B_3O_3 rings are perpendicularly linked by the common $B(3)O_4$ tetrahedron. The B–O bond lengths are in the region of 1.326(8)–1.481(9) Å and O–B–O bond angles are distributed in the range of 116.8(6)–123.0(5)° and 106.7(5)–111.0(4)° for BO_3 and BO_4 units, respectively.

The alternate connectivity between the B_5O_{10} clusters and the AlO_4 tetrahedra through their vertices creates a three-dimensional architecture with multidirectional channels. In this structure, each B_5O_{10} cluster is connected to 10 neighboring B_5O_{10} clusters through four bridging AlO_4 groups, and each AlO_4 group is also connected to 10 neighbors through four bridging B_5O_{10} clusters (Fig. 3). Thus, no Al–O–Al connection exists in the structure. Fig. 4a shows the regular 8- and 14-ring channels viewed down the [010] direction. The largest 14-ring channels are elliptical in shape and delimited by four AlO_4 , two BO_4 and eight BO_3 units in the linkage of the $-AlO_4-BO_3-BO_4-BO_3-AlO_4-BO_3-BO_3-AlO_4-BO_3-BO_4-BO_3-AlO_4-BO_3-BO_3-$ sequence. Similarly, the openings of the 8-ring channels are made up from two AlO_4 , two BO_4 and four BO_3 units with two repeating $-AlO_4-BO_3-BO_4-BO_3-$ linkages. The oxygen-to-oxygen dimensions of 8- and 12-ring apertures in the structure are approximately $6.6 \times 4.5 \text{ \AA}^2$ and $12.6 \times 6.5 \text{ \AA}^2$, respectively.

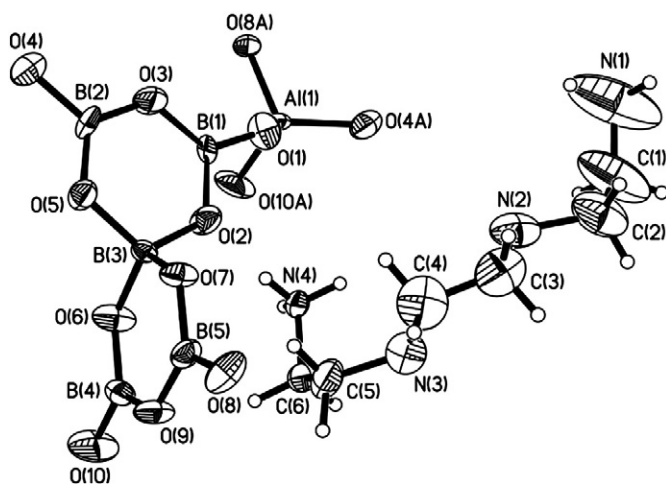


Fig. 2. ORTEP view of the asymmetric unit of **1**, showing the atom-labeling scheme and 50% thermal ellipsoids.

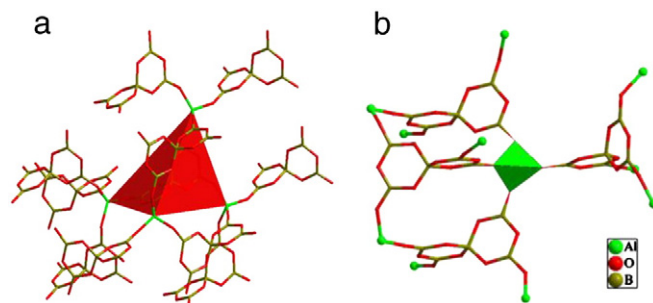


Fig. 3. (a, b) Views of the linkage of B_5O_{10} and AlO_4 groups in **1**. Each B_5O_{10}/AlO_4 unit is bridged by four AlO_4/B_5O_{10} groups to 10 other B_5O_{10}/AlO_4 units. Color code: B_5O_{10} cluster, red; AlO_4 , green.

The simultaneous presence of large odd 11-ring channels along the [100] direction is also noteworthy (Fig. 4b). Except for the recently reported aluminoborates with larger 13- and 15-ring channels [13d], luminescence and nonlinear optical (NLO) materials, the odd 11-ring opening is the largest and scarcely observed in ICMM6 and XA-1 [8,17]. The apertures of the 11-ring channels are bound by three AlO_4 , two BO_4 and six BO_3 units with the $-AlO_4-BO_3-BO_4-BO_3-AlO_4-BO_3-BO_4-BO_3-AlO_4-BO_3-BO_3-$ sequence. If the AlO_4 tetrahedra and B_5O_{10} clusters are viewed as 4-connected nodes, **1** has a familiar $sra-4^26^38$ net (Fig. 4c). The H_2TETA templates reside in the 14-ring channels and interact with the framework through extensive N–H...O hydrogen bonds (Fig. 5). A void space analysis using the program PLATON indicates that these extra-framework organic cations occupy 57.2% of the unit cell volume.

Considering the noncentrosymmetric structure of **1**, the second harmonic generation (SHG) measurement is carried out on the powder sample by the Kurtz–Perry method at room temperature [18]. The intensity of the green light (frequency doubled output: $\lambda = 532 \text{ nm}$)

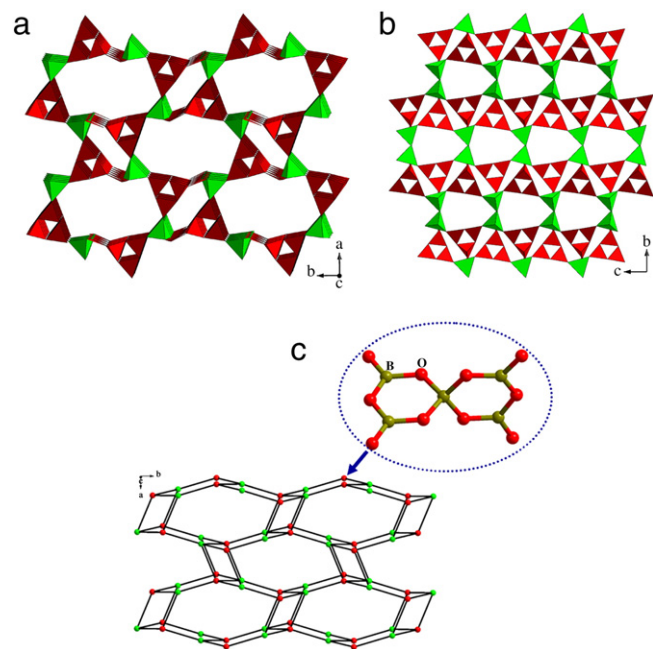


Fig. 4. Polyedral view of the 3D structure of **1**, showing the elliptical 8- and 14-ring channels along the c axis (a), and the odd 11-ring channels along the a axis (b). Color code: AlO_4 , green; BO_4 and BO_3 , red. (c) The sra topology of **1** with 4^26^38 net.

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