Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cs1	0.23511 (7)	0.12217 (3)	0	0.01346 (16)
Mn1	1/2	0	1/4	0.0100 (3)
Mn2	0	0.24009 (8)	1/4	0.0096 (2)
Te1	0.23314 (5)	0.37052 (2)	0.14642 (2)	0.00973 (15)

Table 2. *Selected geometric parameters (Å, °)*

Cs1—Te1	3.8865 (10)	Mn1—Te1^{ii}	2.7442 (6)
Cs1—Te1^{i}	3.9263 (10)	Mn2—Te1^{iv}	2.7379 (7)
Cs1—Te1^{ii}	3.9262 (10)	Mn2—Te1^{v}	2.7515 (8)
Cs1—Te1^{iii}	3.9471 (10)		
Te1^{ii}—Mn1—Te1^{vi}	106.02 (2)	Te1^{iv}—Mn2—Te1^{v}	107.73 (2)
Te1^{ii}—Mn1—Te1^{vii}	113.49 (2)	Te1^{vii}—Mn2—Te1^{v}	108.56 (2)
Te1^{vi}—Mn1—Te1^{vii}	108.99 (2)	Te1^{v}—Mn2—Te1	105.62 (4)
Te1^{iv}—Mn2—Te1^{vii}	117.98 (4)		

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, z$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, -z$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (v) $-x, y, \frac{1}{2}-z$; (vi) $\frac{1}{2}+x, y-\frac{1}{2}, \frac{1}{2}-z$; (vii) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$.

Cell parameters were taken from a least-squares fit to 24 reflections automatically centered in the range $34 < 2\theta$ (Mo $K\alpha_1$) $< 37°$. Intensity data were processed (Waters & Ibers, 1977) and corrected for absorption (de Meulenaer & Tompa, 1965) on an IBM RS/6000 series computer. The initial Cs, Mn and Te atom positional parameters were obtained from the structure of the isostructural compound $Cs_2Mn_3S_4$ (Bronger, Hendriks & Müller, 1988). The structure was refined with the program *SHELXL*93 (Sheldrick, 1993). The refinement included anisotropic displacement parameters and an extinction parameter. The final difference electron density map shows no feature with a height greater than 1.6% that of a Cs atom.

Data collection: local program. Cell refinement: local program. Data reduction: local program. Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OH1099). Services for accessing these data are described at the back of the journal.

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Potassium Strontium Tetraborate Decahydrate and Ammonium Calcium Tetraborate Octahydrate

XAVIER SOLANS, JOAQUIM SOLANS AND M. VICTORIA DOMÈNECH

Departament de Cristallografia i Mineralogia, Universitat de Barcelona, Martí i Franquès s/n, E-08028 Barcelona, Spain. E-mail: xavier@natura.geo.ub.es

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Abstract

The crystal structures of potassium strontium tetraborate decahydrate, $K_2Sr[H_4B_4O_9]_2.10H_2O$, and ammonium calcium tetraborate octahydrate, $(NH_4)_2Ca[H_4B_4O_9]_2.8H_2O$, have been determined. The two structures have similar cell parameters but different space groups. The first compound is homeotypic and the second is isotypic with potassium calcium tetraborate octahydrate and rubidium strontium tetraborate octahydrate. The structures contain alternate layers of tetraborate ions and two of the water molecules, along with the cations and the remaining water molecules. The cation size and the hydrolysis constant of each cation define the space group and the number of water molecules of hydration.

Comment

The crystal structures of tetraborate compounds have been extensively explored in recent years. The structures the following monovalent-ion tetraborates have been solved: NH_4 (Janda, Heller & Pickardt, 1981), Na (Menchetti & Sabelli, 1978; Powell, Gaines, Zerella & Smith, 1991), K (Marezio, Plettinger & Zachariasen, 1963) and Tl (Touboul, Bois & Amoussou, 1983). Only the structures of tetraborates containing Mg (Wan & Ghose, 1977) and Mn (Berzinja, Ozols & Ievinsh, 1975) as divalent ions and [K,Ca] (Solans, Font-Altaba, Solans & Domènech, 1982) and [Rb,Sr] (Ivchenko & Kurkutova, 1975) as mixed monovalent and divalent ions have been solved. The last two compounds are orthorhombic with cell parameters close to a = 16.7, b = 12.7 and c = 11.6 Å, space group $P2_12_12_1$. Potassium strontium tetraborate decahydrate, (1), and ammonium calcium tetraborate octahydrate, (2), have similar cell parameters to the [K,Ca] and [Rb,Sr] compounds but the space group of (1) is $Pna2_1$ while (2) has the same space group as the [K,Ca] tetraborate ($P2_12_12_1$).

The crystal structures of four of the mixed monovalent and divalent compounds and the NH_4 and K compounds contain alternate layers of tetraborate anions and two of the water molecules, and are completed by the cations and the remaining water molecules. Different

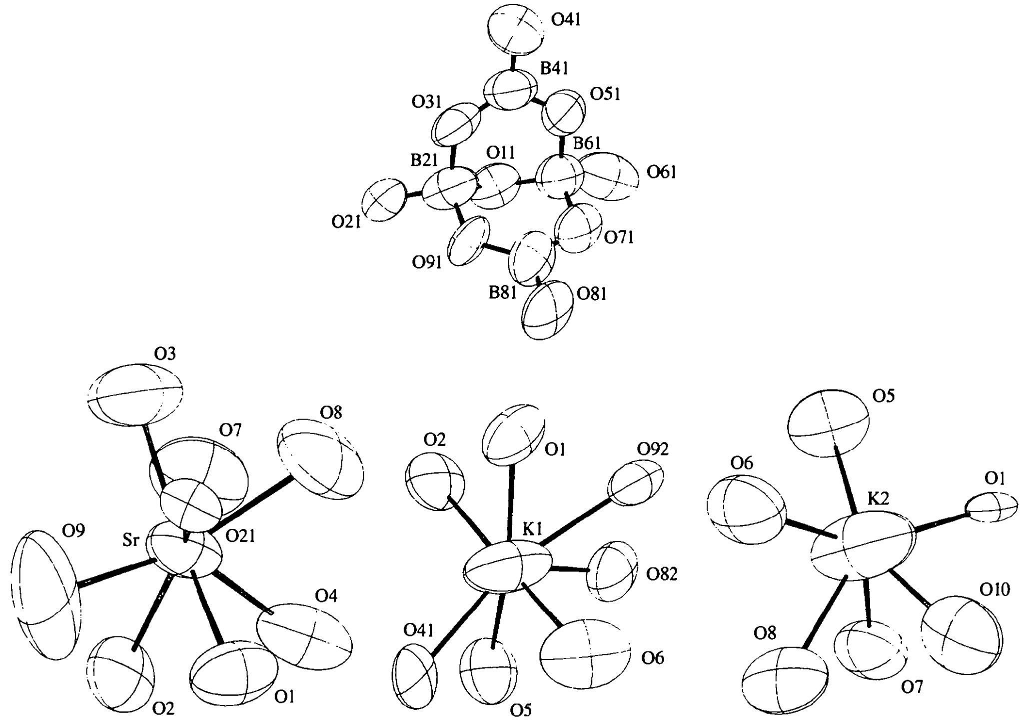

Fig. 1. *ORTEP* (Brueggemann & Schmid, 1990) drawing of the tetraborate ion and the K and Sr coordination polyhedra in (1) showing the atomic labelling scheme. Ellipsoids are drawn at the 50% probability level.

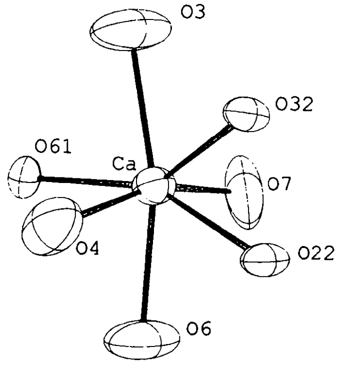

Fig. 2. The coordination polyhedron of Ca in (2) showing the atomic labelling scheme and ellipsoids at the 50% probability level.

coordination results in different space groups, while different cation sizes and different hydrolysis constants result in different degrees of hydration. Thus, the Sr^{2+} ion is eight-coordinate (four sites occupied by water molecules) while the K^+ ion displays sevenfold coordination in potassium tetraborate, eight- and sixfold coordination in the [K,Ca] compound, and seven- and sixfold coordination in the [K,Sr] compound.

The tetraborate ions show bond lengths and angles typical of those found in the literature (average values: $B_{tetra}—O_{tetra}$ = 1.455, $B_{tetra}—O_{tri}$ = 1.496, $B_{tri}—O_{tri}$ = 1.369 Å, $O—B_{tetra}—O$ = 109.4 and $O—B_{tri}—O$ 120.0°)

Experimental

Compound (1) was prepared by adding H_3BO_3 to a water solution of $SrCl_2$. When most of the starting material had dissolved, KOH was added and the resulting mixture was stirred at room temperature for 1 h. The colourless precipitate formed was collected by filtration, washed with water and air-dried. The crystals were grown by slow evaporation of a water solution of the compound at 293 K. Compound (2) was prepared by adding H_3BO_3 to a water solution of $CaCl_2$. When most of the starting material had dissolved, NH_4OH was added and the resulting mixture was stirred at room temperature for 1 h. The colourless precipitate formed was collected by filtration, washed with water and air-dried. The crystals were grown by slow evaporation of a water solution of the compound at 293 K.

Compound (1)

Crystal data

$K_2Sr[H_4B_4O_9]_2.10H_2O$
M_r = 728.52
Orthorhombic
$Pna2_1$
a = 16.746 (2) Å
b = 12.974 (2) Å
c = 11.582 (2) Å
V = 2516.3 (7) Å^3
Z = 4
D_x = 1.923 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 8–12°
μ = 2.588 mm^{-1}
T = 293 (2) K
Prismatic
0.2 × 0.1 × 0.1 mm
Colourless

Data collection

Philips PW1100 diffractometer
ω scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.964$, $T_{\max} = 0.984$
2202 measured reflections
2202 independent reflections
1880 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 24.94°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.076$
$S = 0.994$
2202 reflections
352 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 1.2961P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.288$
$\Delta\rho_{\max} = 0.380$ e Å^{-3}
$\Delta\rho_{\min} = -0.648$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0008 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.00 (2)

Table 1. *Selected geometric parameters (Å, °) for (1)*

Sr—O3	2.546 (6)	K1—O1	2.786 (6)
Sr—O9	2.568 (7)	K1—O82	2.893 (6)
Sr—O2	2.570 (6)	K1—O41^{ii}	3.001 (7)
Sr—O1	2.585 (6)	K1—O92	3.031 (5)
Sr—O8	2.626 (6)	K2—O10	2.779 (7)
Sr—O7	2.644 (6)	K2—O5	2.790 (7)
Sr—O4	2.748 (6)	K2—O6	2.800 (7)
Sr—O21^{i}	2.915 (5)	K2—O7^{iii}	2.918 (7)
K1—O6	2.698 (7)	K2—O8^{iii}	3.031 (7)
K1—O5	2.742 (6)	K2—O91	2.909 (5)
K1—O2	2.781 (6)		
O3—Sr—O9	89.3 (3)	O8—Sr—O7	80.1 (2)
O3—Sr—O2	129.0 (2)	O3—Sr—O4	134.8 (2)
O9—Sr—O2	70.6 (2)	O9—Sr—O4	133.2 (2)
O3—Sr—O1	140.5 (2)	O2—Sr—O4	68.5 (2)
O9—Sr—O1	77.7 (3)	O1—Sr—O4	74.8 (2)
O2—Sr—O1	81.7 (2)	O8—Sr—O4	76.8 (2)
O3—Sr—O8	74.1 (2)	O7—Sr—O4	70.8 (2)
O9—Sr—O8	142.6 (2)	O3—Sr—O21^{i}	75.0 (2)
O2—Sr—O8	145.0 (2)	O9—Sr—O21^{i}	71.2 (2)
O1—Sr—O8	93.9 (2)	O2—Sr—O21^{i}	133.7 (2)
O3—Sr—O7	70.6 (2)	O1—Sr—O21^{i}	65.5 (2)
O9—Sr—O7	126.2 (2)	O8—Sr—O21^{i}	72.2 (2)
O2—Sr—O7	84.3 (2)	O7—Sr—O21^{i}	140.5 (2)
O1—Sr—O7	145.6 (2)	O4—Sr—O21^{i}	126.8 (2)

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (iii) $x, y, z-1$.

Compound (2)

Crystal data

$(NH_4)_2Ca[H_4B_4O_9]_2.8H_2O$
$M_r = 602.84$
Orthorhombic
$P2_12_12_1$
$a = 16.659$ (2) Å
$b = 12.571$ (2) Å
$c = 11.588$ (2) Å
$V = 2426.8$ (6) Å^3
$Z = 4$
$D_x = 1.650$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8$–$12°$
$\mu = 0.370$ mm^{-1}
$T = 293$ (2) K
Prismatic
0.2 × 0.1 × 0.1 mm
Colourless

Data collection

Philips PW1100 diffractometer
ω scans
Absorption correction: none
2191 measured reflections
2191 independent reflections
2188 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 24.96°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.067$
$S = 1.020$
2191 reflections
344 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.2553P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.126$
$\Delta\rho_{\max} = 0.201$ e Å^{-3}
$\Delta\rho_{\min} = -0.243$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0106 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.00 (4)

Table 2. *Selected geometric parameters (Å, °) for (2)*

Ca—O22	2.340 (2)	Ca—O61^{i}	2.405 (2)
Ca—O3	2.3760 (7)	Ca—O6	2.4219 (7)
Ca—O7	2.3809 (7)	Ca—O32	2.489 (2)
Ca—O4	2.3915 (7)		
O22—Ca—O3	128.05 (5)	O3—Ca—O6	157.49 (2)
O22—Ca—O7	89.51 (5)	O7—Ca—O6	79.02 (2)
O3—Ca—O7	93.51 (2)	O4—Ca—O6	82.54 (2)
O22—Ca—O4	88.22 (5)	O61^{i}—Ca—O6	81.01 (5)
O3—Ca—O4	102.47 (2)	O22—Ca—O32	56.86 (6)
O7—Ca—O4	161.30 (3)	O3—Ca—O32	72.55 (4)
O22—Ca—O61^{i}	154.22 (7)	O7—Ca—O32	105.58 (5)
O3—Ca—O61^{i}	77.71 (5)	O4—Ca—O32	88.61 (5)
O7—Ca—O61^{i}	89.65 (5)	O61^{i}—Ca—O32	147.16 (6)
O4—Ca—O61^{i}	84.42 (5)	O6—Ca—O32	129.85 (4)
O22—Ca—O6	73.54 (5)		

Symmetry code: (i) $\frac{1}{2}-x, -y, z-\frac{1}{2}$.

28 H atoms in (1) and 26 H atoms in (2) were determined from a difference synthesis. The coordinates of the remaining eight H atoms in (2) were computed from the geometry. The H-atom parameters were not refined in order to provide an acceptable ratio of parameters to measured intensity data.

For both compounds, data collection: Philips software; cell refinement: Philips software; data reduction: *CFEO* (Solans, 1978); program used to solve structures: *SHELXS*86 (Sheldrick, 1990): program used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP* (Brueggemann & Schmid, 1990); software used to prepare material for publication: *CIFTAB* (Sheldrick, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1150). Services for accessing these data are described at the back of the journal.

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A Synthetic Hydrated Zinc Arsenate Constructed from Tetrahedral, Trigonal Bipyramidal and Octahedral Zinc Polyhedra: $[Zn_3(AsO_4)_2]_3.4H_2O$

PINGYUN FENG, XIANHUI BU AND GALEN D. STUCKY

Chemistry Department, University of California, Santa Barbara, CA 93106, USA. E-mail: pingyun@sbxray.ucsb.edu

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Abstract

The synthesis and crystal structure of the first synthetic hydrated zinc arsenate, tris(zinc arsenate) tetrahydrate, are described.

Comment

There has been an increased interest in the divalent metal phosphates and arsenates since the discovery of zeolite structural analogs and other open-framework structures (Gier & Stucky, 1991; Feng, Bu & Stucky, 1995). In our search for novel framework structures based on divalent metal phosphates and arsenates (Bu, Feng & Stucky, 1996; Bu, Gier & Stucky, 1996; Feng, Bu & Stucky, 1997*a*,*b*; Feng, Bu, Tolbert & Stucky, 1997) we discovered a new hydrated zinc arsenate. The synthesis, structure and thermal properties of this first synthetic hydrated zinc arsenate are reported here.

The examination of the local coordination environment (Fig. 1) is helpful to the understanding of the three-dimensional connectivity of this rather dense framework structure. There are five unique zinc sites. Zn1 and Zn2 are tetrahedral and trigonal bipyramidal, respectively, with all corner O atoms bonded to one As cation and, with the exception of O2, to another Zn cation. Zn3, Zn4 and Zn5 are all octahedrally bonded. Zn5 has a pendant water molecule (O14) whereas another water molecule (O12) bridges Zn3 and Zn4. O9 and O11 on Zn3 are bicoordinated between one Zn cation and one As cation while the remaining O-atom corners are trigonally coordinated between two Zn cations and one As cation.

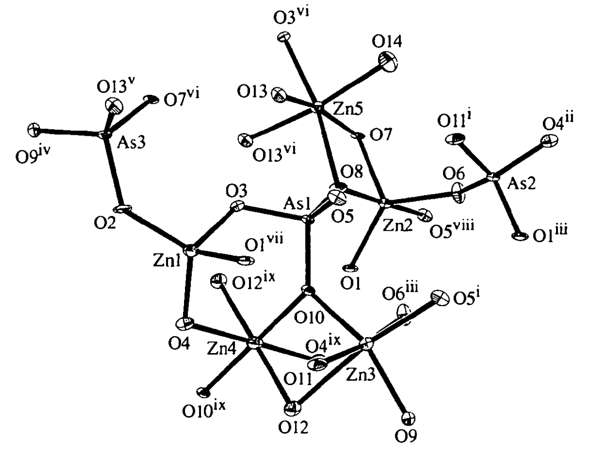

Fig. 1. An *ORTEP* (Johnson, 1976) drawing showing the local coordination environment. Ellipsoids are drawn at the 50% probability level. O12 and O14 are water molecules. O2, O9 and O11 are bicoordinated between Zn and As. Other O atoms are trigonally coordinated between two Zn atoms and one As atom. Only Zn4 is located on the inversion center. See Table 2 for symmetry codes.

The framework can be broken down into two structural units: a cluster of eight tetrahedra and an infinite chain of edge-sharing polyhedra (Fig. 2). The cluster consists of eight tetrahedra and is located at the center of inversion. All four crystallographically unique tetrahedral sites are part of this cluster. Three unique zinc octahedra and one unique zinc trigonal bipyramid form an infinite zigzag edge-sharing chain along the crystallographic $[\bar{1}11]$ direction. One of the unique zinc sites in the chain is located at the unit-cell body center. As a result the chain also has the symmetry of inversion. The framework can be regarded as rows of one-dimensional chains interconnected by clusters of tetrahedra.

Two other hydrated zinc arsenates, both of which are minerals, are known. The most hydrated form, koettigite (Hill, 1979), with the formula $Zn_3(AsO_4)_2.8H_2O$ (also contains of a small amount of Co and Ni), possesses a monoclinic structure which is adopted by a variety of divalent metal phosphates and arsenates including $M_3(PO_4)_2.8H_2O$ (M = Mg, Fe, Co) (Takagi, Mathew & Brown, 1986; Fejdi, Poullen & Gasperin, 1980; Riou, Cudennec & Gerault, 1989) and $Fe_3(AsO_4)_2.8H_2O$