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$(NH_3CH_2CH_2NH_3)B_6O_9(OH)_2$: Synthesis and crystal structure of a novel layered borate templated by ethylenediamine

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Abstract

A novel intercalated borate compound $(NH_3CH_2CH_2NH_3)B_6O_9(OH)_2$, has been solvothermally synthesized, and structurally characterized by single crystal X-ray diffraction. Compound crystallizes in the monoclinic, space group $P2(1)/c$, $a = 8.6200(17)$ Å, $b = 15.656(3)$ Å, $c = 8.8386(18)$ Å, $\beta = 93.32(3)°$, $V = 1190.8(4)$ Å^3, $Z = 4$. Its oxoborate structure is built up from 1-D polyborate chains with 3, 11-membered boron rings bonded diamine molecules through electrostatic attraction and hydrogen bond interactions to construct 2-D layered compound. Other characterizations by IR, element analysis, thermal analysis and specific surface area are also discussed.

Keywords: Solvothermal synthesis; Crystal structure; Intercalated borate

1. Introduction

The metal borates, such as β-BaB_2O_4 (BBO) [1], LiB_3O_5 (LBO) [2], $CsLiB_6O_{10}$ [3], $Sr_2Be_2B_2O_7$ [4] and $K_2Al_2B_2O_7$ [5] have a practical application in optical, electrooptical, ferroelectric applications and UV laser materials. Moreover, the basic building blocks of these borates (BO_3 and BO_4) are similar to the building units of silicates, aluminosilicates (AlO_4 and SiO_4), and aluminophosphates (AlO_4 and PO_4), which have considerable mineralogical and industrial importance. The main difference is the flexibility of boron bound to oxygen not only in triangular coordination but also in tetrahedral coordination. These phenomena made chemists to pursue the designed preparation of the borates materials and related to materials with defined architecture and useful chemophysical properties. As expected, Stucky et al. had reported the borate with any degree of porosity [6]. A new cobalt borate containing both exchangeable cations and redox-active metal sites and borophosphates with microporous structure had recently been reported [7,8]. Over the past decade many hydrated and anhydrous metal borates had been obtained [9]. The structure chemistry of the borates with the anionic components composed of BO_3 and BO_4 groups that may link together by sharing oxygen atoms extents from isolated rings and cages or polymerize to infinite chains, sheets, and networks. And, based on the linkage of BO_3 and BO_4 groups Burns et al. developed a comprehensive description based on fundamental building blocks "FBB" to have a clearer nomenclature for more complicated polyanions [10]. Of the reported borates only one exception was very recently described in the structure of $Dy_4B_6O_{15}$ where the exclusively appearing BO_4 tetrahedra can link together not only via common corners but also via common edges [11]. In spite of considerable efforts being made in synthesizing organically templated borates, the amount of the compounds is still less explored [12]. To our awareness, the organically intercalated borate is not reported yet. In our experiment, by employing solvothermally synthesized condition we have obtained a organically intercalated borate $(NH_3CH_2CH_2NH_3)B_6O_9(OH)_2$. The compound contains the polyborates $[B_6O_9(OH)_2]^{2-}$ and protonated ethylenediamine ions. Its oxoborate structure is

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build up from polyborate chains with 3, 11-membered boron rings bonded diamine molecules through electrostatic attraction and H-bonding pair interactions to construct 2-D layered compound. In this paper, we describe the synthesis and structure of this novel material.

2. Experimental

All reagents were commercially available and no further purification was carried out. IR spectrum was recorded on a BRUKER Vertex 70 FTIR plus spectrometer in the KBr matrix in the range of 400–4000 cm^{-1}. The element analysis results were obtained with Elementar Analysensysteme GmbH instrument. Thermal analysis was carried out at a heating rate of 5 °C/min in nitrogen atmosphere from 25 to 800 °C with a TGA/SDTA851^{e}. The absorption–desorption isotherm and specific surface area were performed on a Quantachrome NOVA 1000 analyzer. The surface area was determined by a multipoint BET method using the adsorption data in the partial pressure range P/P_0 of 0.05–0.35.

The compound was initially obtained in an attempt to hydrothermally synthesize organically templated titanium borophosphate, and therefore the starting materials included tetrabutyltitanium and H_3PO_4 according to procedure reported by Guo et al. [13]. Unexpectedly, this compound was obtained. The synthesis procedures were as follows: 3.79 g tetrabutyltitanium and 4.50 g H_3BO_3 were dispersed in 20 mL of 1-butanol under vigorous stirring and then 4.3 mL of phosphoric acid (85 wt%) was added dropwise. A gel was formed and was stirred at room temperature for 24 h, and then 4.3 mL of ethylenediamine was added. The final reaction mixture was sealed in a Teflon-lined stainless steel autoclave and heated at 170 °C for 6 days. The colorless prism crystal yield of 49.89% based on B was obtained by ultrasonication and filtration, washed with distilled water and acetone. Later, the reaction conditions were optimized, and we were failed to get this product. Instead of, a new phase was obtained, and will be reported elsewhere. IR (KBr pellet, cm^{-1}): 3320 (s), 3111 (s), 2931 (w), 2760(w), 2482 (w), 2097 (w), 1649 (s), 1601 (w), 1569 (s), 1382 (s), 1356 (s), 1254 (s), 1232 (s), 1088 (s), 980 (s), 935 (s), 860 (s), 834 (s), 806 (w), 755 (s), 718 (w), 629 (w), 587 (w) and 488 (s) cm^{-1}. Elemental analysis results for N, C, H: calcd.: N, 9.18; C, 7.88; H, 3.93; found: N, 10.10; C, 9.00; H, 3.90.

The data for the crystals (0.20 mm × 0.18 mm × 0.16 mm was collected on a Rigaku AXIS-IV imaging plate area detector with graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). The data were collected at a temperature of 291(2) K to a maximum 2θ value of 55°. Of the 3461 reflections that were collected, 1924 reflections were unique ($R_{\text{int}} = 0.0220$). The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement on F^2 was based on 1924 observed reflections as well as 223 variable parameters and converged. All calculations were performed using the SHELXL-97 crystallographic software package. Details of the data collection, structure solution and refinement are given in Table 1. The CIF file of single-crystal refinement is deposited. CCDC-295562.

Table 1
Crystal data and structure refinement

Empirical formula	$(NH_3CH_2CH_2NH_3)B_6O_9(OH)_2$
Formula weight	305.00
Temperature (K)	291(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions (Å)	$a = 8.6200(17)$ $b = 15.656(3)$, $\beta = 93.32(3)°$ $c = 8.8386(18)$
Volume (Å^3)	1190.8(4)
Z	4
Calculated density (g/cm^3)	1.701
Absorption coefficient (mm^{-1})	0.157
$F(000)$	624
Crystal size (mm)	0.20 × 0.18 × 0.16
Index ranges	$0 \leqslant h \leqslant 9$; $-18 \leqslant k \leqslant 18$; $-10 \leqslant l \leqslant 10$
Reflections collected/unique	3461/1924 [$R(\text{int}) = 0.0220$]
Max. and min. transmission	0.9753 and 0.9693
Data/restraints/parameters	1924/0/223
Goodness-of-fit on F^2	1.171
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0482$; w$R_2 = 0.0923$
R indices (all data)	$R_1 = 0.0667$; w$R_2 = 0.0985$
Extinction coefficient	0.0049(16)
Largest diff. peak and hole (e Å^{-3})	0.216 and −0.220

3. Results and discussion

The non-hydrogen coordinates, the thermal motion parameters, the selected bond lengths and angles as well as hydrogen bonds are listed in Tables 2–5, respectively. The structure of this compound contains six boron atoms, 11 oxygen atoms, two nitrogen atoms and two carbon atoms as shown in Fig. 1. The compound consists of 1-D polyborate chains and protonated amine molecules. These chains are built up from $[B_6O_9(OH)_2]^{2-}$ fundamental building blocks containing two different boroxyl rings, which are linked together through oxygen atoms to neighboring units. The linkage of these rings by further alternatively corner-sharing BO_3 groups and BO_4 groups leads to novel layers containing 3, 11-membered boron rings, as shown in Fig. 2. In this layer each three-coordinated boron atom, which is sp^2 hybridization is nearly coplanar with O–B–O bond angles in the range from 116.3(2)° to 123.9(2)°, and whereas, four-coordinated B atom is in a distorted tetrahedral environment due to sp^3 hybridization with O–B–O bond angles in the range from 105.95(19)° to 112.7(2)°. IR spectra bands at 1649 and 3320 cm^{-1} confirm the presence of OH groups in the B_3O_3 boroxyl rings.

Strong H-bonding interactions between adjacent chains lead to 2-D layered structure within microporous channels

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}*
B(1)	−5454(3)	3181(2)	−3361(3)	12(1)
B(2)	−3108(3)	3787(2)	−1984(3)	17(1)
B(3)	−2384(3)	5331(2)	−2147(4)	19(1)
B(4)	−345(3)	4279(2)	−2051(3)	15(1)
B(5)	1975(3)	3293(2)	−2268(3)	13(1)
B(6)	2324(3)	2626(2)	−4801(3)	14(1)
N(1)	−1522(3)	2953(2)	4662(3)	21(1)
N(2)	−3482(3)	4567(2)	2005(3)	19(1)
C(2)	−3287(3)	4007(2)	3352(3)	25(1)
C(1)	−1739(3)	3566(2)	3390(4)	34(1)
O(1)	−6366(2)	3476(1)	−2272(2)	15(1)
O(2)	−6070(2)	2741(1)	−4625(2)	19(1)
O(3)	−3894(2)	3319(1)	−3237(2)	19(1)
O(4)	−3525(2)	3464(1)	−497(2)	21(1)
O(5)	−1432(2)	3648(1)	−2093(2)	19(1)
O(6)	−3486(2)	4716(1)	−2100(2)	25(1)
O(7)	−2872(2)	6150(1)	−2313(3)	33(1)
O(8)	−815(2)	5131(1)	−2055(2)	25(1)
O(9)	1197(2)	4133(1)	−2088(2)	17(1)
O(10)	1593(2)	2720(1)	−1041(2)	21(1)
O(11)	1400(2)	2899(1)	−3702(2)	19(1)

U_{eq} is defined as one-third of the trace of the orthogonaliz.

Table 3
Selected bond lengths (Å) and angles (°)

B(1)–O(1)	1.357(3)	O(1)–B(1)–O(3)	120.0(2)
B(1)–O(3)	1.361(3)	O(1)–B(1)–O(2)	121.9(2)
B(1)–O(2)	1.391(3)	O(3)–B(1)–O(2)	118.2(2)
B(2)–O(3)	1.461(3)	O(3)–B(2)–O(5)	106.9(2)
B(2)–O(5)	1.470(3)	O(3)–B(2)–O(4)	112.2(2)
B(2)–O(4)	1.473(3)	O(5)–B(2)–O(4)	107.4(2)
B(2)–O(6)	1.493(3)	O(3)–B(2)–O(6)	110.3(2)
B(3)–O(6)	1.354(3)	O(5)–B(2)–O(6)	110.6(2)
B(3)–O(7)	1.355(3)	O(4)–B(2)–O(6)	109.4(2)
B(3)–O(8)	1.386(3)	O(6)–B(3)–O(7)	117.5(2)
B(4)–O(9)	1.351(3)	O(6)–B(3)–O(8)	121.5(2)
B(4)–O(5)	1.360(3)	O(7)–B(3)–O(8)	121.0(2)
B(4)–O(8)	1.394(3)	O(9)–B(4)–O(5)	123.6(2)
B(5)–O(1)#1	1.459(3)	O(9)–B(4)–O(8)	116.6(2)
B(5)–O(10)	1.460(3)	O(5)–B(4)–O(8)	119.7(2)
B(5)–O(11)	1.469(3)	O(1)#1–B(5)–O(10)	112.7(2)
B(5)–O(9)	1.489(3)	O(1)#1–B(5)–O(11)	111.21(19)
B(6)–O(10)#2	1.345(3)	O(10)–B(5)–O(11)	107.69(19)
B(6)–O(11)	1.361(3)	O(1)#1–B(5)–O(9)	105.95(19)
B(6)–O(2)#1	1.396(3)	O(10)–B(5)–O(9)	109.94(19)
O(1)–B(5)#3	1.459(3)	O(11)–B(5)–O(9)	109.37(19)
O(2)–B(6)#3	1.396(3)	O(10)#2–B(6)–O(11)	116.3(2)
O(7)–H(7E)	0.83(4)	O(10)#2–B(6)–O(2)#1	123.9(2)
O(10)–B(6)#4	1.345(3)	O(11)–B(6)–O(2)#1	119.8(2)

Symmetry transformations used to generate equivalent atoms: #1 $x+1$, y, z; #2 x, $-y+1/2$, $z-1/2$; #3 $x-1$, y, z; #4 x, $-y+1/2$, $z+1/2$.

Table 4
Anisotropic displacement parameters ($Å^2 \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B(1)	9(1)	13(1)	14(2)	3(1)	2(1)	0(1)
B(2)	10(1)	14(2)	27(2)	−1(1)	1(1)	1(1)
B(3)	18(2)	15(2)	25(2)	0(1)	4(1)	3(1)
B(4)	16(1)	15(2)	15(2)	−2(1)	1(1)	0(1)
B(5)	9(1)	16(2)	13(2)	−1(1)	2(1)	−2(1)
B(6)	12(1)	11(1)	17(2)	2(1)	1(1)	−1(1)
N(1)	17(1)	21(1)	26(1)	4(1)	−2(1)	−2(1)
N(2)	17(1)	16(1)	23(1)	1(1)	0(1)	1(1)
C(2)	22(1)	28(2)	25(2)	8(1)	4(1)	2(1)
C(1)	27(2)	36(2)	40(2)	19(2)	11(1)	7(1)
O(1)	10(1)	19(1)	16(1)	−3(1)	1(1)	−2(1)
O(2)	12(1)	29(1)	17(1)	−8(1)	1(1)	−2(1)
O(3)	10(1)	26(1)	21(1)	−4(1)	3(1)	−2(1)
O(4)	15(1)	26(1)	21(1)	−1(1)	−1(1)	−4(1)
O(5)	10(1)	11(1)	36(1)	−2(1)	−1(1)	0(1)
O(6)	14(1)	13(1)	48(1)	3(1)	2(1)	2(1)
O(7)	25(1)	14(1)	60(2)	3(1)	4(1)	3(1)
O(8)	14(1)	13(1)	49(1)	0(1)	7(1)	−2(1)
O(9)	9(1)	14(1)	30(1)	−2(1)	1(1)	−1(1)
O(10)	14(1)	29(1)	21(1)	12(1)	−2(1)	−1(1)
O(11)	10(1)	31(1)	17(1)	−8(1)	1(1)	−2(1)

Table 5
Hydrogen-bonds (Å) and bond angles (°)

D–H···A	d(D–H)(Å)	d(H···A)(Å)	d(D···A)(Å)	<(DHA) (deg)
N(2)–H(2E)···O(9)#5	0.93(3)	1.90(3)	2.831(3)	175(3)
N(2)–H(2E)···O(1)#6	0.93(3)	2.56(3)	3.078(3)	116(2)
N(2)–H(2F)···O(6)#6	0.98(3)	1.88(3)	2.850(3)	170(3)
N(1)–H(1F)···O(4)#4	0.95(4)	1.86(4)	2.809(3)	177(4)
N(1)–H(1F)···O(5)#4	0.95(4)	2.42(4)	2.952(3)	115(3)
N(1)–H(1E)···O(10)#4	0.88(6)	2.14(6)	2.984(3)	161(5)
O(4)–H(4E)···O(2)#4	0.85(4)	2.28(4)	3.027(2)	147(3)
N(1)–H(1E)···O(11)#7	0.88(6)	2.16(6)	2.832(3)	133(5)
N(1)–H(1G)···O(3)#7	0.95(7)	2.07(6)	2.897(3)	144(5)
N(1)–H(1G)···O(5)#7	0.95(7)	2.21(6)	3.064(3)	149(5)
O(7)–H(7E)···O(10)#8	0.83(4)	2.42(4)	3.091(3)	139(4)
O(7)–H(7E)···O(11)#8	0.83(4)	2.44(4)	3.127(3)	141(4)
N(2)–H(2G)···O(4)	0.96(3)	1.85(4)	2.804(3)	173(3)
O(4)–H(4E)···O(1)	0.85(4)	2.23(4)	2.830(2)	128(3)

Symmetry transformations used to generate equivalent atoms: #1 $x+1$, y, z; #2 x, $-y+1/2$, $z-1/2$; #3 $x-1$, y, z; #4 x, $-y+1/2$, $z+1/2$; #5 $-x$, $-y+1$, $-z$; #6 $-x-1$, $-y+1$, $-z$; #7 x, y, $z+1$; #8 $-x$, $y+1/2$, $-z$-1/2.

as shown in Fig. 3. The amine templates located between layers reinforce the polyborate connectivity via electrostatic and H-bonding interactions (see Table 5). In this case, the borate layers are alternatively intercalated by onium ions to balance the charge of the polyborate layers.

It is noteworthy that the crystal structure of this compound has a unidimensional channels (viewed along the c-axis) and 11-membered window system similar to those in aluminosilicate zeolites and in certain detemplated aluminophosphates. Another remarkable feature of the structure is organic molecules being intercalated between the layers of borate anionic ions compared with the intercalated clay exchanged by amine molecules [14]. These results suggest that the borate compound

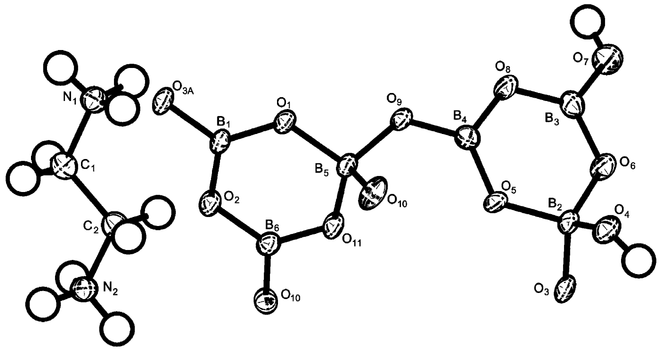

Fig. 1. ORTEP plot of the title compound $(NH_3CH_2CH_2NH_3)B_6O_9(OH)_2$.

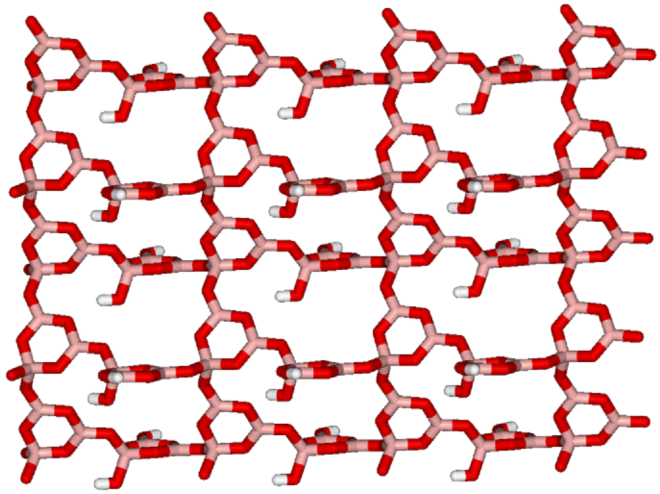

Fig. 2. Layered connectivity of polyborate for the title compound.

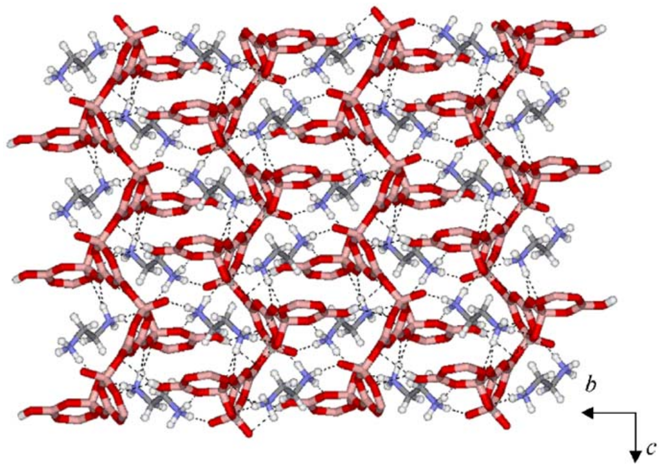

Fig. 3. Viewing structural network along *a*-axis direction.

$(NH_3CH_2CH_2NH_3)B_6O_9(OH)_2$, maybe not only provides a rich structural chemistry of borates but also likely possesses some influence on the dimension-controlled properties and intergallery guest, which have proven to be useful in catalysis and nanocomposite.

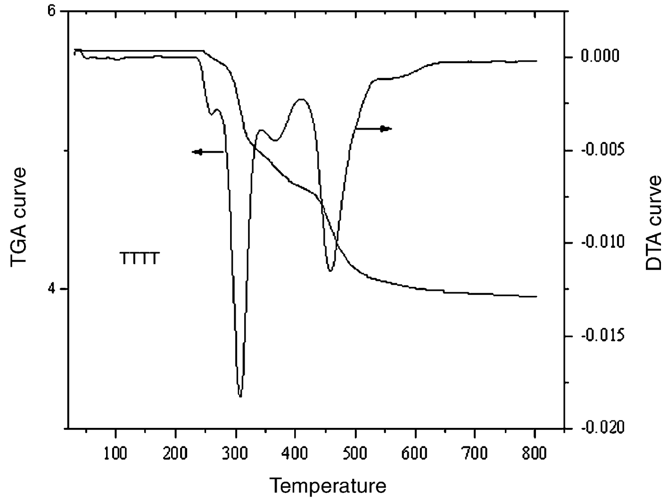

Fig. 4. Thermal study of the title compound.

Thermal loss weight is a two-stage process accompanied by two obvious endothermic DTA peaks as shown in Fig. 4. The first weight loss of 19.10% is observed between 240 and 435 °C and attubuted to the removal of the organic amine (cal. 20.32%). A gradual loss of mass 11.05% (cal. 11.15%) at the second stage in the range from 435 to 600 °C is attributed to the dehydration of hydroxyl. This result is identical with the structural refinement of single crystal X-ray diffraction. From N_2 adsorption–desorption isotherms obtained with an automated physisorption instrument the calculated specific surface area is $37.76\,m^2/g$, which also indicates a microporous materials.

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