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Structural Characterization and Chemistry of the Industrially Important Zinc Borate, $Zn[B_3O_4(OH)_3]$

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Several unique crystalline zinc borates are known, a few of which find industrial use in significant tonnages. Although the most important of these has been a commercial product for more than 3 decades, it was never before structurally characterized. The structure of $Zn[B_3O_4(OH)_3]$ (**1**) was determined for the first time by single-crystal X-ray diffraction, revealing it to be a complex network consisting of infinite polytriborate chains cross-linked by coordination with zinc and further integrated by hydrogen bonding. The structure of **1** bears similarities to certain borate minerals, most notably, studenitsite ($Ca[B_3O_4(OH)_3]$) and colemanite ($Ca[B_3O_4(OH)_3]\cdot H_2O$); however, significant differences are described. Hydrolytic and thermochemical properties of **1** are discussed. This compound illustrates the important role played by metal cations in directing the spatial arrangement of anionic polyborate structural units in metal borates. This new structural information leads to a revision in the chemical formula, $2ZnO\cdot 3B_2O_3\cdot 3.5H_2O$, typically used to describe this material as an article of commerce, to $2ZnO\cdot 3B_2O_3\cdot 3H_2O$. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 6.845(2)$ Å, $b = 9.798(2)$ Å, $c = 7.697(2)$ Å, $\beta = 106.966(4)°$, $V = 493.8\ (2)$ Å^3, and $Z = 4$.

Introduction

Occurring in both mineral and synthetic forms, metal borates in which boron is bound only to oxygen are numerous and find extensive industrial use. Many synthetic metal borates resemble minerals in structure, containing isolated polyborate anions or complex polyborate rings, chains, sheets, or networks. However, structure−stability theories recently developed for borate minerals do not consistently apply to synthetic borates. Understanding how cations direct borate structural units in borate compounds is fundamental to the development of synthetic strategies for metal borates having useful properties.

Metal borates can be divided into two categories, hydrated and anhydrous. So-called hydrated borates, which account for the majority of known boron-containing minerals and synthetic borates consumed by industry, have structures containing B−OH groups (hydroxyl-hydrated borates) and may also contain interstitial water. Although structural details for most commercially relevant crystalline hydrated borates are known, the structures of several important zinc borates, including the title compound **1**, have not been described.

There is good evidence for the existence of at least eight unique crystalline hydrated zinc borates. These have compositions $4ZnO\cdot B_2O_3\cdot H_2O$ (**2**),[1] $ZnO\cdot B_2O_3\cdot {\sim}1.12H_2O$ (**3**),[2] $ZnO\cdot B_2O_3\cdot {\sim}2H_2O$ (**4**),[2] $6ZnO\cdot 5B_2O_3\cdot 3H_2O$ (**5**),[3] $2ZnO\cdot 3B_2O_3\cdot 7H_2O$ (**6**),[4] $2ZnO\cdot 3B_2O_3\cdot 3H_2O$ (≡**1**), $3ZnO\cdot 5B_2O_3\cdot 14H_2O$,[5] and $ZnO\cdot 5B_2O_3\cdot 4.5H_2O$,[3] spanning a range of B_2O_3/ZnO mole ratios from 0.25 to 5.0. Each of these compounds can be prepared selectively by reactions of zinc oxide with boric acid in water, the specific product obtained determined by reactant concentrations and temperature. Aside from the title compound, to date only the structures of **3** and **6** have been reported; the latter has the structural formula $Zn[B_3O_3(OH)_5]\cdot H_2O$ and contains a monomeric triborate dianion.[4]

Zinc borates have found industrial use since the 1940s,[6] with $2ZnO\cdot 3B_2O_3\cdot 7H_2O$ and $3ZnO\cdot 5B_2O_3\cdot 14H_2O$ primarily utilized in the earlier period. However, these compounds had a limited range of applications owing to their low dehydration temperatures. The most important commercial zinc borate today, **1**, was introduced more than 30 years ago and now has a worldwide annual production exceeding 10 000 metric tons. It is primarily used as a polymer additive and as a preservative in wood composites. As a polymer additive, it serves as a fire retardant synergist, char promoter, antidrip agent, smoke and afterglow suppressant, and modifier of electrical and optical properties. Addition of **1** to ceramic bodies can improve green strength and reduce firing times, temperatures, and pyroplastic deformation.

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(1) Schubert, D. M. U.S. Patent 5,342,533, 1994.

(2) Choudhury, A.; Neeraj, S.; Natarajan, S.; Rao, C. N. *J. Chem. Soc., Dalton Trans.* **2002**, *7*, 1535−1538. The recently characterized **3** is apparently a different compound from **4**, also known in trade literature as $2ZnO\cdot 2B_2O_3\cdot 3H_2O$, which has been an article of commerce for many years.

(3) Lehmann, H.-A.; Sperscheider, K.; Kessler, G. *Z. Anorg. Allg. Chem.* **1967**, *354*, 37−43.

(4) Ozols, J.; Tetere, I.; Ievins, A. *Izv. Akad. Latv. Nauk. SSR, Ser. Kim.* **1973**, *1*, 3−7.

(5) Putnins, J.; Ievins, A. *Latv. Valsts Univ. Kim. Fak. Zinat. Raksti* **1958**, *22*, 69. This compound has been referred to as $2ZnO\cdot 3B_2O_3\cdot 9H_2O$ in trade literature.

(6) *The Crown* **1944**, *9*, 31.

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It is also added to coatings where it functions as a corrosion inhibitor, fire retardant, preservative, mildewstat, and tannin-stain blocker. Important attributes of **1** include relatively low water solubility, as discussed below, and a relatively high dehydration onset temperature (>290 °C). The latter property permits processing in a wide range of polymer systems. Its low refractive index (1.58) permits the manufacture of transparent or translucent articles.

Zinc borate **1** is produced by reaction of zinc oxide and boric acid, or reactions of zinc and borate salts, in hot water ($\gtrsim$65 °C); the composition $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ was assigned to it by workers who first prepared it and recognized its usefulness.[7] This composition is used extensively in technical and trade literature to describe this compound as an article of commerce. However, this composition is inconsistent with more recent physical data. For example, both elemental analysis and TGA data indicate a lower water content. The TGA data was usually explained by a minor loss of steam-volatile $B(OH)_3$, which is known to occur when large samples of **1** are dehydrated. Other early workers independently prepared this compound by hydrothermal methods and assigned the composition $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$, which we now confirm as correct.[3] This lower level of hydration has implications regarding structure since hydration relates to the degree of condensation of the borate structural unit. The composition $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ suggests a tetrameric structure, which has been proposed repeatedly in trade literature, whereas $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$ (**1**) corresponds to a fully polymerized structural unit.

Solid state ^{11}B NMR and NQR data indicate that **1** is a member of the triborate class, with a 2:1 ratio of tetrahedral to trigonal boron atoms, but are insufficient in establishing further structural details.[8,9] Although the composition and structure of **1** has been a subject of speculation for some time, a detailed structure determination was not previously reported because single crystals large enough for X-ray work were unattainable, the compound consistently forming as small, intergrown crystallites. The compound also exhibits incongruent solubility, making recrystallization impractical. We now have succeeded in preparing single crystals of **1** of sufficient size for X-ray structure determination, revealing this compound to have the composition Zn[$B_3O_4(OH)_3$] ($\equiv 2ZnO \cdot 3B_2O_3 \cdot 3H_2O$).

Experimental Section

Preparation of Crystals. Single crystals of **1** were grown using the following procedure. An aqueous zinc chloride solution, prepared by dissolving enough zinc oxide in 6 M HCl to produce a solution having pH 4, was added dropwise to a quiescent, concentrated boric acid solution at 95 °C. Mixing these solutions results in a significant pH decrease, which was corrected by subsequent slow dropwise addition of an aqueous suspension of zinc oxide. Single crystals of **1** grew on the vessel walls after maintaining the solution at 95 °C for 1 day. The X-ray powder pattern calculated from the single-crystal X-ray data reproduces the pattern observed for bulk samples (commercial product) in all details, showing that the single crystal used for structure determination is representative of this specific zinc borate. The IR spectrum obtained from a sample of single crystals prepared by the above method also agrees well with that of the bulk material. The specific gravity calculated from X-ray data of 2.9 is close to the value 2.8 obtained for bulk material by the flotation method.

Table 1. Crystal Data and Structure Refinement for 1

empirical formula	$H_{12}B_{12}O_{28}Zn_4$
formula weight	851.30
temperature	298(2) K
wavelength	0.71073 Å
crystal system	monoclinic
space group	$P2_1/n$
unit cell dimensions	$a = 6.8452(16)$ Å, $\alpha = 90°$ $b = 9.798(2)$ Å, $\beta = 106.966(4)°$ $c = 7.6970(18)$ Å, $\gamma = 90°$
volume	493.8(2) Å^3
Z	4
density (calculated)	2.863 mg/m^3
absorption coefficient	4.949 mm^{-1}
$F(000)$	416
crystal size	$0.15 \times 0.1 \times 0.05$ mm^3
θ range for data collection	3.46−28.26°
index ranges	$-8 \le h \le 8, -13 \le k \le 8, -9 \le l \le 10$
reflections collected	3045
independent reflections	1173 [R(int) = 0.0236]
completeness to $\theta = 28.26°$	96.1%
absorption correction	SADABS
max. and min. transmission	1.000 and 0.828
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	1173/0/109
goodness-of-fit on F^2	0.988
final R indices [$I > 2\sigma(I)$]	R1 = 0.0226, wR2 = 0.0504
R indices (all data)	R1 = 0.0340, wR2 = 0.0528
largest diff. peak and hole	0.586 and −0.554 e·Å^{-3}

Collection and Reduction of X-ray Data for 1. A colorless parallelepiped was mounted on a thin glass fiber on a Bruker SMART ccd diffractometer. Unit cell parameters were determined from a least-squares fit of 559 reflections ($8.16° < 2\theta < 53.60°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table 1. Intensities did not decay during the course of the experiment. Of the 1173 unique reflections measured, 941 were considered observed ($I > 2\sigma(I)$), but all reflections were used in the subsequent structure analysis. The final discrepancy index was $R = 0.023$, $R_w = 0.050$ for the 941 independent reflections with $I > 2\sigma(I)$. Data were corrected for Lorentz and polarization effects and for absorption. Atoms were located by statistical methods. All nonhydrogen atoms were included with anisotropic displacement parameters. Positional parameters of hydrogen atoms were refined. The isotropic displacement parameters for hydrogen atoms were based on the values for the attached atoms. Scattering factors for H were obtained from Stewart et al.[10] and for other atoms from *The International Tables for X-ray Crystallography*.[11] The maximum and minimum values on a final difference electron density map were 0.59 and −0.55 e·Å^{-3}. Programs used in this work are those supplied with the Bruker SMART ccd diffractometer.

Results and Discussion

Description of Structure. Zinc borate **1** is a complex inoborate (containing a borate structural unit that is an infinite chain) composed of linked triborate moieties, interconnected by coordination with pseudotetrahedral zinc centers and a network of H-bonds. Interatomic distances and angles for **1** are given in Table 2. The asymmetric unit in **1** includes one zinc atom (Figure 1a) and one triborate moiety (Figure 1b). There are three unique boron sites, present as one

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(7) Nies, N. P.; Hulbert, R. W. U.S. Patent 3,549,316, 1970. Nies, N. P.; Hulbert, R. W. U.S. Patent 3,649,172, 1972.

(8) Mao, De Gen, Ph.D. Dissertation, Brown University, 1991.

(9) Mertens, V.; Eckert, H.; Schubert, D. To be published.

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(11) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table 2. Bond Lengths (Å) and Bond Angles (deg) for 1[a]

Zn(1)−O(5)	1.919(2)	O(5)−Zn(1)−O(6)	105.91(9)
Zn(1)−O(6)	1.9473(19)	O(5)−Zn(1)−O(7)	110.00(9)
Zn(1)−O(7)	1.965(2)	O(6)−Zn(1)−O(7)	117.66(8)
Zn(1)−O(1)	1.9663(17)	O(5)−Zn(1)−O(1)	119.48(8)
O(1)−B(1)	1.386(4)	O(6)−Zn(1)−O(1)	108.04(8)
O(1)−B(3)	1.526(3)	O(7)−Zn(1)−O(1)	96.24(8)
O(2)−B(1)	1.361(3)	B(1)−O(1)−B(3)	120.6(2)
O(2)−B(2)	1.474(3)	B(1)−O(1)−Zn(1)	119.39(16)
O(3)−B(3)	1.430(3)	B(3)−O(1)−Zn(1)	118.42(15)
O(3)−B(2)	1.440(3)	B(1)−O(2)−B(2)	123.8(2)
O(4)−B(1)[#1]	1.363(3)	B(3)−O(3)−B(2)	120.3(2)
O(4)−B(3)	1.465(3)	B(1)[#1]−O(4)−B(3)	134.8(2)
O(5)−B(2)[#2]	1.484(3)	B(2)[#2]−O(5)−Zn(1)	116.02(16)
O(6)−B(2)[#3]	1.482(3)	B(2)[#3]−O(6)−Zn(1)	130.81(16)
O(7)−B(3)[#4]	1.477(3)	B(3)[#4]−O(7)−Zn(1)	126.62(16)
B(3)−O(7)[#1]	1.477(3)	O(3)−B(3)−O(4)	114.3(2)
B(1)−O(4)[#4]	1.363(3)	O(3)−B(3)−O(7)[#1]	112.4(2)
B(2)−O(6)[#3]	1.482(3)	O(4)−B(3)−O(7)[#1]	108.2(2)
B(2)−O(5)[#5]	1.484(3)	O(3)−B(3)−O(1)	110.6(2)
		O(4)−B(3)−O(1)	104.5(2)
		O(7)[#1]−B(3)−O(1)	106.2(2)
		O(2)−B(1)−O(4)[#4]	117.9(2)
		O(2)−B(1)−O(1)	119.5(2)
		O(4)[#4]−B(1)−O(1)	122.6(2)
		O(3)−B(2)−O(2)	112.9(2)
		O(3)−B(2)−O(6)[#3]	108.6(2)
		O(2)−B(2)−O(6)[#3]	109.3(2)
		O(3)−B(2)−O(5)[#5]	114.2(2)
		O(2)−B(2)−O(5)[#5]	103.7(2)
		O(6)[#3]−B(2)−O(5)[#5]	107.9(2)

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

trigonal BO_3 and two tetrahedral BO_4 groups. These groups share oxygen vertexes to form a B_3O_3 boroxyl ring. One BO_4 group has one attached OH group and the other has two, producing the $B_3O_4(OH)_3$ subunit (Figure 1b). These triborate moieties link into infinite chains parallel to [101] by sharing an exocyclic oxygen (O4/O4A) between BO_3 and BO_4 polyhedra. The $BO_2(OH)_2$ group is not involved in chain extension. Each zinc atom (Figure 1a) is pseudotetrahedrally coordinated by oxygens of three different polyborate chains. Two zinc coordination positions are satisfied by one endocyclic boroxyl oxygen (O1) and one hydroxyl oxygen (O7) that is attached to the adjacent triborate moiety in the same chain, producing the six-membered ZnB_2O_3 rings, seen in Figure 2.

The boroxyl oxygen involved in zinc coordination lies between the BO_3 and BO_4 polyhedra involved in chain extension. The remaining two zinc coordination sites are occupied by hydroxyl oxygens of $BO_2(OH)_2$ groups in two separate polyborate chains. In this way, all hydroxyl groups are involved in zinc coordination.

Compound **1** exhibits a complex higher order structure. Not only does each zinc center link three separate polyborate chains, but also these chains are interconnected by H-bonds. All three OH hydrogens are involved in H-bonding with oxygen atoms of adjacent chains. Chains are connected via O5−H5···O3, O6−H6···O4, and O7−H7···O2 hydrogen bonds. Notably, all three H-bonds involve B−O−B acceptor oxygen atoms and not B−O−H oxygens, which may explain the relatively high dehydration onset temperature of **1**. Details of H-bonds are given in Table 3. The three hydrogens atoms in **1** are observed in the ^1H MAS NMR spectrum, shown in Figure 3. Owing to their distinct differences in H-bonding strengths, the three proton sites yield clearly resolved resonances at 4.6, 7.0, and 8.6 ppm. There are regular 4-fold centrosymmetric connections between alternating complementary pairs of triborate moieties in neighboring chains. These interactions involve two zinc centers, one in each chain, that link adjacent triborate rings via 2-fold O6−Zn−O1 coordination (corner sharing of zinc tetrahedra and borate polyhedra). The same triborate moieties are also linked by pairs

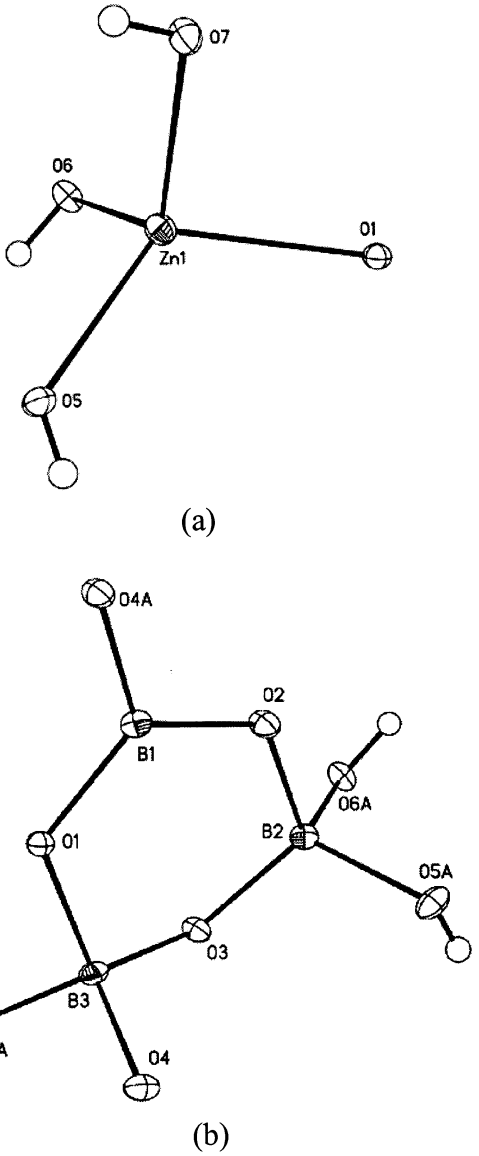

Figure 1. (a) Zn center and (b) $B_3O_4(OH)_3$ units in **1**. Thermal ellipsoids are drawn at 30% probability level.

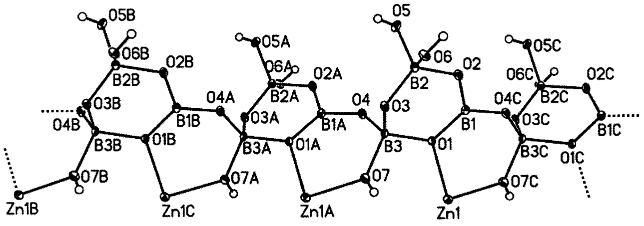

Figure 2. A segment of the infinite polytriborate chains in **1** showing zinc interactions. Zinc atoms are shown with only two coordination positions occupied for clarity. Thermal ellipsoids are drawn at 30% probability level.

Table 3. Details of Hydrogen Bonds for 1[a]

D−H···A	d(D−H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (deg)
O(5)−H(5)···O(3)[#6]	0.61(3)	2.09(3)	2.705(3)	175(4)
O(6)−H(6)···O(4)[#2]	0.74(3)	2.03(3)	2.766(3)	174(3)
O(7)−H(7)···O(2)[#7]	0.69(3)	2.39(3)	3.073(3)	170(3)

[a] D and A signify donor and acceptor oxygens, respectively. Symmetry transformations used to generate equivalent atoms: [#2] $x + {}^1/_2, -y + {}^3/_2, z - {}^1/_2$; [#6] $-x + {}^1/_2, y - {}^1/_2, -z + {}^5/_2$; [#7] $-x - {}^1/_2, y - {}^1/_2, -z + {}^3/_2$.

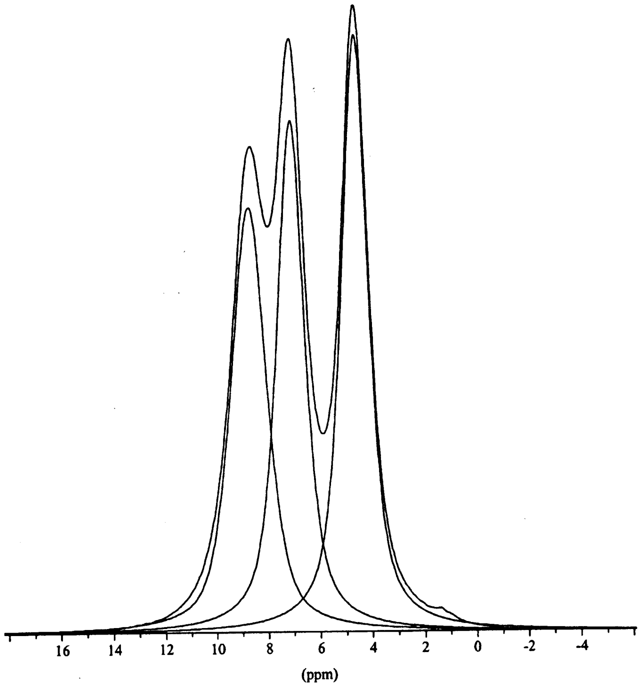

Figure 3. ^1H MAS NMR spectrum of **1** recorded at a field strength of 11.7 T, using a 20-kHz rotation frequency.

of O7−H7···O2 H-bonds. Zinc atoms lie very roughly in layers positioned between repeating pairs of polyborate chains.

Borate structures can be described in terms of compact, insular groups, referred to as fundamental building blocks (FBBs), forming the basis of classification schemes for crystalline borate compounds.[12,13] These schemes define FBBs according to the number of boron atoms, the number of trigonal BO_3 and tetrahedral BO_4 groups, and the mode of polymerization between the FBBs, to give isolated, modified isolated, chain, modified chain, sheet, modified sheet, and three-dimensional network structures. Using the classification scheme devised by Christ and Clark, the borate structural unit of **1** is described as $\infty{:}3(\Delta + 2T)$, indicating a three-boron FBB containing one trigonal and two tetrahedral boron centers.[12] Using the more recent classification scheme proposed by Burns and Hawthorne, the structural unit in **1** is described as 1△2□:<△2□>, where △ and □ refer to BO_3 and BO_4 polyhedra, respectively.[13]

Comparison with Mineral Structures. The structure of **1** bears similarities to some borate minerals, notably the industrially important colemanite, $Ca[B_3O_4(OH)_3]\cdot H_2O$, and the lesser known studenitsite, $Ca[B_3O_4(OH)_3]$.[14−16] The industrial mineral hydroboracite, $CaMg[B_3O_4(OH)_3]_2\cdot 3H_2O$, is also related.[17] These minerals also contain infinite polytriborate chains of the ⟨△2□⟩ type that are cross-linked by coordination with metal cations. However, significant differences exist between the structures of these minerals and **1** resulting from the different coordination demands of their metal cations.

In colemanite, calcium atoms link together by sharing oxygen to form chains running parallel to the polytriborate chains (parallel to [100]).[14,15] These calcium-containing chains share oxygen of the polytriborate chains and thereby interconnect them into infinite sheets. These sheets are connected by H-bonding and a relatively small number of Ca−O bonds, resulting in the perfect [101] cleavage characteristic of colemanite.[15] In contrast, the tetrahedral zinc centers in **1** do not form chains by sharing oxygen between zinc and instead interconnect the polyborate chains into a three-dimensional network rather than sheets. Consequently, **1** is a much less friable material than colemanite.

The closest mineral analogue to **1** in composition is studenitsite, $Ca[B_3O_4(OH)_3]$.[16] In contrast, however, this mineral contains corrugated calcium oxide sheets lying between and interconnecting parallel polytriborate chains. Some notable differences between studenitsite and colemanite are the absence of interstitial water and a helical rather than translational extension of borate chains in the former, with $B_3O_4(OH)_3$ groups within a chain related by a 2-fold screw axis parallel to the *b*-axis of the crystal. Although colemanite contains one water in the coordination environment of calcium, this water uses one hydrogen to H-bond to adjacent water with the result that the total number of bonds from the interstitial complex, $[Ca(H_2O)]^{2+}$, to the borate structural unit is the same as that for Ca^{2+} in studenitsite if each metal center is assigned the same coordination number.

Borate and polyborate structural units have associated basicities that are approximately proportional to the percentage of tetrahedral boron in their FBBs.[18] This is also a function of the solution pH prevailing during borate crystallization since specific borate anions are stable only within a given pH range.[18] Empirical methods based on the analysis of borate mineral structures were developed recently to estimate Lewis basicities of borate structural units.[18] According to the *valence matching principle,* to have a stable structure, the Lewis basicity of the (anionic) borate structural unit must match closely the Lewis acidity of the (cationic) interstitial complex.[19] Correlations of structural features found in minerals suggest that borate structural units adjust to varying acid−base conditions, within stability ranges, by changing the average coordination number of oxygen atoms (O−CN) in the structural unit, counting hydrogen bonds and bonds to cations.[18] Higher average

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(12) Christ, C. L.; Clark, J. R. *Phys. Chem. Miner.* **1977**, *2*, 59−87.

(13) Burns, P. C. *Can. Mineral.* **1995**, *33*, 1167−1176.

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O−CN values are associated with higher borate basicities.[18] These correlations depend heavily on the assignment of coordination number to cations since this largely defines average O−CN.

Colemanite, studenitsite, and **1** have chemically equivalent borate structural units and thus have the same Lewis basicities. However, Zn^{2+} has substantially higher Lewis acidity than Ca^{2+}.[19] The structure of colemanite was analyzed by others with the conclusion that it has an average O−CN of 3.6, considering calcium to be 8-coordinated, and examination of the studenitsite structure indicates that it also has an average O−CN of 3.6.[15,16,18] The O−CN value of these minerals correlates well with the overall pattern for borate mineral structures.[18] Zinc favors four-coordination and we consider the zinc atom in **1** to be four-coordinate. Each structural unit oxygen in **1** is coordinated once by either an H-bond or zinc, resulting in an O−CN of 3.0. This O−CN value is significantly below the range reported for borate minerals.[18] Only by considering the coordination number of zinc to be higher than 4 can the O−CN be higher.

For metal coordination, some authors have included all oxygens having a metal−oxygen bond valence greater than 0.05 vu with metal−oxygen distances less than the metal−metal distance, with consideration of distance gaps.[18,19] Application of the distance rules alone can overcount the number of oxygens actually involved in bonding interactions with the metal. In **1**, there are 24 oxygen atoms having Zn−O distances shorter than the Zn−Zn distance (4.391 Å). The immediate coordination environment around zinc (Figure 1a) contains four oxygen atoms, at distances from 1.919 to 1.966 Å, with geometry close to an idealized tetrahedron. Valence analysis gives a sum of bond valences for zinc of 3.8 vu, counting only these four Zn−O bonds. There is a large gap between the closest four oxygens and the next two, which have Zn−O distances of 2.707 Å (O2) and 2.918 Å (O7). Beyond these, the next closest oxygen lies at a distance of 3.179 Å (O4).

For the borate structural unit in colemanite, studenitsite, and **1**, it has been argued that the boroxyl oxygen linking the two tetrahedral boron atoms should receive two additional bonds, either from the metal or H-bonds, to satisfy its valence requirements.[15] In colemanite this oxygen receives two H-bonds and in studenitsite it is bonded to two calcium atoms.[15,16] However, the corresponding oxygen in **1**, O(3), receives only one H-bond and is not within the tetrahedral coordination environment of zinc. The shortest three O(3)−Zn distances are 3.282, 3.771, and 3.885 Å. Valence analysis, counting one H-bond and two $^{[4]}$B−O bonds, gives a sum of valences for O(3) of 1.81 vu, somewhat less than the 1.90 vu calculated for colemanite.[15,19] The two $^{[4]}$B−O bonds to these oxygen atoms are both slightly shorter by 0.021−0.022 Å in **1** than in colemanite.[15]

The related synthetic monomeric triborate **6**, $Zn(H_2O)[B_3O_3(OH)_5]$, is an analogue of the mineral meyerhofferite, $Ca(H_2O)[B_3O_3(OH)_5]$.[4,20,21] Here, the tetracoordination of zinc also results in a significantly lower average O−CN in the synthetic material compared to that in the mineral. Explanations offered for why synthetic borates may not match the patterns observed for borate minerals refer to the greater range of options available in nature compared with more restricted synthetic systems.[18] Hydrolytic stability under geologic conditions may also be a factor. Clearly, geological conditions, as well as those used to crystallize most anhydrous borates, favor more thermodynamically stable products. Nevertheless, improved understanding of structure−stability relationships is important to the development of synthetic methodologies for borates having useful properties.

Solubility and Hydrolysis. Details of the hydrolytic behavior of **1**, which are important to industrial applications, have not been described previously in the literature. Compound **1** is sparingly soluble in water and exhibits incongruent solubility. Less than 50 mg of **1** will dissolve in a liter of water at 20 °C (0.005 wt %). Concentrated aqueous slurries of solid **1** (e.g., 10 wt %) are stable indefinitely, the bulk of the solids persisting as crystalline **1** in contact with its solution. However, very dilute slurries of **1** hydrolyze at room temperature to boric acid and highly insoluble $Zn(OH)_2$. Owing to the thermal instability of $Zn(OH)_2$, hydrolysis at elevated temperatures (boiling water) gives boric acid and ZnO, the reverse of the reaction used for commercial production of **1**. Room-temperature hydrolysis is relatively slow. A stirred 10 wt % slurry of **1** required $\approx$3 weeks to reach equilibrium, ultimately giving a supernatant solution that is saturated in boric acid (800−850 ppm B) and has 10−15 ppm Zn. This solution has an approximately neutral pH, which is below the pH at which $Zn(OH)_2$ exhibits minimum solubility. The stability of concentrated slurries of **1** is attributable to the high concentration of boric acid in solution resulting from partial hydrolysis. Incongruent solubilities can be expressed in various ways. If we define solubility as the weight percent of the hypothetical anhydrous components, ZnO and B_2O_3, in solution at equilibrium, calculated from observed B and Zn concentrations, then the solubility of **1** is $\approx$0.28 wt %. However, at very low slurry concentrations, the undissolved solids resulting from hydrolysis of **1** are primarily $Zn(OH)_2$.

Under appropriate conditions, **1** can be converted to other crystalline hydrated zinc borates, including **2**, **4**, and **5**. For example, **1** converts to **4** (dehydration onset $\approx$200 °C) when aqueous slurries are heated in the presence of excess zinc oxide, and **4** converts to **1** in the presence of excess boric acid in the appropriate temperature range. Also, prolonged reflux of a 5 wt % aqueous slurry of **1** results in quantitative conversion to **2** after 1 week (eq 3).[1] Continued reflux of this system for 1 month results in further quantitative conversion of **2** to **5** (eq 4) with the net reaction given by eq 5. Slurry concentrations of **1** must be relatively low to allow conversion to **2**, as high concentrations of boric acid product inhibit formation of **2**. We proposed the structural formula $Zn_2(BO_3)(OH)$ for **2**, supported by detection of only three-coordinate boron in MAS solid state ^{11}B NMR spectra.[8,9] This structure was confirmed by the structural characterization of the OH/F disordered compound $Zn_2(BO_3)(OH)_{0.75}F_{0.25}$, which exhibits an X-

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ray diffraction pattern identical to that of **2**.[22] Compound **2** is notable in that it exhibits a dehydration onset temperature of ≈415 °C, which is unusually high for a hydroxy-hydrated borate crystallized under nonhydrothermal conditions. This property allows for processing in engineering thermoplastics and other relatively high temperature systems. Despite containing 78.8 wt % ZnO, **2** has a relatively low refractive index: 1.65. Practical methods for the synthesis of **2** have been devised, including direct preparation from zinc oxide and boric acid with short reaction time.[1] These methods have been used to manufacture **2** in multiton quantities. In contrast, **5**, which has not yet been structurally characterized, exhibits a relatively low dehydration onset temperature.

$$\underset{\mathbf{1}}{2[2ZnO\cdot 3B_2O_3\cdot 3H_2O]} + 10H_2O \rightarrow \underset{\mathbf{2}}{4ZnO\cdot B_2O_3\cdot H_2O} + 10B(OH)_3 \tag{3}$$

$$\underset{\mathbf{2}}{3[4ZnO\cdot B_2O_3\cdot H_2O]} + 14B(OH)_3 \rightarrow \underset{\mathbf{5}}{2[6ZnO\cdot 5B_2O_3\cdot 3H_2O]} + 3H_2O \tag{4}$$

$$\underset{\mathbf{1}}{3[2ZnO\cdot 3B_2O_3\cdot 3H_2O]} + 15H_2O \rightarrow \underset{\mathbf{5}}{6ZnO\cdot 5B_2O_3\cdot 3H_2O} + 8B(OH)_3 + 3H_2O \tag{5}$$

Thermochemistry. The thermal behavior of **1** is important to industrial applications, particularly, uses in fire retardancy and ceramics manufacture. Dehydration of **1** commences upon heating above 290 °C, observed in TGA experiments as three overlapping endothermic events that are complete by ≈420 °C. Complete dehydration requires ≈445 J/g, as measured by DSC experiments. The dehydration sequence, involving loss of three molar equivalents of water through condensation of B−OH groups, yields a substantially amorphous material of composition $2ZnO\cdot 3B_2O_3$. This material undergoes a sharp exothermic event (≈270 J/g) at ≈640 °C corresponding to crystallization of two anhydrous zinc borate phases, $3ZnO\cdot B_2O_3$ and $4ZnO\cdot 3B_2O_3$, presumably in the presence of liquid B_2O_3, as determined by XRD analysis of quenched samples.[23,24] Upon further heating, $3ZnO\cdot B_2O_3$ decomposes at ≈870 °C to a liquid and crystalline $4ZnO\cdot 3B_2O_3$, which subsequently melts at ≈960 °C.

Conclusions

Borate compounds exhibit considerable structural variability, having spatial arrangements directed by the demands of interstitial cations. Hydrogen bonding plays an additional important role in integrating and stabilizing structures.[25] Borates differ from other oxide materials, such as aluminates and silicates, in which the main group element oxide components play a more dominant role in directing structure. Theories recently developed for borate minerals advance our understanding of borate materials, but do not consistently apply to synthetic borates. A current challenge is the extension and adaptation of these principles to synthetic systems. Finally, elucidation of the structure of **1** leads to a revision of the chemical formula from $2ZnO\cdot 3B_2O_3\cdot 3.5H_2O$, used to describe this material as an article of commerce for more than 30 years, to $2ZnO\cdot 3B_2O_3\cdot 3H_2O$.

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Supporting Information Available: Crystallographic information files (CIF) and figures showing details of H-bonding (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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