Inorg. Chem. **2007**, *46*, 7503–7508

Inorganic Chemistry
Article

$CsSc[B_2P_3O_{11}(OH)_3]$: A New Borophosphate Oligomer Containing Boron in Three- and Fourfold Coordination†

Prashanth W. Menezes, Stefan Hoffmann, Yurii Prots, and Rüdiger Kniep*

Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Strasse 40,
01187 Dresden, Germany

Received May 11, 2007

$CsSc[B_2P_3O_{11}(OH)_3]$ was obtained by hydrothermal synthesis and represents the first alkali-metal scandium borophosphate containing boron with coordination numbers 3 and 4. The crystal structure was determined from single-crystal X-ray data: orthorhombic, space group *Pnna* (No. 52), $a = 13.0529(15)$ Å, $b = 18.3403(17)$ Å, $c = 10.3838(12)$ Å, $Z = 8$. The crystal structure contains the oligomeric unit $[B_2P_3O_{11}(OH)_3]^{4-}$ in which a central borate tetrahedron is open-branched by two $(OH)PO_3$ tetrahedra and cyclobranched by one PO_4 tetrahedron and a trigonal-planar $(OH)BO_2$ by sharing common apexes. The borophosphate oligomers together with the ScO_6 octahedra are condensed to form layers. Simultaneous difference thermal analysis and thermogravimetry revealed the stepwise decomposition of the compound in the temperature range between 333 and 973 K. Partly dehydrated samples do not show any substantial rehydration behavior. The crystal structure of $CsSc[B_2P_3O_{11}(OH)_3]$ is discussed in connection with structural motifs of related borates and borophosphates.

Introduction

Borates have been a subject of interest for many decades because of their rich structural chemistry and their potential applications[1−4] such as nonlinear optics.[5] They exhibit complex structures[6] and tend to crystallize in noncentrosymmetric space groups.[7] In general, the B atoms reveal two kinds of coordination modes, either triangular or tetrahedral. The BO_3 and BO_4 groups favor condensation via common corners to form polynuclear anionic units including isolated clusters,[2,8−10] infinite chains,[2,11−13] sheets,[2,14−18] and frameworks.[2,19−23]

For further classification of borates, fundamental building blocks (FBBs) with certain numbers (*N*) of borate units are determined, which then allow a simple grouping into mono-, di-, tri-, tetra-, penta-, and hexaborates and higher. It was found that even though there exists a considerable number of theoretically possible FBBs,[2] only a few are realized in borate crystal structures. For instance, the FBB of pentaborates ($N = 5$) always consists of one BO_4 tetrahedron as well as at least one B_3O_3 ring that is formed by adjacent BO_3 and/or BO_4 units (Figure 1).[24] This general principle can be overcome by introducing PO_4 tetrahedra as shown in Figure

---

† Dedicated to Prof. Dieter Fenske on the occasion of his 65th birthday.

* To whom correspondence should be addressed. E-mail: Kniep@cpfs.mpg.de. Phone: +49(0)35146463000. Fax: +49(0)35146463002.

(1) Burns, P. C. *Can. Mineral.* **1995**, *33*, 1167.
(2) Burns, P. C.; Grice, J. D.; Hawthorne, F. C. *Can. Mineral.* **1995**, *33*, 1131.
(3) Christ, C. L.; Clark, J. R. *Phys. Chem. Miner.* **1977**, *2*, 59.
(4) Grice, J. D.; Burns, P. C.; Hawthorne, F. C. *Can. Mineral.* **1999**, *37*, 731.
(5) Chen, C. T.; Wang, Y. B.; Wu, B. C.; Wu, K. C.; Zeng, W. L.; Yu, L. H. *Nature* **1995**, *373*, 322.
(6) Heller, G. *Top. Curr. Chem.* **1986**, *131*, 39.
(7) Becker, P. *Adv. Mater.* **1998**, *10*, 979.
(8) Salentine, C. G. *Inorg. Chem.* **1987**, *26*, 128.
(9) Schubert, D. M.; Visi, M. Z.; Knobler, C. B. *Inorg. Chem.* **2000**, *39*, 2250.
(10) Touboul, M.; Penin, N.; Nowogrocki, G. *J. Solid State Chem.* **1999**, *143*, 260.
(11) Park, H.; Barbier, J.; Hammond, R. P. *Solid State Sci.* **2003**, *5*, 565.
(12) Schubert, D. M.; Alam, F.; Visi, M. Z.; Knobler, C. B. *Chem. Mater.* **2003**, *15*, 866.
(13) Yu, Z. T.; Shi, Z.; Jiang, Y. S.; Yuan, H. M.; Chen, J. S. *Chem. Mater.* **2002**, *14*, 1314.
(14) Bubnova, R. S.; Fundamensky, V. S.; Anderson, J. E.; Filatov, S. K. *Solid State Sci.* **2002**, *4*, 87.
(15) Emme, H.; Huppertz, H. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2165.
(16) Penin, N.; Seguin, L.; Touboul, M.; Nowogrocki, G. *Solid State Sci.* **2002**, *4*, 67.
(17) Penin, N.; Touboul, M.; Nowogrocki, G. *J. Solid State Chem.* **2002**, *168*, 316.
(18) Penin, N.; Touboul, M.; Nowogrocki, G. *Solid State Sci.* **2003**, *5*, 559.
(19) Harrison, W. T. A.; Gier, T. E.; Stucky, G. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 724.
(20) Huppertz, H.; von der Eltz, B. *J. Am. Chem. Soc.* **2002**, *124*, 9376.
(21) Huppertz, H.; Heymann, G. *Solid State Sci.* **2003**, *5*, 281.
(22) Penin, N.; Seguin, L.; Touboul, M.; Nowogrocki, G. *J. Solid State Chem.* **2001**, *161*, 205.
(23) Rowsell, J. L. C.; Taylor, N. J.; Nazar, L. F. *J. Am. Chem. Soc.* **2002**, *124*, 6522.
(24) Touboul, M.; Penin, N.; Nowogrocki, G. *Solid State Sci.* **2003**, *5*, 1327.

10.1021/ic700914v CCC: $37.00

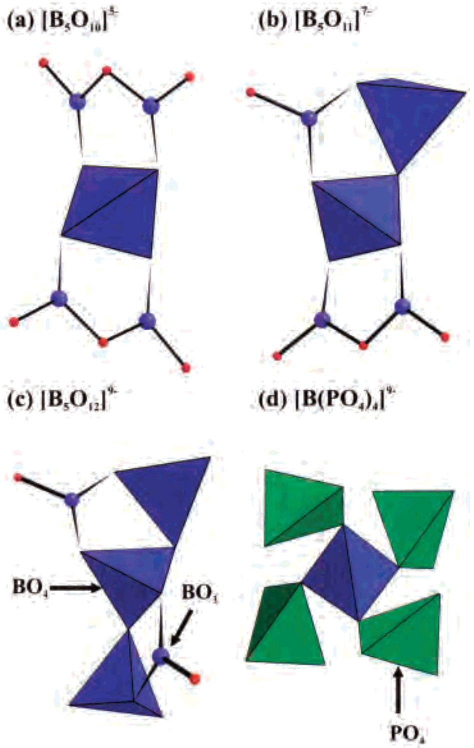

Figure 1. FBBs in pentaborates (a) $[B_5O_{10}]^{5-}$ (one BO_4 tetrahedron and four BO_3 groups), (b) $[B_5O_{11}]^{7-}$ (two BO_4 tetrahedra and three BO_3 groups), and (c) $[B_5O_{12}]^{9-}$ (three BO_4 tetrahedra and two BO_3 groups). An example for a pentameric FBB in borophosphates: (d) $[B(PO_4)_4]^{9-}$ (one BO_4 tetrahedron and four PO_4 tetrahedra).

1d, which then leads to the large group of borophosphates with new condensation patterns of complex anions. Here we report on our investigations on scandium−alkali-metal borophosphates, in particular on the respective cesium compound exhibiting a new type of a pentameric oligomer with three- and fourfold-coordinated boron extending the patterns given in Figure 1.

Experimental Section

Synthesis of $CsSc[B_2P_3O_{11}(OH)_3]$. The title compound was prepared under hydrothermal conditions. Single crystals of $CsSc[B_2P_3O_{11}(OH)_3]$ used for the structure determination were isolated from a sample synthesized hydrothermally from a mixture of 0.2500 g of Sc_2O_3 (99%, ABCR), 1.009 g of CsOH (99%, Alfa Aesar), 0.6043 g of H_3BO_3 (99.9%, Alfa Aesar), and 2.8126 g of H_3PO_4 (85%, Merck) in the molar ratio Cs:Sc:B:P = 3:1:4:10. The pH value was adjusted to 1 by the addition of 1.0 mL of HCl (37%). The mixture was then transferred to a 10 mL Teflon autoclave (filling degree 30%), treated under autogenous pressure at 443 K for 10 days, cooled down to 333 K, and kept there for 12 h before cooling down to room temperature. The reaction product was separated by filtration, washed with hot water/acetone, and dried in air at 333 K. The product consisted of transparent platy crystals with dimensions ranging from 0.1 to 0.4 mm.

Powder X-ray Diffraction (XRD). The powder XRD data were collected on a STOE Stadi MP diffractometer equipped with a primary-beam germanium monochromator. The radiation used was Cu Kα_1 (λ = 1.540 60 Å). The powdered sample was filled in a glass capillary with a 0.3 mm inner diameter. Continuous scan data were collected in the 2θ range of 5−110° with a step width of 0.02° and a counting time of 460 s/step. The lattice parameters of $CsSc[B_2P_3O_{11}(OH)]$ were determined by using lanthanum hexaboride (LaB_6) as the internal standard, and the WinCSD program package was used for least-squares refinements.[25]

Table 1. Crystal Data and Refinement Parameters for $CsSc[B_2P_3O_{11}(OH)_3]$

empirical formula	$CsSc[B_2P_3O_{11}(OH)_3]$
temperature (K)	295
radiation, λ (Å)	Mo Kα, 0.71073
space group	*Pnna* (No. 52)
unit cell parameters:	
a (Å)	13.0529(15)
b (Å)	18.3403(17)
c (Å)	10.3838(12)
V (Å^3)	2485.8(5)
Z	8
μ (mm^{-1})	3.94
ρ_{calc} (g/cm^3)	2.773
R1/wR2^a [$I > 2\sigma(I)$]	0.044/0.115
R1/wR2, all data	0.049/0.121

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0700P)^2 + 7.26P]$ with $P = \max(F_o^2 + 2F_c^2)/3$.

Single-Crystal Structure Analysis. A suitable colorless single crystal of $CsSc[B_2P_3O_{11}(OH)_3]$ with the dimensions 0.2 × 0.1 × 0.4 mm^3 was selected for single-crystal XRD analysis. The data with index ranges of $-18 \le h \le 15$, $-11 \le k \le 11$, $-14 \le l \le 9$, and $6° \le 2\theta \le 61°$ were collected on a Rigaku AFC7 (Mercury CCD) diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at a temperature of 295 K. The crystal structure was solved in the space group *Pnna* (No. 52) with the program *SHELX* by direct methods (program package *WinGX*).[26] Subsequent difference Fourier analysis unequivocally located the atomic coordinates of all of the atoms including H. In Table 1, the crystallographic data and refinement parameters are summarized. The final fractional atomic coordinates and equivalent/ isotropic displacement factors are listed in Table 2.

Chemical Analysis. The chemical composition of $CsSc[B_2P_3O_{11}(OH)_3]$ was confirmed by inductively coupled plasma optical emission spectroscopy on a Varian Vista RL spectrometer with radial plasma observation. The sample was dissolved in an acid solution (chloronitrous acid), and the results of three measurements were averaged. The ratio was found to be Cs:Sc:P:B = 24.68:8.61:17.20:3.99 (wt %), which is in good agreement with the chemical formula obtained from the single-crystal structure refinement, Cs:Sc:P:B = 25.58:8.65:17.88:4.16 (wt %).

IR Spectroscopy. A mixture of 1.5 mg of $CsSc[B_2P_3O_{11}(OH)_3]$ and 150 mg of KBr (Merck, Uvasol for IR spectroscopy) was ground and pressed with a pressure of 10 × 10^4 N/cm^2 to a transparent tablet. The IR spectrum was recorded on a Bruker spectrometer (IFS 66v/S; Globar (MIR), KBr, DTGS detector; program Opus/IR 3.0.3) in the wavenumber range 4000−400 cm^{-1}. The observed broad IR absorption band at 3200 cm^{-1} clearly indicates the presence of −OH groups in the crystal structure of $CsSc[B_2P_3O_{11}(OH)_3]$.

Thermal Analysis. Simultaneous constant rate thermogravimetry (TG) and difference thermal analysis (DTA) was performed on a Netzsch STA 449 in a glovebox filled with argon. The powdered

---

(25) Akselrud, L. G.; Zavalii, P. Y.; Grin, Y.; Pecharski, V. K.; Baumgartner, B.; Woelfel, E. *Mater. Sci. Forum* **1993**, *335*, 133.

(26) (a) Farrugia, L. *J. Appl. Crystallogr.* **1999**, *32*, 837. (b) Sheldrick, G. *Acta Crystallogr.* **1990**, *A46*, 467. (c) Sheldrick, G. *SHELXL-97, a computer program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent/Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $CsSc[B_2P_3O_{11}(OH)_3]$

atom	Wyckoff position	*x*	*y*	*z*	U_{eq}/U_{iso}
Cs	8e	−3610(1)	−3839(1)	6086(1)	38(1)
Sc	8e	−6143(1)	−2316(1)	5021(1)	15(1)
*P*1	8e	−5650(1)	−1326(1)	2194(1)	16(1)
*P*2	8e	−1592(1)	−1316(1)	2282(1)	15(1)
*P*3	8e	−3639(1)	−1895(2)	5005(1)	17(1)
B1	8e	−3642(4)	−1180(5)	2718(6)	15(3)
B2	8e	−3708(4)	−464(7)	4782(7)	19(3)
O1	8e	−3673(3)	−1092(3)	5543(4)	21(2)
O2	8e	−2688(2)	−2258(3)	5493(3)	21(1)
O3	8e	−945(3)	−646(3)	1828(3)	23(1)
O4	8e	−2714(2)	−1135(3)	1918(3)	21(1)
O5	8e	−3608(2)	−1828(3)	3527(4)	16(2)
O6	8e	−4582(2)	−2286(3)	5463(3)	22(1)
O7	8e	−1233(3)	−1943(3)	1504(4)	25(2)
O8	8e	−1466(2)	−1397(3)	3732(3)	18(2)
O9	8e	−3722(2)	−507(3)	3474(4)	20(2)
O10	8e	−6182(3)	−555(3)	2133(4)	25(2)
O11	8e	−4506(2)	−1218(2)	1825(3)	18(1)
O12	8e	−5766(2)	−1603(3)	3543(3)	21(1)
O13	8e	−6130(3)	−1776(3)	1163(3)	22(2)
O14	8e	−3727(3)	179(4)	5396(4)	32(2)
H3	8e	−1034	−326	2270	28[a]
H10	8e	−6188	−405	2923	29[a]
H14	8e	−3730	505	4854	39[a]

[a] U_{iso} values of the H atoms were kept at $1.2U_{eq}$ of the O atoms to which they are attached.

sample was placed in an open 85 μL PtRh crucible (Netzsch) and then heated at 2 K/min to 1273 K in a continuous argon flow (200 mL/h, Messer-Griesheim 99.999% purified with ALPHAGAZ O2-Free-System). After cooling with the same rate, the slightly sintered powder was examined by powder XRD. For examination of the rehydration behavior, a new sample was heated under the same conditions up to 583 K. The obtained product was then exposed to atmospheric moisture for several days and reheated to 1273 K in a continuous argon flow. All measurements were corrected by buoyancy.

Results

Crystal Structure. The crystal structure of $CsSc[B_2P_3O_{11}(OH)_3]$ contains a novel complex anion, $[B_2P_3O_{11}(OH)_3]^{4-}$, which is built of a central borate tetrahedron open-branched by two $(OH)PO_3$ tetrhedra and cyclobranched by one PO_4 tetrahedron and a trigonal-planar $(OH)BO_2$ group by sharing common apexes, as shown in Figure 2. All of the atoms of the oligomeric unit represent independent crystallographic sites. The bond distances within the oligomeric unit are listed in Table 3. The lengths of the bridging B−O bonds ($B-O_{br}$) for the borate tetrahedron (B1) range from 1.457(1) to 1.470(6) Å. In the case of the trigonal-planar boron unit, the bridging B−O bonds ($B-O_{br}$) are notably shorter, with 1.361(8) and 1.397(1) Å. The shortest B−O bond is observed for the terminal B−OH, with 1.342(1) Å.

The shortest P−O distances are found for the terminal P−O bonds ($P-O_t$) in the phosphate tetrahedron (P3) and the hydrogen phosphate groups (P1 and P2), varying from 1.4821(6) to 1.522(4) Å. The bridging P−O bonds ($P-O_{br}$) are in the range from 1.540(4) to 1.576(6) Å, and the two P−OH (P1 and P2) bond lengths are 1.562(5) and 1.577(5) Å, respectively. This is in accordance with the trend observed for pure phosphates.[27]

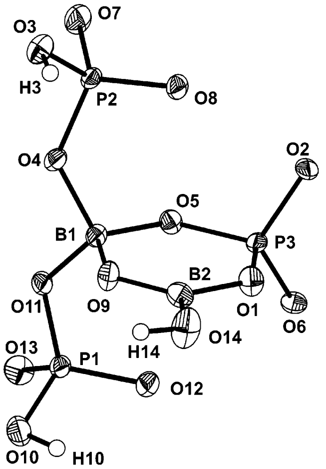

Figure 2. Borophosphate complex $[B_2P_3O_{11}(OH)_3]^{4-}$ in the compound $CsSc[B_2P_3O_{11}(OH)_3]$ containing a central BO_4 tetrahedron (B1) open-branched by two $(OH)PO_3$ tetrahedra (P1 and P2) and cyclobranched by one PO_4 tetrahedron (P3) and a trigonal-planar $(OH)BO_2$ (B2) by sharing common apexes (displacement ellipsoids are drawn at the 50% probability level).

Table 3. P−O and B−O Bond Distances in $CsSc[B_2P_3O_{11}(OH)_3]$, Standard Deviations in Units of Last Decimal in Brackets (O_t Denotes Terminal, O_{br} Bridging, and O_{OH} Hydroxyl O Atoms)

atom−atom contact		*d*/Å
P1	$-O13_t$	1.490(4)
	$-O12_t$	1.498(4)
	$-O11_{br}$	1.555(3)
	$-O10_{OH}$	1.577(5)
P2	$-O7_t$	1.482(6)
	$-O8_t$	1.522(4)
	$-O4_{br}$	1.548(4)
	$-O3_{OH}$	1.562(5)
P3	$-O2_t$	1.497(4)
	$-O6_t$	1.503(4)
	$-O5_{br}$	1.540(4)
	$-O1_{br}$	1.576(6)
B1	$-O5_{br}$	1.457(1)
	$-O11_{br}$	1.462(6)
	$-O9_{br}$	1.466(1)
	$-O4_{br}$	1.470(6)
B2	$-O14_{OH}$	1.342(1)
	$-O9_{br}$	1.361(8)
	$-O1_{br}$	1.397(1)

The oligomeric units are interlinked via common O corners of ScO_6 octahedra. By this, each scandium octahedron (ScO_6) is surrounded by six phosphate tetrahedra belonging to four different borophosphate oligomers (Figure 3). The lengths of the Sc−O bonds range from 2.058(5) to 2.166(5) Å. As shown in Figure 4, two borophosphate anions are connected to four ScO_6 octahedra, resulting in the formation of a cavity. A detailed analysis of this cavity (Figure 5) reveals similarities to a common secondary building unit (SBU) encountered in zeolites,[28] which can be described as a hexagonal prism 6−6 in SBU nomenclature. The shortest interatomic distance within the cavity is 3.25 Å (O5−O5′). The Cs ions

---

(27) Baur, W. H. *Acta Crystallogr.* **1974**, *B30*, 1195.

(28) http://topaz.ethz.ch/IZA-SC.

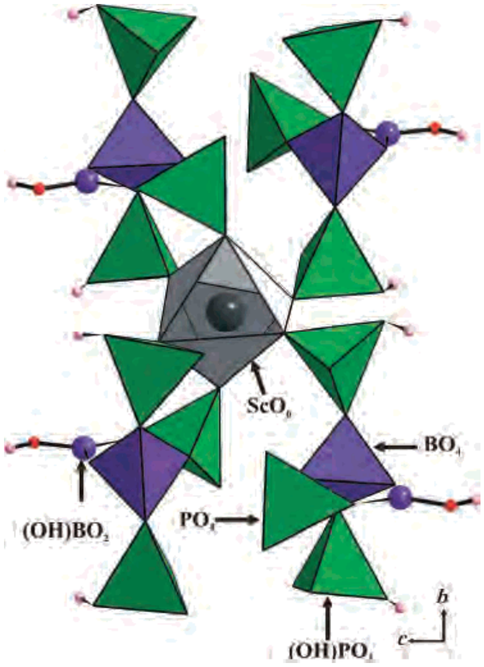

Figure 3. Linkage of six (OH)PO_3 tetrahedra to one ScO_6 octahedron via common corners shared with four surrounding borophosphate oligomeric units.

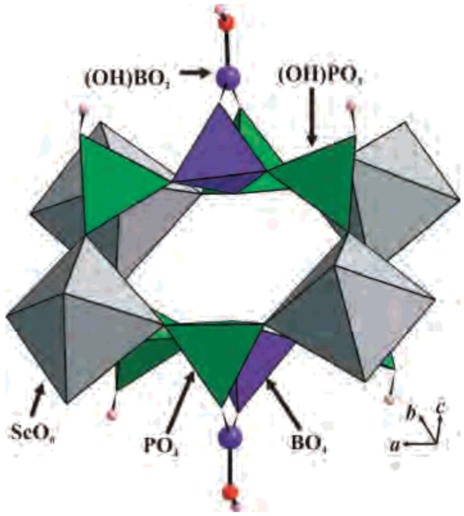

Figure 4. Cavity formed by four ScO_6 octahedra and two borophosphate anions $[B_2P_3O_{11}(OH)_3]^{4-}$ in the crystal structure of $CsSc[B_2P_3O_{11}(OH)_3]$.

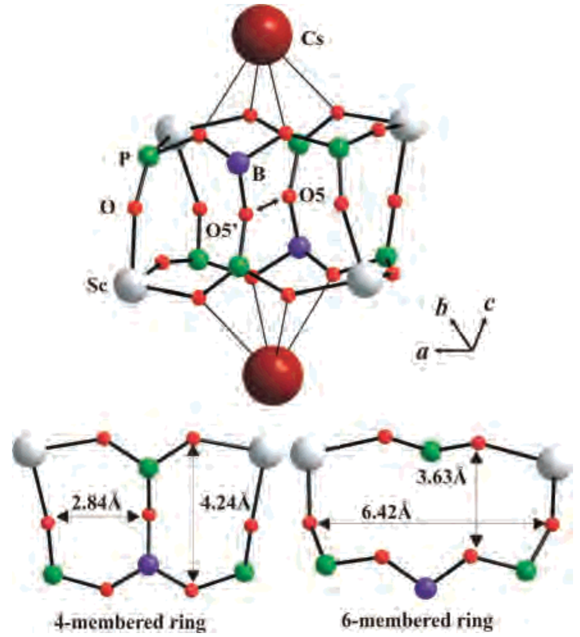

Figure 5. Details of the cage formed by six four-membered rings (according to zeolite nomenclature) and two six-membered rings with $d(O5\cdots O5') = 3.25$ Å in the crystal structure of $CsSc[B_2P_3O_{11}(OH)_3]$.

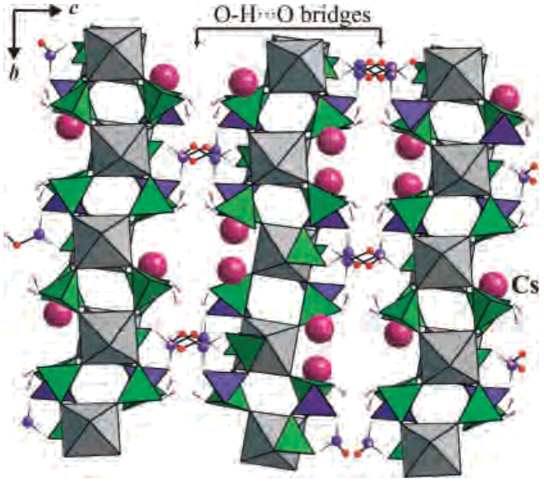

Figure 6. Crystal structure of $CsSc[B_2P_3O_{11}(OH)_3]$ (view along [100]): layers of interconnected borophosphate anions and ScO_6 octahedra linked via hydrogen bonds. The Cs^+ ions (large red spheres) are located in between the layers.

are situated above and below the six-membered rings with four contacts to neighboring O atoms [3.181(5)−3.334(4) Å] of the rings (Figure 5). The borophosphate oligomers together with the ScO_6 octahedra are condensed to form layers running parallel (001), as shown in Figure 6. The Cs cations are located in between the layers. Hydrogen bonds O−H···O with O···O distances of 2.66, 2.76, and 2.83 Å (angles (O−H···O) of 169°, 174°, and 179°) are formed between the layers.

Thermal Behavior. The TG curve of $CsSc[B_2P_3O_{11}(OH)_3]$ reveals a stepwise mass loss during heating, which is completed at about 973 K with an overall mass loss of 6.3 wt %. Assuming that only water is released under the chosen experimental conditions, a value of 5.2 wt % (1.5 mol of H_2O per formula unit) is expected. During heating, a broad structured endothermic effect is observed with maxima (513, 583, and 723 K) coinciding with the individual steps of the mass loss. At 1113 K, an exothermic effect occurs without a change in the sample weight. The powder XRD pattern of the decomposition product shows sharp reflections that could not be assigned to any known crystalline phase or a phase mixture. A sample that was heated to approximately the end of the second TG step at about 583 K did not show any rehydration behavior. For details, see the Supporting Information.

Discussion

In the course of our systematic investigation on the existence of alkali-metal scandium borophosphates, three different compounds were synthesized and structurally

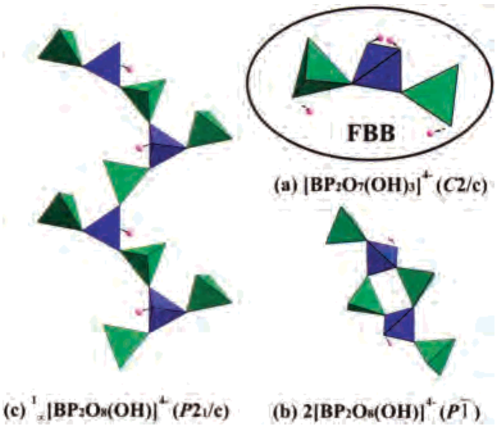

Figure 7. Anionic partial borophosphate structures in compounds with element combinations M^I (Na, K, Rb, and Cs) and M^{III} (Al, Ga, In, V, and Fe): (a) M^IM^{III}[$BP_2O_7(OH)_3$]; (b) M^IM^{III}[$BP_2O_8(OH)$] (SPR: $P\bar{1}$); (c) M^IM^{III}[$BP_2O_8(OH)$] (SPG: $P2_1/c$). All three anionic partial structures are built up from a common FBB [$BP_2O_7(OH)_3$]$^{3-}$.

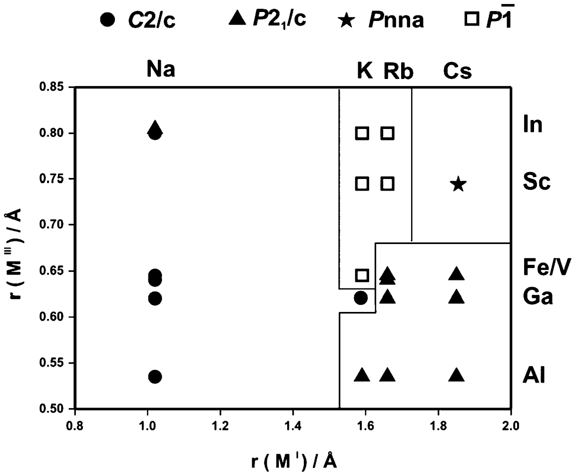

Figure 8. Structure map for the known borophosphates of the general formulas M^IM^{III}[$BP_2O_7(OH)_3$], M^IM^{III}[$BP_2O_8(OH)$] (SPR: $P\bar{1}$), M^IM^{III}[$BP_2O_8(OH)$] (SPG: $P2_1/c$), and CsSc[$B_2P_3O_{11}(OH)_3$] (monovalent as well as trivalent cations in the molar ratio 1:1).

characterized by single-crystal XRD data: KSc[$BP_2O_8(OH)$],[29] RbSc[$BP_2O_8(OH)$],[30] and CsSc[$B_2P_3O_{11}(OH)_3$].[31] The borophosphates KSc[$BP_2O_8(OH)$] and RbSc[$BP_2O_8(OH)$] were found to be isotypic to KFe[$BP_2O_8(OH)$] (triclinic, $P\bar{1}$),[32] which belongs to the group of borophosphates with B:P = 1:2. On the other hand, CsSc[$B_2P_3O_{11}(OH)_3$] exhibits a new crystal structure with B:P = 2:3, although the molar ratio of the educts and the reaction conditions used for the preparation of all three compounds were kept invariant. Attempts to synthesize lithium– and sodium–scandium borophosphates ended up with phosphates only.

The anionic partial structure of ASc[$BP_2O_8(OH)$] (A = K, Rb)[29,30] is built up from two unbranched tetrahedral triples (Figure 7a) and comprises an open-branched four-membered ring [$B_2P_4O_{16}(OH)_2$]$^{8-}$ (Figure 7b), which is formed by alternating hydrogen borate and phosphate tetrahedra by sharing common corners with two additional open-branching phosphate tetrahedra. The resulting three-dimensional framework contains channels running along [100] filled with K^+ or Rb^+, respectively.

With the successful synthesis of the scandium compounds under consideration, the group of borophosphates containing M^I as well as M^{III} species (M^I = Na, K, Rb, Cs; M^{III} = Al, Ga, V, Fe, Sc, In) is now represented by a total number of 21 members, which are ordered in Figure 8 according to their cationic radii. Three types of borophosphate anions were already observed for the known M^IM^{III} borophosphates, namely, M^IM^{III}[$BP_2O_8(OH)$] ($P2_1/c$; Figure 7c),[33] M^IM^{III}[$BP_2O_7(OH)_3$] ($C2/c$; Figure 7a),[34] and M^IM^{III}[$BP_2O_8(OH)$] ($P\bar{1}$; Figure 7b),[29,30,35] which all consist of the same FBB as the borophosphate trimer [BP_2O_{10}] (Figure 7a).

In the crystal structure of M^IM^{III}[$BP_2O_7(OH)_3$],[34] the anionic partial structure (Figure 7a) consists of an unbranched tetrahedral triple [$BP_2O_7(OH)_3$]$^{4-}$, built of a dihydrogen borate tetrahedron sharing common corners with two hydrogen phosphate tetrahedra. This unit is present in all members containing sodium. Condensation of such units accompanied by the loss of one molecule of H_2O per unit can lead to the formation of either open-branched four-membered rings [$B_2P_4O_{16}(OH)_2$]$^{8-}$ (Figure 7b) or single chains $^1_\infty$[$BP_2O_8(OH)$]$^{4-}$ (Figure 7c). Examples with a higher degree of condensation are unknown for the combination M^IM^{III} so far but can be realized using M^IM^{II},[36] $M_{0.5}{}^{II}M^{II}$,[37]

---

(29) Menezes, P. W.; Hoffmann, S.; Prots, Yu.; Kniep, R. *Z. Kristallogr.—New Cryst. Struct.* **2006**, *221*, 251.

(30) Menezes, P. W.; Hoffmann, S.; Prots, Yu.; Kniep, R. *Z. Kristallogr.—New Cryst. Struct.* **2006**, *221*, 253.

(31) Part of this paper was presented at the 13th Vortragstagung, Fachgruppe Festkoerperchemie und Materialforschung, Aachen, Germany, 20.09-22.09.2006. Menezes, P. W.; Hoffmann, S.; Prots, Yu.; Kniep, R. *Z. Anorg. Allg. Chem.* **2006**, *32*, 2131.

(32) Boy, I.; Cordier, G.; Eisenmann, B.; Kniep, R. *Z. Naturforsch. B: Chem. Sci.* **1998**, *53*, 165.

(33) (a) Engelhardt, H.; Borrmann, H.; Kniep, R. *Z. Kristallogr.—New Cryst. Struct.* **2000**, *215*, 203. (b) Kniep, R.; Koch, D.; Hartmann, T. *Z. Kristallogr.—New Cryst. Struct.* **2002**, *217*, 186. (c) Mi, J. X.; Zhao, J. T.; Huang, Y. X.; Deng, J. F.; Borrmann, H.; Kniep, R. *Z. Kristallogr.—New Cryst. Struct.* **2002**, *217*, 171. (d) Mi, J. X.; Huang, Y. X.; Deng, J. F.; Borrmann, H.; Zhao, J. T.; Kniep, R. *Z. Kristallogr.—New Cryst. Struct.* **2002**, *217*, 169. (e) Mi, J. X.; Borrmann, H.; Huang, Y. X.; Mao, S. Y.; Zhao, J. T.; Kniep, R. *Z. Kristallogr.—New Cryst. Struct.* **2003**, *218*, 171. (f) Mi, J. X.; Borrmann, H.; Mao, S. Y.; Huang, Y. X.; Zhang, H.; Zhao, J. T.; Kniep, R. *Z. Kristallogr.—New Cryst. Struct.* **2003**, *218*, 17. (g) Kniep, R.; Boy, I.; Engelhardt, H. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1512. (h) Engelhardt, H.; Kniep, R. *Z. Kristallogr.—New Cryst. Struct.* **1999**, *214*, 443. (i) Mao, S. Y.; Li, M.-R.; Wei, Z.-B.; Mi, J.-X.; Zhao, J.-T. *Wuji Huaxue Xuebao* **2004**, *20*, 53.

(34) (a) Koch, D.; Kniep, R. *Z. Kristallogr.—New Cryst. Struct.* **1999**, *214*, 441. (b) Huang, Y. X.; Mao, S. Y.; Mi, J. X.; Wei, Z. B.; Zhao, J. T.; Kniep, R. *Z. Kristallogr.—New Cryst. Struct.* **2001**, *216*, 15. (c) Mi, J. X.; Huang, Y. X.; Mao, S. Y.; Borrmann, H.; Zhao, J. T.; Kniep, R. *Z. Kristallogr.—New Cryst. Struct.* **2002**, *217*, 167. (d) Huang, Y. X.; Mi, J. X.; Mao, S. Y.; Wei, Z. B.; Zhao, J. T.; Kniep, R. *Z. Kristallogr.—New Cryst. Struct.* **2002**, *217*, 7. (e) Zhang, L. R.; Zhang, H.; Borrmann, H.; Kniep, R. *Z. Kristallogr.—New Cryst. Struct.* **2002**, *217*, 477. (f) Boy, I.; Cordier, G.; Eisenmann, B.; Kniep, R. *Z. Naturforsch. B: Chem. Sci.* **1998**, *53*, 165.

(35) Mao, S. Y.; Li, M. R.; Huang, Y. X.; Mi, J. X.; Wei, Z. B.; Zhao, J. T.; Kniep, R. *Z. Kristallogr.—New Cryst. Struct.* **2002**, *217*, 3.

(36) Kniep, R.; Will, H. G.; Boy, I.; Rohr, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1013.

(37) Menezes, P. W.; Hoffmann, S.; Prots, Yu.; Kniep, R., in preparation.

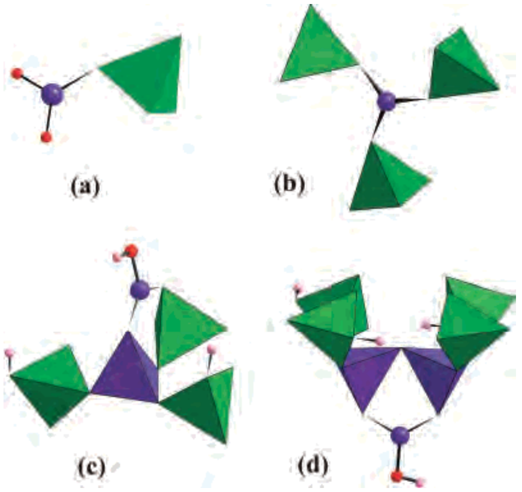

Figure 9. Borophosphate complexes (B:P < 1) containing boron in the coordination numbers 3 and 4 (see the text for references): (a) $Co_5[BP_3O_{14}]$ (one PO_4 tetrahedron and one BO_3 group); (b) $Cr_2[BP_3O_{12}]$ and $V_2[BP_3O_{12}]$ (three PO_4 tetrahedra and one BO_3 group); (c) $[C_6H_{12}N_2]_2VO(PO_3(OH)_4$-$(B_3O_3OH)\cdot 4H_2O$ (four PO_4 tetrahedra, two BO_4 tetrahedra, and one BO_3 group); (d) $CsSc[B_2P_3O_{11}(OH)_3]$ (three PO_4 tetrahedra, one borate tetrahedron, and one BO_3 group).

or M^{III} [38] and result in a helical anion ${}^{1}_{\infty}[BP_2O_8]^{3-}$. For all of these M^IM^{III} borophosphates under consideration, the coordination number of boron and phosphorus is 4 (Figure 7). For the title compound (also with B:P < 1), a completely different anionic partial structure is observed containing boron in coordination numbers 3 and 4, respectively. Up to now, the occurrence of mixed coordination for boron was only reported for compounds with B:P > 1 containing complex chain anions[39−41] and the trigonal borate unit exclusively bonded to borate species.

Considering borophosphates containing triangular borate units with B:P < 1, only four members are reported so far: $Co_5[BP_3O_{14}]$,[42] $Cr_2[BP_3O_{12}]$,[43] $V_2[BP_3O_{12}]$[44] (prepared via a solid-state route), and the templated compound ($[C_6H_{12}N_2]_2$-$VO(PO_3(OH)_4(B_3O_3OH)\cdot 4H_2O$) ($C_6H_{12}N_2$ = DABCO)[45] (Figure 9). In $Co_5[BP_3O_{14}]$ (SPG: $P2_1/c$),[42] the anionic partial structure (Figure 9a) consists of a trigonal-planar borate unit that is connected to one phosphate tetrahedron, whereas in $Cr_2[BP_3O_{12}]$ (SPG: $P3$)[43] and $V_2[BP_3O_{12}]$[44] (SPG: $P6_3/m$), the anionic partial structure (Figure 9b) consists of a trigonal-planar borate unit that is connected to three phosphate tetrahedra. The only known example for an oligomeric templated borophosphate containing boron in coordination 3 and 4, respectively, is given by $[C_6H_{12}N_2]_2VO(PO_3(OH)_4$-$(B_3O_3OH)\cdot 4H_2O$ ($P2_1/c$)[45]containing an oligomer (Figure 9d) built of a trimeric hydrogen borate group $(OH)B_3O_3$ and four hydrogen phosphate groups $((OH)PO_3)_4$. The trigonal-planar borate unit in this oligomer is connected to two borate tetrahedra, which are further connected to four hydrogen phosphate groups. In the crystal structure of the title compound, $CsSc[B_2P_3O_{11}(OH)_3]$, the trigonal-planar borate unit is attached to one borate and one phosphate tetrahedron, as shown in Figure 9c. This arrangement of polyhedra was already predicted for borates[2] but never observed.

Considering the structural similarity of indium and scandium (see Figure 8), several attempts have already been made to prepare a corresponding cesium−indium borophosphate containing the novel oligomer, but despite all efforts, they were unsuccessful up to now.

Conclusions

The first approach for the classification of the known borophosphate crystal structures in 1998 led to the conclusion that hydrated borophosphates with a molar ratio B:P ≤ 1 are exclusively built of borate and phosphate tetrahedra and do not contain boron in trigonal-planar coordination.[46] Interestingly, we ascertained that the predicted principles does not hold for our novel borophosphate (templated borophosphates are not under consideration). In $CsSc[B_2P_3O_{11}(OH)_3]$, the B:P ratio is less than 1 (B:P < 1) and we do observe BO_3 units, which are furthermore linked not only to borate species but also to a phosphate tetrahedron. Moreover, this arrangement of polyhedra in $CsSc[B_2P_3O_{11}(OH)_3]$ was already predicted for borates[2] but never observed. This itself proves that $CsSc[B_2P_3O_{11}(OH)_3]$ is a special compound with regard to the structural building principles of borates and borophosphates.

Acknowledgment. We thank Ms. Anja Völzke and Dr. G. Auffermann for chemical analyses, Mrs. P. Scheppan for energy-dispersive X-ray analyses, Ms. Susann Müller for DTA/TG measurements, Dr. R. Cardoso for XRD measurements, and Dr. B. Ewald for IR measurements.

Supporting Information Available: Crystallographic data for $CsSc[B_2P_3O_{11}(OH)_3]$ in CIF format, the IR spectrum and TG/DTA of $CsSc[B_2P_3O_{11}(OH)_3]$, and a table containing all known M^IM^{III} borophosphates (M^I:M^{III} = 1:1). This material is available free of charge via the Internet at http://pubs.acs.org.

IC700914V

---

(38) Yilmaz, A.; Bu, X. H.; Kizilyalli, M.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 3243.
(39) Hauf, C.; Kniep, R. *Z. Kristallogr.−New Cryst. Struct.* **1997**, *212*, 313.
(40) Hauf, C.; Kniep, R. *Z. Kristallogr.* **1996**, *211*, 705.
(41) Hauf, C.; Kniep, R. *Z. Kristallogr.* **1996**, *211*, 707.
(42) Bontchev, R. P.; Sevov, S. C. *Inorg. Chem.* **1996**, *35*, 6910.
(43) Mi, J. X.; Zhao, J. T.; Mao, S. Y.; Huang, Y. X.; Engelhardt, H.; Kniep, R. *Z. Kristallogr.−New Cryst. Struct.* **2000**, *215*, 201.
(44) Meisel, M.; Pach, M.; Lutz, L. W. B.; Wulff-Molder, D. *Z. Anorg. Allg. Chem.* **2004**, *630*, 983.
(45) Bontchev, R. P.; Do, J.; Jacobson, A. J. *Inorg. Chem.* **1999**, *38*, 2231.
(46) Kniep, R.; Engelhardt, H.; Hauf, C. *Chem. Mater.* **1998**, *10*, 2930.