Inorg. Chem. **1992,** *31,* 4679–4682

Framework Alkali Metal Zinc Orthoborates: $AZn_4(BO_3)_3$ (A = K, Rb, Cs)

Robert W. Smith, Jeanne L. Luce, and Douglas A. Keszler*

Department of Chemistry and Center for Advanced Materials Research, Gilbert Hall 153, Oregon State University, Corvallis, Oregon 97331-4003

Received April 1, 1992

The new family of alkali metal zinc orthoborates $AZn_4(BO_3)_3$ (A = K, Rb, Cs) have been synthesized, and the structures of the K and Rb analogs have been established by single-crystal X-ray methods. Each compound crystallizes in a monoclinic cell, space group *P*2/*c*, with *Z* = 2. Cell parameters for the K analog: *a* = 6.876 (2) Å, *b* = 4.990 (1) Å, *c* = 12.574 (1) Å, *β* = 92.92 (1)°, *V* = 430.9 (2) Å^3. Cell parameters for the Rb analog: *a* = 6.849 (2) Å, *b* = 5.000 (2) Å, *c* = 12.718 (2) Å, *β* = 92.53 (2)°, *V* = 435.1 (4) Å^3. For the Cs analog, a cell of dimensions *a* = 6.871 (2) Å, *b* = 5.019 (2) Å, *c* = 12.961 (3) Å, *β* = 92.50 (3)°, and *V* = 446.5 (4) Å^3 has been obtained from refinement of powder X-ray data. The structure is a new type composed of tetrahedral ZnO_4 and triangular BO_3 groups that are arranged in a three-dimensional framework by sharing O vertices. The framework affords channels having rectangular cross sections of dimensions 3.5 × 5.6 Å that extend in the [010] direction; the alkali metal ions occupy sites in these channels. The ions in these channels are not exchanged with other cations.

Introduction

In this contribution, we describe the preparation of the isomorphous series of compounds $AZn_4(BO_3)_3$ (A = K, Rb, Cs) and the crystal structures of the K and Rb analogs. The compounds were synthesized as ordered derivatives of the phase $BaLiZn_3(BO_3)_3$;[1] we found the Li and Zn atoms in this material to be disordered over the available tetrahedral sites whereas substitution of Li by a Zn atom and Ba by a K, Rb, or Cs atom affords a regular arrangement.

This work has resulted from our ongoing interests in the optical and catalytic properties[2,3] of borates and the curious structures that result from collocation of metal-centered O tetrahedra and BO_3 triangles.[4] The structure found in the present series provides a unique framework of tetrahedra and triangles that affords rectangular channels occupied by alkali metal atoms. Results of attempts to ion-exchange the K atoms in the channels are described.

Experimental Section

Each compound was prepared by grinding a stoichiometric mixture of KNO_3 (Spectrum, reagent grade), Rb_2CO_3 (Morton Thiokol, 99.9%), or Cs_2CO_3 (Johnson Matthey, 99%) with $Zn(NO_3)_2 \cdot 4.36H_2O$ (Morton Thiokol, reagent grade) and B_2O_3 (Johnson Matthey, 99.99%) under hexane to a fine powder, followed by heating at 600 °C for 1 h to decompose the salts. These samples were then reground and annealed at 750 °C for 12 h. All samples were single phase, as determined by powder X-ray diffraction measurements that were obtained with an automated Philips diffractometer equipped with a diffracted-beam monochromator set for Cu K*α* radiation. Single crystals of the K and Rb analogs were grown with the compound PbO as a flux. A solute–flux mixture, 4:1 by mass, was heated in a Pt crucible to 930 °C, cooled at 6 °C/h to 600 °C, and then rapidly cooled to room temperature. Clear, colorless crystals were physically removed from the crucible for structure determinations.

Unit-cell parameters were determined from a K crystal having dimensions 0.20 × 0.08 × 0.04 mm by least-squares analysis of 15 reflections in the range $30 < 2\theta < 39°$ that were automatically centered on a Rigaku AFC6R diffractometer equipped with monochromatic Mo K*α* radiation. Intensity data covering the range of indices $-9 \le h \le 9$, $0 \le k \le 7$, and $0 \le l \le 17$ were collected with the *ω*–2*θ* scan technique at a speed of 16°/min and a width $\Delta\omega = (1.50 + 0.3 \tan\theta)°$. From 1041 reflections measured to $2\theta = 60°$, 994 unique data with $F_o^2 \ge 3\sigma(F_o^2)$ were obtained.

Similarly, lattice parameters were refined for a Rb crystal having dimensions 0.16 × 0.10 × 0.05 mm from 17 reflections in the range $30 < 2\theta < 43°$; intensity data were collected with the same scan speed and width over the range of indices $-8 \le h \le 8$, $0 \le k \le 6$, and $0 \le l \le 16$. From 791 reflections measured to $2\theta = 55°$, 752 unique data were obtained.

All calculations were performed on a *μ*Vax II computer with programs from the TEXSAN crystallographic software package.[5] The systematically absent reflections *h*0*l*, $l = 2n + 1$, are consistent with the noncentrosymmetric space group *Pc* and the centrosymmetric group *P*2/*c*. We favor the centric group because of the distribution of intensities[6] and the successful solution and refinement of the structure in this group. For the K analog, positional parameters for the K and Zn atoms were determined with the computer program MITHRIL,[7] and the remaining atomic positions were subsequently identified from analyses of difference electron density maps. The positional parameters of the atoms in this model were used as the trial solution for the Rb compound.

Following refinement with isotropic thermal parameters, each set of data was corrected for absorption with the computer program DIFABS.[8] Final least-squares refinement on F_o with those data having $F_o^2 \ge 3\sigma(F_o^2)$ and anisotropic displacement factors on each atom resulted in the residuals $R = 0.029$ and $R_w = 0.043$ for the K compound and $R = 0.028$ and $R_w = 0.039$ for the Rb compound; extinction parameters were refined to 9.72×10^{-8} and 3.36×10^{-7} for the K and Rb derivatives, respectively. The final difference maps contain no features greater than 0.6% of a Zn or Rb atom in the K or Rb derivative, respectively. Crystal data and atomic parameters are summarized in Tables I and II, respectively.

Unit cell parameters were also refined from powder data by least-squares analysis of 2*θ* values for 16–18 intense reflections in the range $19 < 2\theta < 55°$; powdered Si (NIST Standard Reference Material 640b) was used as the internal standard.

Results and Discussion

A labeled sketch of the unit-cell contents that represents both the K and Rb derivatives is shown in Figure 1. The structure is a new brand of orthoborate, exhibiting a three-dimensional

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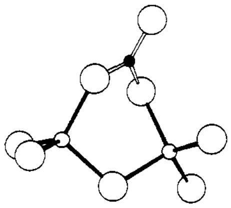
Table I. Crystallographic Data for $KZn_4(BO_3)_3$ and $RbZn_4(BO_3)_3$

formula	$KZn_4(BO_3)_3$	$RbZn_4(BO_3)_3$
fw	477.04	523.41
a, Å	6.876 (2)	6.849 (2)
b, Å	4.990 (1)	5.000 (2)
c, Å	12.574 (1)	12.718 (2)
β, °	92.92 (1)	92.53 (2)
V, Å^3	430.9 (3)	435.1 (4)
Z	2	2
space group	$P2/c$	$P2/c$
λ, Å	0.710 69	0.710 69
T, °C	25	25
μ, cm^{-1}	118.01	166.19
ρ_{calcd}, g cm^{-3}	3.68	3.99
$R(F_o)^a$	0.029	0.028
$R_w(F_o)^b$	0.043	0.039

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$.

framework built from two independent types of distorted ZnO_4 tetrahedra and BO_3 triangles that are fused through common O vertices (Figure 2). The framework may be viewed as a condensation of the six-membered rings contained in the simple Zn_2BO_8 unit, **1**. Two types of these units are present in the structure—one contains two Zn1 atoms and a B1 atom, while the other contains one Zn1, one Zn2, and one B2 atom. The former type propagates along the b axis by sharing vertex O1, which is the terminal atom of the BO_3 triangle in **1**; the latter type propagates along the a axis by sharing vertices O4 and O5. Because atom Zn1 is common to both units, the six-membered rings of each type are fused through the edge Zn1–O3. Whereas the independent orthoborate groups stand alone, the zinc-centered tetrahedra share vertices to form a two-dimensional zinc oxide matrix that extends in the bc plane (Figure 3). Atom B2 bridges adjacent matrices along the a direction, while atom B1 occupies a triangular hollow of O1 × 2O3 atoms within the matrix. The framework affords rectangular channels of approximate dimensions 3.5 × 5.6 Å that extend in the [010] direction; cf. Figure 2. The channel dimensions are defined by the O5···O5 distance projected along the c axis and the O3···O3 distance projected along the a axis. The alkali metal atoms reside in the center of these channels and bind primarily to atoms O4 and O5.



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Selected interatomic distances and angles are listed in Table III. The ZnO_4 and BO_3 groups are metrically regular and statistically equivalent in the two structures. The Zn–O distances in the K derivative average 1.95 (2) Å, a length that is similar to the value 1.97 Å in the compound $Zn_3(BO_3)_2$[9] and the expected value of 1.96 Å determined from crystal radii.[10] The average B–O distance, 1.38 (2) Å, is typical for orthoborates.[11]

Refinement of the K and Rb atoms in the center of the channel on the C_2 special position 0, y, $^1/_4$ affords large displacement coefficients and irregular coordination environments for each atom. Four O5 atoms and two O4 atoms are positioned at distances ranging from 2.892 (4) to 3.221 (4) Å for the K analog and from 2.998 (4) to 3.159 (5) Å for the Rb analog. From a cursory examination of the framework and consideration of the large thermal parameter, we attempted to place and refine the position of the K atom off the special position, but all of these refinements afforded larger residuals. Additional evidence that the alkali metal atoms occupy the special position (or are only slightly displaced from it) is obtained from consideration of the geometries about the O atoms.

Atoms O1, O2, and O3 at the periphery of the channels are three-coordinate, binding only to Zn and B atoms of the framework in a triangular manner, as indicated by interatomic angles near 120°. Bond valence sums[12] computed from consideration of only framework atoms afford agreement to within 7% of expected formal integer values; hence, no strong interactions between these O atoms and the alkali metal atom are apparent. Atom O4 exhibits typical tetrahedral angles in binding to the K (Rb) atom and the framework atoms Zn1, Zn2, and B2. Atom O5 binds to only two atoms—Zn2 amd B2—in the framework with irregular angles that range from 87.1 (1) to 132.2 (3)° observed in the K derivative. From bond valence sums, the bonding requirements of atom O5 appear to be satisfied by placing the K atom in the center of the channel. The interactions O5–Zn2 and O5–B2 are the shortest distances in the framework. Because the K–O5 interaction is primarily ionic, considerable electron density is available to the O5 atom for covalent interactions. Since this electron density is available and distributed primarily to only two other atoms, the Zn2–O5 and B2–O5 distances are shortened.

We have been unable to grow single crystals of the Cs derivative suitable for X-ray analysis by using the fluxes PbO, $LiBO_2$, and NaCl. Analysis of powder X-ray diffraction patterns indicates that the Cs derivative is isostructural with the K and Rb analogs. The powder diffractogram was indexed with a similar monoclinic cell, and the cell parameters were successfully refined. No extraneous peaks were observed from visual comparison of an experimental pattern with a pattern simulated from the atomic coordinates of the Rb analog with Cs replacing the Rb atom.[13] Considering the size of the alkali metal site in the channels and a Cs–O distance near 3.0 Å computed from crystal radii, the Cs atom should comfortably reside in the structure.

We could not form the Na analog by using $NaNO_3$ as a reactant and processing as described in the Experimental Section. Instead, the crystalline products were identified from X-ray analysis as $Zn_3(BO_3)_2$ and ZnO. The Na atom apparently is too small to occupy the large site in the channels, at least under the high-temperature preparative conditions employed here.

Unit-cell parameters refined from powder data are listed in Table IV. Comparison of cell volumes among the three derivatives reveals the expected expansion as the crystal radius of the alkali metal atom increases. The larger difference between the Cs and Rb analogs as compared with that between the K and Rb analogs reflects the greater difference in crystal radii for Cs vs Rb as compared with K vs Rb. Expansion of the unit cell occurs primarily from a lengthening of the c axis; in fact, the a axis of the Rb analog is smaller than that of the K compound.

The ion-exchange capacity of $KZn_4(BO_3)_3$ was examined by several simple procedures. A 2-g sample of $KZn_4(BO_3)_3$ was heated at 150 °C in 150 g of benzoic acid for 44 h.[14] The liquid acid was decanted, and the resultant powder was washed three times with 100 mL of methanol and once with 100 mL of hot water and then dried in an oven at 135 °C. The only crystalline product identified by X-ray analysis was ZnO. Heating the compound $KZn_4(BO_3)_3$ in molten ammonium nitrate in a similar manner also afforded crystalline ZnO.

We next attempted exchange in a concentrated aqueous solution by heating a 3:1 molar ratio of NH_4NO_3 and $KZn_4(BO_3)_3$ with several drops of water in a digestion bomb at 135 °C for 1 day. A white powder was obtained by washing with water and drying.

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Table II. Positional Parameters and B_{eq} Values for $KZn_4(BO_3)_3$ and $RbZn_4(BO_3)_3$

	$KZn_4(BO_3)_3$				$RbZn_4(BO_3)_3$			
atom	*x*	*y*	*z*	B_{eq},[a] Å^2	*x*	*y*	*z*	B_{eq},[a] Å^2
A[b]	0	0.7047 (4)	$^1/_4$	2.73 (7)	0	0.7253 (2)	$^1/_4$	1.93 (4)
Zn1	0.48956 (7)	0.6532 (1)	0.12396 (4)	0.87 (2)	0.4879 (1)	0.6513 (1)	0.12507 (6)	0.89 (3)
Zn2	0.20828 (7)	0.1649 (1)	0.06022 (4)	0.92 (2)	0.2089 (1)	0.1666 (1)	0.06101 (6)	0.94 (3)
B1	$^1/_2$	0.160 (1)	$^1/_4$	0.8 (2)	$^1/_2$	0.156 (2)	$^1/_4$	0.9 (4)
B2	0.1881 (7)	0.346 (1)	0.4507 (4)	0.9 (2)	0.192 (1)	0.346 (1)	0.4539 (6)	1.0 (3)
O1	$^1/_2$	0.8831 (9)	$^1/_4$	1.2 (2)	$^1/_2$	0.878 (1)	$^1/_4$	1.2 (2)
O2	0.2764 (5)	0.7955 (7)	0.0352 (3)	1.4 (1)	0.2758 (7)	0.7977 (9)	0.0383 (4)	1.4 (2)
O3	0.4069 (5)	0.2965 (6)	0.1679 (2)	1.2 (1)	0.4060 (7)	0.2945 (9)	0.1694 (4)	1.2 (2)
O4	0.2591 (5)	0.6068 (6)	0.4351 (2)	1.0 (1)	0.2627 (6)	0.6027 (8)	0.4387 (3)	1.0 (2)
O5	0.0412 (5)	0.2451 (7)	0.3894 (2)	1.4 (1)	0.0466 (7)	0.242 (1)	0.3920 (4)	1.3 (2)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i{\cdot}a_j$. [b] A = K or Rb.

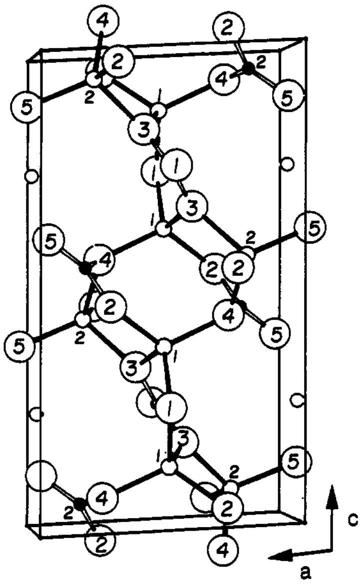

Figure 1. Labeled sketch of the structure of $AZn_4(BO_3)_3$ (A = K, Rb) viewed along the *b* axis. The A atom is indicated as a small open circle with no bonds, the Zn atoms are small open circles with shaded bonds, and the B atoms are small shaded circles, in this and in ensuing figures.

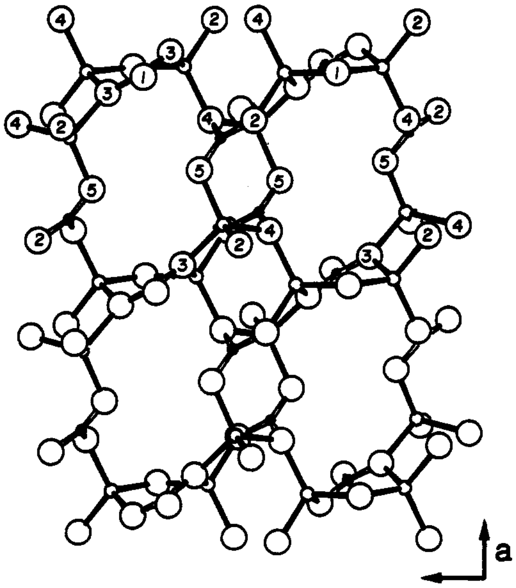

Figure 2. Perspective view of the framework $[Zn_4(BO_3)_3]^-$.

We were unable to identify the product from comparison of the X-ray data with those reported for anhydrous and hydrous zinc borates. Heating the powder at 750 °C for 1 h produced the crystalline product $Zn_3(BO_3)_2$ with a mass loss that was equivalent to one water molecule per formula unit of the anhydrous product.

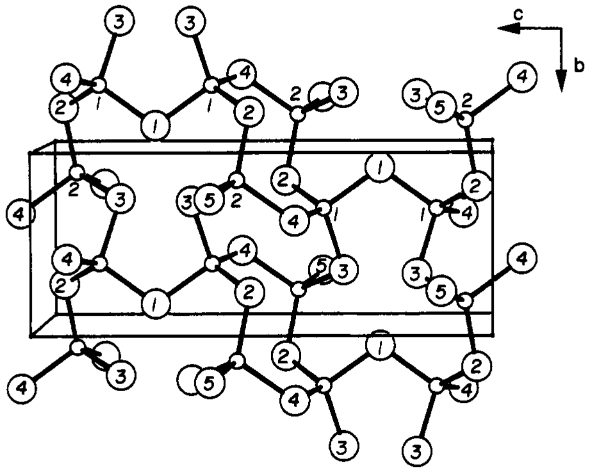

Figure 3. Two-dimensional zinc–oxide matrix in $AZn_4(BO_3)_3$.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $KZn_4(BO_3)_3$ and $RbZn_4(BO_3)_3$

	distance			angle	
	A = K	A = Rb		A = K	A = Rb
A–O5 × 2	2.892 (4)	3.026 (5)			
A–O4 × 2	2.900 (3)	2.998 (4)			
A–O5 × 2	3.221 (4)	3.159 (5)			
Zn1–O1	1.955 (3)	1.950 (4)	O1–Zn1–O2	104.4 (1)	104.5 (2)
Zn1–O2	1.932 (3)	1.929 (5)	O1–Zn1–O3	107.7 (1)	107.2 (2)
Zn1–O3	1.957 (3)	1.960 (5)	O1–Zn1–O4	112.7 (1)	114.0 (1)
Zn1–O4	1.929 (3)	1.938 (5)	O2–Zn1–O3	106.0 (1)	107.0 (2)
			O2–Zn1–O4	119.3 (1)	117.6 (2)
			O3–Zn1–O4	106.2 (1)	106.0 (2)
Zn2–O2	1.932 (3)	1.926 (5)	O2–Zn2–O3	105.2 (1)	104.6 (2)
Zn2–O3	1.985 (3)	1.992 (4)	O2–Zn2–O4	111.4 (1)	112.7 (2)
Zn2–O4	1.988 (3)	1.985 (4)	O2–Zn2–O5	119.0 (2)	117.6 (2)
Zn2–O5	1.901 (3)	1.912 (5)	O3–Zn2–O4	102.0 (1)	102.3 (2)
			O3–Zn2–O5	107.7 (1)	108.8 (2)
			O4–Zn2–O5	110.0 (1)	109.6 (2)
B1–O1	1.380 (7)	1.39 (1)	O1–B1–O3	119.9 (3)	120.2 (4)
B1–O3 × 2	1.369 (4)	1.372 (7)	O3–B1–O3	120.1 (5)	119.6 (8)
B2–O2	1.390 (6)	1.394 (8)	O2–B2–O4	115.8 (4)	116.6 (6)
B2–O4	1.408 (5)	1.390 (8)	O4–B2–O5	121.7 (4)	122.0 (6)
B2–O5	1.337 (6)	1.345 (9)	O5–B2–O2	122.5 (4)	121.4 (6)

Table IV. Cell Parameters Refined from Powder Data

	a, Å	*b*, Å	*c*, Å	*β*, deg	*V*, Å^3
$KZn_4(BO_3)_3$	6.878 (1)	4.989 (1)	12.576 (4)	92.93 (2)	431.0 (2)
$RbZn_4(BO_3)_3$	6.849 (2)	4.999 (2)	12.741 (5)	92.56 (3)	435.8 (4)
$CsZn_4(BO_3)_3$	6.871 (2)	5.019 (2)	12.961 (3)	92.50 (3)	446.5 (4)

A mixture of the unknown material and ZnO was also obtained by using $NaNO_3$ instead of NH_4NO_3. Finally, heating either $KZn_4(BO_3)_3$ or $Zn_3(BO_3)_2$ with several drops of water in a digestion bomb at 80 °C produced a mixture of the unknown material and ZnO, the latter being the major phase in each case.

Therefore, we believe the unknown phase to be a new hydrated zinc borate. Of course, decomposition of $KZn_4(BO_3)_3$ precludes ion-exchange reactions from occurring in heated aqueous solutions.

Acknowledgment. This research was supported by the National Science Foundation, Solid-State Chemistry Program (Grant DMR-8814432). Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of the work. D.A.K. thanks the Alfred P. Sloan Foundation for a research fellowship.

Supplementary Material Available: Tables of crystal and refinement details and anisotropic displacement coefficients (2 pages). Ordering information is given on any current masthead page.