

Electronic Supporting Information

NaK₁₅[B₄O₅(OH)₄]₆(NO₂)₂(CO₃)·7H₂O: Assembly of an unprecedented mixed anion inorganic compounds via a facile hydrothermal route

Yuchen Cao,^a Bingbing Zhang,^a Hongkun Liu,^a Danni Li,^a Ying Wang^{*a}

†Key Laboratory of Medicinal Chemistry and Molecular Diagnosis of the Ministry of Education, Key Laboratory of Analytical Science and Technology of Hebei Province, College of Chemistry and Environmental Science, Hebei University, Baoding 071002, China.

Corresponding Author

*wangy@hbu.edu.cn

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SYNTHESIS AND METHODS

Synthesis. All chemicals were obtained from Aladdin Chemical Industry Co., Ltd, and were used as received. Single crystals of the title compound were obtained by hydrothermal reactions. For I, a mixture of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (0.549 g, 1.20 mmol), KNO_3 (0.093 g, 0.76 mmol), KNO_2 (0.003 g, 0.04 mmol), and K_2CO_3 (0.299 g, 1.8 mmol) was thoroughly ground and then sealed into a Teflon autoclave (23 mL). The autoclave was heated at 205 °C for 4 days, and then cooled slowly to ambient temperature in 3 days. Transparent block crystals of I were obtained after washing with alcohol to remove unreacted raw materials, and the yield is about 20% (based on K). It should be noted that the crystal waters in $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ act as solvent thus the title compound cannot be obtained in an open crucible.

Methods. Single crystal XRD data were recorded on a Bruker SMART APEX II diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data integration and absorption corrections were carried out using the *SAINT*¹ program. The single crystal data were analyzed with the *Olex2* program². The structures were solved using Intrinsic Phasing method³, and refined using the least-squares technique. All H atoms were identified from difference Fourier map. The structures were checked for possible higher symmetry using the program *PLATON*.⁴ Crystal data and structure refinement information are given in Table 1. The final refined atomic positions (exclude H atoms) and isotropic thermal parameters are summarized in Table S2. Selected bond distances and angles are listed in Table S3. Hydrogen coordinates and isotropic displacement parameters are present in Table S4. The possible hydrogen bonds are indicated in Table S5. Powder X-ray Diffraction (PXRD) measurements were performed on a Bruker D8 advance X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at room temperature (2θ range: 10–70°, scan step width: 0.02°, counting time: 2 s). Thermal gravimetric (TG) analysis and differential scanning calorimetry (DSC) were measured on a NETZSCH simultaneous STA 449 F5 thermal analyzer in a flowing N_2 atmosphere (room temperature to 900 °C at a rate of 10 °C min^{-1}). The Infrared spectrum was recorded with a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in the range of 400 - 4000 cm^{-1} with a resolution of 4 cm^{-1} . Pellets for measurement were prepared by pressing a thoroughly ground mixture of sample and dried KBr (weight ratio = 1:100). The UV–Vis–NIR diffuse reflectance spectrum was measured at room temperature with a Shimadzu SolidSpec-3600 spectrophotometer in the 190–1100 nm wavelength range. The reflectance spectra were converted to absorbance using the e Kubelka–Munk relation. The powder SHG response was measured by means of the Kurtz–Perry method⁵ with a Q-switched Nd: YAG solid-state laser at 1064 nm. The α - SiO_2 samples were used as a reference.

ADDITIONAL TABLES AND FIGURES

Table S1. Crystal data and structure refinements for **I**.

Empirical formula	NaK ₁₅ [B ₄ O ₅ (OH) ₄] ₆ (NO ₂) ₂ (CO ₃)·7H ₂ O
Formula weight	2035.26
Crystal system	Hexagonal
space group	$P\bar{6}2c$
$a / \text{\AA}$	11.1399(9)
$c / \text{\AA}$	30.495(5)
Volume / \AA^3	3277.3(7)
$Z, \rho_{\text{calcd}} / \text{g}\cdot\text{cm}^{-3}$	2, 2.062
μ / mm^{-1}	1.117
$F(000)$	2036
Crystal size / mm^3	$0.209 \times 0.158 \times 0.135$
Theta range for data collection	0.668 to 27.504
Limiting indices	$-13 \leq h \leq 14, -14 \leq k \leq 8, -39 \leq l \leq 39$
Reflections collected / unique	23200 / 2576 [$R_{\text{int}} = 0.0531$]
Completeness	99.5 %
Data / restraints / parameters	2576 / 33 / 217
Goodness-of-fit on F^2	1.106
Final R indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.0316, wR_2 = 0.0801$
R indices (all data) ^a	$R_1 = 0.0384, wR_2 = 0.0844$
Absolute structure parameter	-0.01(2)
Largest diff. peak and hole/ $e\cdot\text{\AA}^{-3}$	0.467 and -0.246

^a $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for **I**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>S.O.F</i>	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
K(1)	1	0.6015(1)	0.8194(1)	0.5217(1)	0.030(1)
K(2)	1	0.8117(1)	0.7401(1)	0.2500	0.026(1)
K(3)	1	0.9222(1)	0.4910(1)	0.3117(1)	0.028(1)
Na(1)	1	1.0000	1.0000	0.5000	0.017(1)
B(1)	1	0.5107(4)	0.5933(5)	0.4239(1)	0.018(1)
B(2)	1	0.7303(4)	0.8109(4)	0.4235(1)	0.015(1)
B(3)	1	0.5996(4)	0.7389(4)	0.3576(1)	0.015(1)
B(4)	1	0.8163(4)	0.7373(5)	0.3604(1)	0.018(1)
C(1)	1	0.6667	0.3333	0.2500	0.018(2)
N(1)	1	0.3333	0.6667	0.5998(2)	0.040(2)
O(1)	1	0.4071(3)	0.4787(3)	0.4450(1)	0.029(1)
O(2)	1	0.6226(3)	0.6875(3)	0.4475(1)	0.018(1)
O(3)	1	0.6662(2)	0.8503(3)	0.3893(1)	0.015(1)
O(4)	1	0.4968(3)	0.6093(3)	0.3798(1)	0.020(1)
O(5)	1	0.5292(3)	0.7720(3)	0.3233(1)	0.019(1)
O(6)	1	0.8303(3)	0.7742(3)	0.4038(1)	0.019(1)
O(7)	1	0.7050(3)	0.7147(3)	0.3359(1)	0.018(1)
O(8)	1	0.9193(3)	0.7240(4)	0.3400(1)	0.029(1)
O(9)	1	1.0674(5)	0.7690(5)	0.2500	0.033(1)
O(10)	0.5	1.0000	1.0000	0.2076(5)	0.060(4)
O(11)	1	0.7177(5)	0.4660(4)	0.2500	0.026(1)
O(12)	1	0.4894(5)	0.6090(4)	0.2500	0.032(1)
O(13)	1	0.8029(3)	0.9231(3)	0.4547(1)	0.017(1)
O(14)	0.804	0.3333	0.6667	0.5587(2)	0.044(2)
O(15)	0.268	0.4374(18)	0.7050(20)	0.6188(5)	0.065(5)
O(16)	0.196	0.3333	0.6667	0.6411(9)	0.040(5)
O(17)	0.065	0.3900(90)	0.7780(40)	0.5849(16)	0.090(30)

Table S3. Selected bond lengths [Å] and angles [deg] for **I**.

K(1)-O(1)#3	2.973(3)	K(3)-O(5)#10	3.228(3)	B(2)-O(2)	1.488(5)
K(1)-O(1)#4	3.033(3)	K(3)-O(7)#11	2.896(3)	B(2)-O(3)	1.452(5)
K(1)-O(2)	2.773(3)	K(3)-O(8)	2.750(3)	B(2)-O(6)	1.492(5)
K(1)-O(2)#2	2.951(3)	K(3)-O(9)	3.278(4)	B(2)-O(13)	1.452(5)
K(1)-O(6)#1	2.939(3)	K(3)-O(11)	2.859(4)		
K(1)-O(13)	2.820(3)	K(3)-O(11)#11	2.864(4)	B(3)-O(3)	1.451(5)
K(1)-O(13)#1	3.076(3)	K(3)-O(12)#11	2.819(3)	B(3)-O(4)	1.484(5)
K(1)-O(14)	2.830(3)	K(3)-O(4)#11	2.919(3)	B(3)-O(5)	1.460(5)
				B(3)-O(7)	1.486(5)
K(2)-O(7)#5	2.830(2)	Na(1)-O(13)#4	2.362(2)		
K(2)-O(7)	2.830(2)	Na(1)-O(13)#1	2.362(2)	B(4)-O(6)	1.373(5)
K(2)-O(8)	3.037(3)	Na(1)-O(13)#8	2.362(2)	B(4)-O(7)	1.358(5)
K(2)-O(8)#5	3.037(3)	Na(1)-O(13)# ¹⁰	2.362(2)	B(4)-O(8)	1.377(5)
K(2)-O(9)#6	2.957(5)	Na(1)-O(13)	2.362(2)		
K(2)-O(9)	2.702(5)	Na(1)-O(13)# ¹³	2.362(2)	C(1)-O(11) #14	1.291(4)
K(2)-O(10)#5	2.883(7)			C(1)-O(11)#11	1.291(4)
K(2)-O(10)	2.883(7)	B(1)-O(1)	1.379(5)	C(1)-O(11)	1.291(4)
K(2)-O(11)	2.685(5)	B(1)-O(2)	1.366(5)		
K(2)-O(12)	3.129(6)	B(1)-O(4)	1.374(5)	N(1)-O(14)	1.253(9)
				N(1)-O(15)	1.170(15)
				N(1)-O(16)	1.260(3)
				N(1)-O(17)	1.170(3)
O(2)-B(1)-O(1)	119.0(3)	O(3)-B(3)-O(4)	110.1(3)	O(11)#8-C(1)-O(11)	120.0
	122.3(3)	O(3)-B(3)-O(5)	111.8(3)	O(11)#8-C(1)-	120.0
O(2)-B(1)-O(4)				O(11)#10	
O(4)-B(1)-O(1)	118.7(4)	O(3)-B(3)-O(7)	109.9(3)	O(11)-C(1)-O(11)#10	119.998(1)
		O(5)-B(3)-O(4)	108.8(3)		
O(2)-B(2)-O(6)	108.2(3)	O(5)-B(3)-O(7)	107.5(3)	O(15)-N(1)-O(14)	119.7(9)
O(3)-B(2)-O(2)	109.9(3)	O(7)-B(3)-O(4)	108.8(3)	O(17)#3-N(1)-O(16)	113(3)
O(3)-B(2)-O(6)	109.9(3)	O(6)-B(4)-O(8)	119.4(3)		
O(13)-B(2)-O(2)	108.6(3)	O(7)-B(4)-O(6)	122.9(3)		
O(13)-B(2)-O(3)	111.0(3)	O(7)-B(4)-O(8)	117.7(3)		
O(13)-B(2)-O(6)	109.2(3)				

Symmetry transformations used to generate equivalent atoms: #1 $y, x, -z+1$; #2 $-x+1, -x+y+1, -z+1$; #3 $-y+1, x-y+1, z$; #4 $x-y+1, -y+2, -z+1$; #5 $-x+y, -x+1, z$; #6 $-y+1, x-y, -z+1/2$; #7 $x, y, -z+1/2$; #8 $-x+y+1, -x+2, z$; #9 $-y+2, x-y+1, -z+1/2$; #10 $-y+2, x-y+1, z$; #11 $-x+y+1, -x+1, z$; #12 $x-y+1, -y+1, -z+1$; #13 $-x+2, -x+y+1, -z+1$; #14 $-y+1, x-y, z$; #15 $-x+y+1, -x+1, -z+1/2$; #16 $-x+1, -x+y, -z+1$; #17 $x-y, -y+1, -z+1$.

Table S4. Hydrogen coordinates and isotropic displacement parameters for **I**.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
H(1)	0.3340(40)	0.4450(50)	0.4273(14)	0.035
H(5)	0.4690(40)	0.7890(50)	0.3352(14)	0.023
H(8)	0.9950(40)	0.7470(50)	0.3537(15)	0.035
H(9)	1.1170(50)	0.7690(50)	0.2732(13)	0.039
H(10)	1.0200(30)	1.0770(11)	0.2220(50)	0.072
H(12)	0.5120(50)	0.6750(40)	0.2687(13)	0.038
H(13)	0.8470(40)	1.0030(30)	0.4427(13)	0.020

Table S5. The possible hydrogen bonds with $H..A < r(A) + 2.000 \text{ \AA}$ and $\angle DHA > 110 \text{ deg}^*$.

D-H	<i>d</i> (D-H)	<i>d</i> (H..A)	\angle DHA	<i>d</i> (D..A)	A
O1-H1	0.890	1.895	165.89	2.766	O3 [-x+y, -x+1, z]
O1-H1	0.865	2.184	157.04	2.999	O13 [-x+y, -x+1, z]
O5-H5	0.865	2.551	142.10	3.277	O4 [-y+1, x-y+1, z]
O5-H5	0.886	2.564	139.05	3.285	O5 [-y+1, x-y+1, z]
O12-H12	0.864	1.941	161.07	2.772	O5
O12-H12	0.864	2.636	121.31	3.172	O9 [-x+y+1, -x+2, z]

*D = donor, A = acceptor

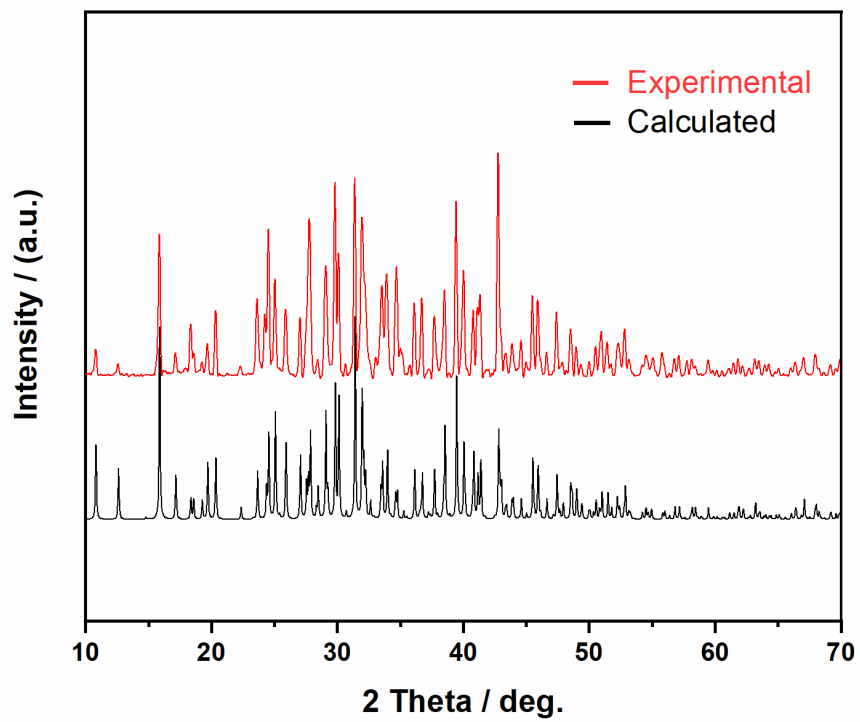


Figure S1. The powder XRD pattern of I.

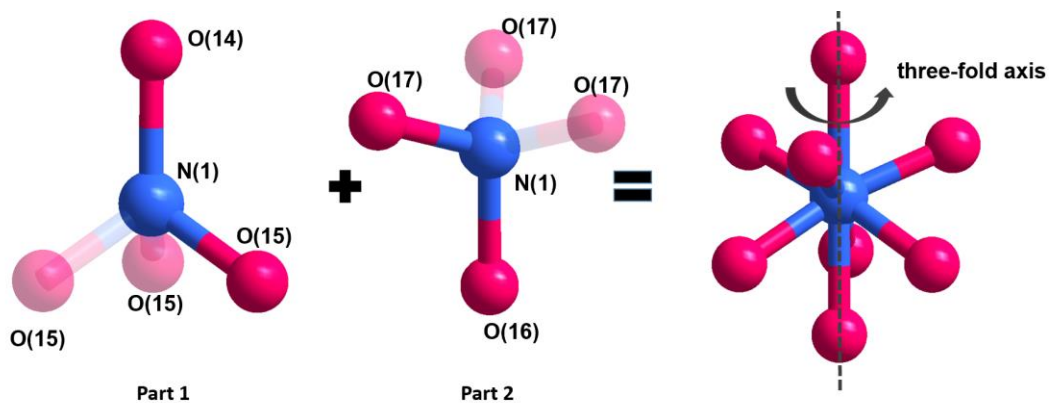


Figure S1. The disorder $[\text{NO}_2]^-$ units around the three-fold axis. Owing to the flexibility of small $[\text{NO}_2]^-$ molecular, a complicated position disorder was found in **I**, which can be divided into two parts. The “O-N-O” (typical $[\text{NO}_2]^-$ molecular, with position possibility of $1/3$) in part 1 and 2 are clearly shown while the transparent atoms/bonds stand for other possible locations in each part. Note that the refined ratio of part 1/part 2 = $0.8/0.2$, and the site occupancy of O(14), O(15), O(16), and O(17) is 0.804, 0.268, 0.196, and 0.065, respectively.

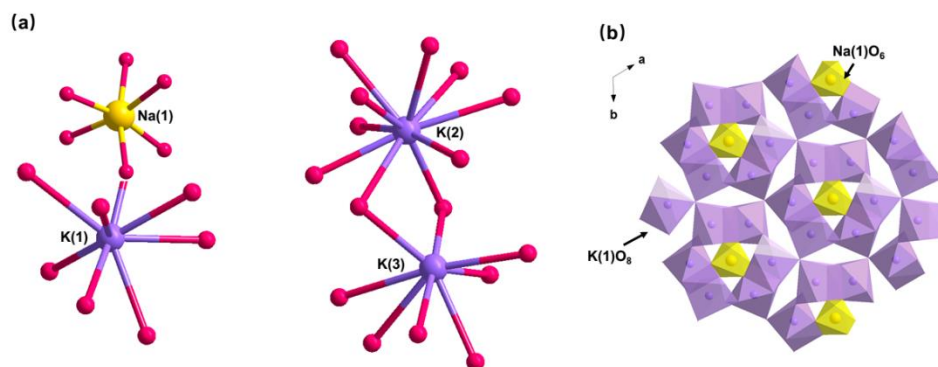


Figure S3. (a) The coordination environment of Na⁺ nad K⁺ cations. (b) Na(1)O₆ and K(1)O₈ polyhedra.

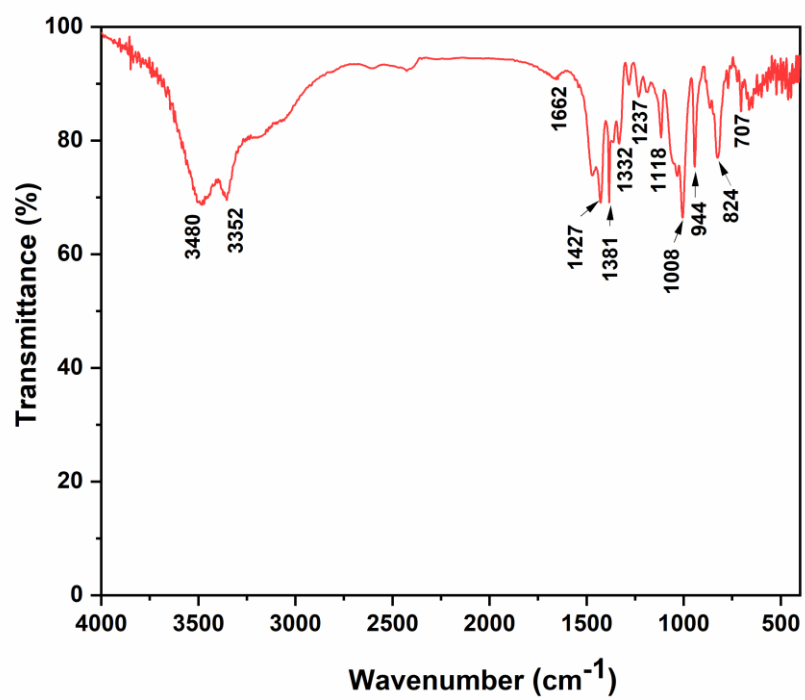


Figure S4. The IR spectrum of I.

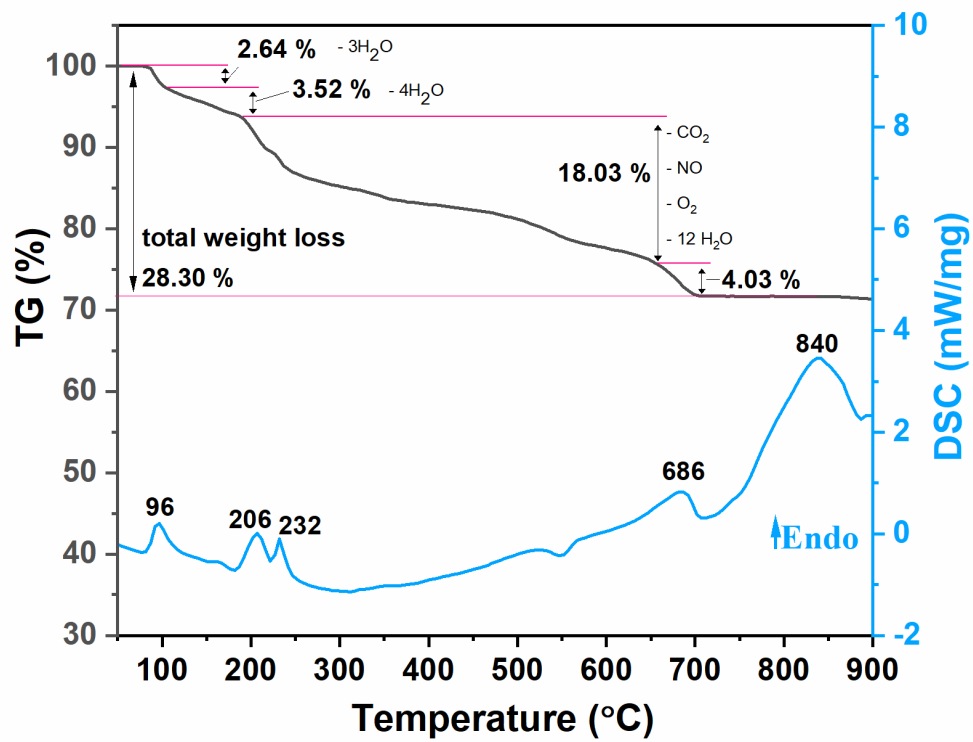


Figure S5. The TG and DSC measurements of I.

Table S6. Summary of borate-based compounds with three or more anionic groups.

Compound	Mineral/Synthetic	Ref
$\text{Ca}_{12}\text{Mg}_4(\text{BO}_3)_7(\text{CO}_3)_4(\text{OH})_2\text{Cl}\cdot\text{H}_2\text{O}$	Mineral	6
$\text{Pb}_{47}\text{O}_{24}(\text{BO}_3)_2(\text{CO}_3)(\text{OH})_{13}\text{Cl}_{25}$	Mineral	7
$\text{Ca}_4\text{CuB}_4\text{O}_6(\text{OH})_6(\text{CO}_3)_2$	Mineral	8
$\text{Ca}_4\text{MgB}_4\text{O}_6(\text{OH})_6(\text{CO}_3)_2$	Mineral	9
$\text{Ca}_3\text{Al}(\text{CO}_3)[\text{B}(\text{OH})_4](\text{OH})_6\cdot 12\text{H}_2\text{O}$	Mineral	10
$\text{Ba}_2(\text{BO}_3)_{1-x}(\text{CO}_3)_x\text{Cl}_{1+x}$	Synthetic	11
$\text{K}_9[\text{B}_4\text{O}_5(\text{OH})_4]_3(\text{CO}_3)(\text{BH}_4)\cdot 7\text{H}_2\text{O}$	Synthetic	12
$\text{Ca}_4(\text{Ca}_{0.7}\text{Na}_{0.3})_3\text{Na}_{0.7}\text{Li}_5[\text{B}_{22}\text{O}_{39}(\text{OH})_3](\text{CO}_3)(\text{OH})_{1.8}\cdot 0.2\text{H}_2\text{O}$	Synthetic	13
$\text{Pb}_7\text{O}(\text{CO}_3)_3(\text{BO}_3)(\text{OH})_3$	Synthetic	14
$\text{Rb}_9[\text{B}_4\text{O}_5(\text{OH})_4]_3(\text{CO}_3)\text{X}\cdot 7\text{H}_2\text{O}$ (X = Cl, Br, and I)	Synthetic	15
$\text{K}_9[\text{B}_4\text{O}_5(\text{OH})_4]_3(\text{CO}_3)\text{X}\cdot 7\text{H}_2\text{O}$ (X = OH and I)	Synthetic	15

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