Communication

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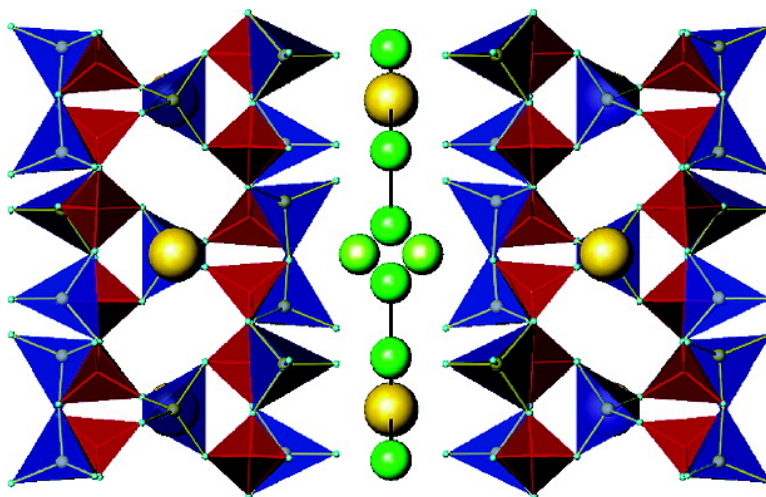# Boroarsenates: A Framework Motif and Family Templated on Cations and Anions

Seth B. Wiggin and Mark T. Weller*

School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK

Received August 22, 2005; E-mail: mtw@soton.ac.uk

Framework materials have been extensively studied due to their important applications in areas as diverse as cation exchangers, catalysts, and nonlinear optical materials. Oxotetrahedral frameworks are the most prevalent structures, as exemplified by the large number of zeolite, aluminophosphate, and zincophosphate structures.[1] Recently, significant developments of oxotetrahedral frameworks have been made with the synthesis of a generation of structures containing less common units, for example, BO_4, FeO_4, and NiO_4 tetrahedra; these normally occur in association with the more traditional species of SiO_4, AlO_4, and PO_4.[2] In some framework structures, tetrahedra may terminate in oxygen or a protonated oxygen, for example, $NaZnSiO_3OH$[3] and the dumortierite analogues, $CoCo_6(OH)_3(AsO_4)(AsO_3OH)$.[4] The quest for structural diversity in framework materials has also led to the use of borate units, with their three- or four-coordinate linking abilities.[5] These borate groups in combination with group 15 oxotetrahedra, such as PO_4, can produce building blocks isoelectronic with silicates and lead to analogous structures, for example, the quartz analogue BPO_4,[6] mixed isolated borate and phosphate units,[7] chain structures,[8] and fully three-dimensional frameworks.[9] In contrast, the area of boroarsenate chemistry has been relatively poorly explored, with very few known examples in the current literature. The minerals Teruggite $[Ca_4Mg(B_6(OH)_6O_8 (AsO_3))_2(H_2O)_{14}]$ and Cahnite $[Ca_2-BAsO_4(OH)_4]$, which contains discrete $B(O,OH)_4$ and $As(OH)_4$ tetrahedra, are known, as are a few dense boroarsenates, prepared at high temperature, including $Ba(BAsO_5)$, $Pb(BAsO_5)$, and $Pb_6-AsO_4(B(AsO_4)_4)$. The combination of the unique framework-forming behaviors of arsenate $(AsO_{4-n}(OH)_n)$ and (fluoro)borate (BO_3, BO_4, BO_3F) has not, hitherto, been studied in any detail. Investigation of these arsenate species provides an opportunity to develop completely new framework types, quite distinct from borophosphates, that can coordinate to anionic species through the proton of the OH unit or hydrogen bond within channels. We present here results that show the wealth of new framework structural types that exist based on (fluoro)borate and arsenate; these are templated around alkali metal ions and, more unusually, alkali metal halide species.

The synthesis of new boroarsenate framework materials was undertaken using low-temperature molten salt reactions at 513 K. A typical reaction mixture consisted of H_3BO_3, $NH_4H_2AsO_4$, and an alkali metal halide in a 3:3:2 molar ratio. These were mixed in a pestle and mortar before being added to a 23 mL Teflon-lined steel autoclave and heated for 240 h. The product was washed with hot deionized water to dissolve the remaining borate flux, leaving colorless crystals of the desired phases as the only solid product. The crystal structures of the new compounds were determined by analysis of single-crystal X-ray diffraction data. We have systematically surveyed materials formed from the systems, as summarized in Table 1, and found many new materials. In this communication, the details of two key new structure types are reported; other phases formed in this system will be described in a later full article.

Potassium boroarsenate, $K_2[B(AsO_3O)_2H]$ (**I**), crystallizes in the tetragonal space group $P4_12_12$ (No. 92). Determination of the hydrogen position shows that the arsenate tetrahedron exists as an $AsO_3OH_{1/2}$ moiety with the hydrogen shared between two equivalent tetrahedra; this distribution is also apparent in the different As–O bond lengths. The framework consists of borate, BO_4, tetrahedra bonded to four arsenate $As(O_3OH_{1/2})$ tetrahedra in a strictly alternating borate–arsenate pattern (Figure 1). The $As(O_3OH_{1/2})$ tetrahedra have two oxygen atoms bridging to borate, one terminal oxygen, and OH. The structure is formed from interconnected 12-rings, with each borate group contributing to three separate rings. The potassium ions occupy the cavities and are coordinated by five framework oxygen atoms at distances of 2.7–2.9 Å, similar to those observed in zeolite-type frameworks templated on K^+. The protons on the $As(O_3OH_{1/2})$ tetrahedra are directed into the cavities containing the potassium ions forming a strong hydrogen bond, $OH\cdots O = 1.74$ Å, with the terminal oxygen on an adjacent $As(O_3OH_{1/2})$ unit.

The product of the reaction involving cesium chloride, (**II**) $(Cs_2[BAsO_3OH]_8[AsO_4]_2[CsCl_4]Cl)_2$, is perhaps the most unusual, forming a tetragonal structure in the $I4/m$ space group (No. 87). The material templates on both anions and cations and the structure can be considered as containing two distinct regions. A boroarsenate layer is formed from a secondary building unit (SBU) consisting of a central arsenate tetrahedra attached to four different borate tetrahedra (Figure 2). Pairs of borate tetrahedra are bridged by two arsenate tetrahedra creating small, empty cages. Four of these SBUs join to create a large central cavity that holds cesium ions (Figure 2). The pendant arsenate tetrahedra have one OH unit, and the oxygen atom of this unit coordinates to a second cesium ion, while the protons are hydrogen bonded to chloride. This cesium ion also coordinates to four chloride ions, and this unit, together with isolated Cl^- ions, form sheets between the boroarsenate layers (Figure 2). The overall composition of the compound can be thus be rewritten as $({Cs_2[BAsO_3OH]_8[AsO_4]_2}{[CsCl_4]Cl})_2$ with alternating layers of a framework structure element and an ionic part.

Many further unique framework structures have been produced as summarized in Table 1. Fluoride salts of larger cations (e.g., K, Cs, Rb, NH_4) gave isostructural products of the stoichiometry M^+-$[BAsO_3F]$ as the sole reaction product; this fluoroboroarsenate is an analogue of the recently reported borophosphate.[10] A similar reaction but using NaF produces a new open-pore material crystallizing in the $F23$ space group, $a = 21$ Å. The use of metal bromide salts also produces boroarsenate frameworks often isostructural with the products formed using chloride, so $({Cs_2[BAsO_3-OH]_8[AsO_4]_2}{[CsBr_4]Br})_2$ adopts the same structure type as **II** but with an expanded unit cell (the c axis increases by ca. 0.25 Å).

In summary, we have synthesized several new (fluoro)boroarsenate framework materials with a variety of structural motifs. Arsenic is incorporated into these frameworks, built from tetrahedra, as AsO_4 or protonated (AsO_3OH) units. The pendent protons may

Table 1. Phases Isolated in the Systems MX, H_3BO_3, $NH_4H_2AsO_4$

	Cation[a]				
	Li	Na	K	Rb	Cs
F		$Na_{11}[B_6(AsO_3OH)_4(AsO_4)_7]$ *F23* $a = 20.995(2)$ Å a high-symmetry framework with 6 and 4 Å pores	$K[BAsO_4F]$ $P2_13$ $a = 7.6842(9)$ Å isostructural with $K[BPO_4F]$[10]	$Rb[BAsO_4F]$ $P2_13$ $a = 7.7725(5)$ Å isostructural with $K[BAsO_4F]$	$Cs[BAsO_4F]$ $P2_13$ $a = 7.8695(4)$ Å isostructural with $K[BAsO_4F]$
Cl, {Br} (Anion)	$Li_2B_5O_5(AsO_3OH)_2(AsO_4)$ *Pna2₁* $a = 24.0901(8)$ Å, $b = 4.5219(1)$ Å, $c = 13.2572(5)$ Å chains comprised of three arsenate and borate tetrahedra and two BO_3 units templated by Li		compound **I** $\{K_2[B_4O_5(AsO_3OH)_2]$ *Pc* $a = 10.792(3)$ Å $b = 4.522(5)$ Å, $c = 12.919(4)$ Å $\beta = 111.9(1)°$ *similar chain-like motif to* $Li_2B_5O_5(AsO_3OH)_2(AsO_4)\}$	$Rb_2[B_2(AsO_4)_2(AsO_3OH)]$ $C2_1/c$ $a = 15.795(3)$ Å, $b = 7.528(2)$ Å, $c = 9.311(2)$ Å $\beta = 106.1(1)°$ boroarsenate layers with bridging AsO_4 tetrahedra	compound **II** $\{$*isostructural with* **II**$\}$

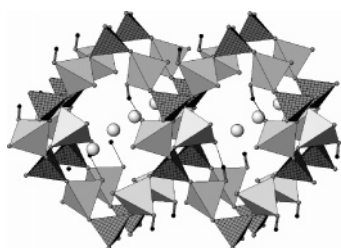[a] Ammonium fluoride produces a material isostructural with the potassium, rubidium, and cesium fluoride systems.

Figure 1. Representation of the structure of $K_2[B(AsO_3O)_2H]$ viewed close to *a*. AsO_4 tetrahedra are shaded pale gray and BO_4 tetrahedra cross-hatched. K^+ ions are shown as pale gray spheres, and hydrogen is shown as small black spheres with hydrogen bonding delineated by a thin black line.
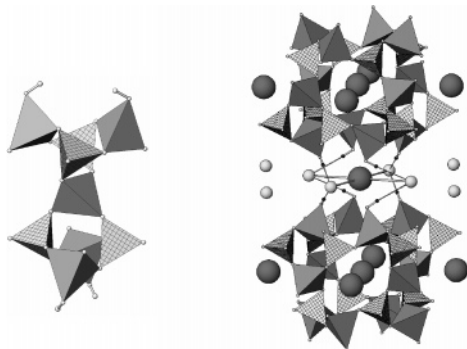

Figure 2. Left: The secondary building unit of $(Cs_2[BAsO_3OH]_8[AsO_4]_2$-$[CsCl_4]Cl]_2$. (AsO_3OH) and AsO_4 tetrahedra (center) are shown shaded gray, and BO_4 tetrahedral are shown with cross-hatching. Right: The structure of $(Cs_2[BAsO_3OH]_8[AsO_4]_2 [CsCl_4]Cl)_2$ viewed down close to [1 1 0]; cesium ions are shown as large dark gray spheres and chloride ions as medium pale gray spheres.

either decorate the channels formed within these structures, as in $K_2[B(AsO_3O)_2H]$, or act as coordination sites for anions, as in $(Cs_2[BAsO_3OH]_8[AsO_4]_2[CsCl_4]Cl)_2$. This leads to an unusual new type of framework structure templated around both anions and cations and which may be considered to be a hybrid structure-type containing elements of both framework and ionic structures. Framework materials containing both anions and cations are relatively rare though examples include the aluminosilicates sodalite[11] and kalborsite.[12] Other routes to anion-containing structures include the insertion of metal halides into layered oxides, such as $FeClLaNb_2O_7$,[13] salt inclusion chemistry, as in $Na_5CsCu_4(AsO_4)_4$-Cl_2,[14] and the formation of hybrid metal oxalates, such as $[RbCl]$-$Cd_6(C_2O_4)_6]\cdot2H_2O$.[15] The materials reported here may thus show the properties associated with these unusual structural features, such as selective anion trapping and exchange.[16] Furthermore the structure of **II** can be considered as having a regularly distributed two-dimensional layer of a simple metal compound, and the use of the AsO_3OH unit, by coordinating to both anions and cations, may provide a synthetic route to functionalized metal halides and oxides of restricted dimensions.

Supporting Information Available: Details of experimental and synthesis methods, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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