Borosulfates

International Edition: DOI: 10.1002/anie.201510612
German Edition: DOI: 10.1002/ange.201510612

The Borosulfates $K_4[BS_4O_{15}(OH)]$, $Ba[B_2S_3O_{13}]$, and $Gd_2[B_2S_6O_{24}]$

*Peter Gross, Arno Kirchhain, and Henning A. Höppe**

Abstract: *$K_4[BS_4O_{15}(OH)]$, $Ba[B_2S_3O_{13}]$, and $Gd_2[B_2S_6O_{24}]$ were obtained by a new synthetic approach. The strategy involves initially synthesizing the complex acid $H[B(HSO_4)_4]$ which is subsequently reacted in an open system with anhydrous chlorides of K, Ba, and Gd to the respective borosulfates and a volatile molecule (HCl). Furthermore, protonated borosulfates should be accessible by appropriate stoichiometry of the starting materials, particularly in closed systems, which inhibit deprotonation of $H[B(HSO_4)_4]$ via condensation and dehydration. This approach led to the successful synthesis of the first divalent and trivalent metal borosulfates ($Ba[B_2S_3O_{13}]$ with band-silicate topology and $Gd_2[B_2S_6O_{24}]$ with cyclosilicate topology) and the first hydrogen borosulfate $K_4[BS_4O_{15}(OH)]$.*

By strict analogy to silicates,[1] one of the structurally most versatile compound classes (with their mother compound SiO_2), borophosphates (based on $BPO_4 \hat{=} Si_2O_4$) also show a rich structural diversity.[2,3] Inspired by the structural principles and synthetic methods of oligosulfates,[4] the first crystalline borosulfates[5–8] were characterized recently, beginning with $K_5[B(SO_4)_4]$.[9] These can be classified, like silicate, as soro-,[9] cyclo-,[7] ino-,[5] phyllo-,[10] and tectosilicate-analogous[5] compounds. Whereas for borophosphates only B-O-P- and B-O-B-connections occur, but to date no P-O-P-connections,[3] -B-O-S- and B-O-B-, and also S-O-S-connections[5] could be found for borosulfates. This raises expectations for a just as broad range of structural possibilities; but therefore, by analogy with borophosphates and silicates, syntheses of borosulfate salts comprising higher charged cations as well as salts with protonated anions must succeed. All hitherto published ionic borosulfates contained merely monovalent cations as well as fully deprotonated anions. Herein we present a systematic and general synthetic approach for the synthesis of protonated, alkaline-earth and rare-earth borosulfates, which additionally opens pathways to novel structural motifs.

Analogously to borosilicates and borophosphates, we name the described compounds borosulfates, although we are well aware that some readers may expect the name boratosulfates according to nomenclature rules.

The first borosulfates where synthesized employing H_3BO_3 and alkali-metal hydrogen sulfates, alkali-metal disulfates, or directly in oleum as solvent. The hitherto always found FBU (fundamental building unit) in form of a super-tetrahedron, which is non-condensed in $K_5[BS_4O_{16}]$,[9] as well as several publications regarding superacids[11–13] suggest the complex acid $H[B(HSO_4)_4]$, which is presumably formed in situ. Thus, our new synthetic approach adopts a strategy of initially synthesizing this acid and reacting it subsequently in an open system with anhydrous salts (for example, anhydrous chlorides of the desired metal) to the respective borosulfates and a volatile molecule (for example, HCl). Furthermore, protonated borosulfates should be accessible by appropriate stoichiometry of the starting materials, particularly in closed systems, which inhibit deprotonation of $H[B(HSO_4)_4]$ via condensation and dehydration. This approach led to the successful synthesis of the first divalent and trivalent metal borosulfates ($Ba[B_2S_3O_{13}]$ and $Gd_2[B_2S_6O_{24}]$) as well as the first protonated alkali borosulfate $K_4[BS_4O_{15}(OH)]$.

$K_4[BS_4O_{15}(OH)]$ crystallizes in a new structure type adopting space group $I2/a$. The crystal structure features non-condensed super-tetrahedra $[B(HSO_4)(SO_4)_3]^{4-}$, resembling the topology of the anions of the alkali borosulfates $A_5[B(SO_4)_4]$ (A = Li, Na, K, Rb) or the alkali boroselenate $HK_4[(B(SeO_4)_4]$[14] (Figure 1). They consist of one borate tetrahedron, which is connected via all corners to four sulfate tetrahedra. But unlike all previously known borosulfates, on average one of the four sulfate tetrahedra is protonated. This is an important extension of the structural diversity of borosulfates, with analogy to borophosphates and boroselenates. Evidence on the position of the hydrogen atoms was initially given by the significant differences in terminal S–O bond lengths (5 pm) and by analysis of the difference Fourier map; subsequently, these positions could be confirmed by calculations based on the MAPLE concept[15–17] and by bond-

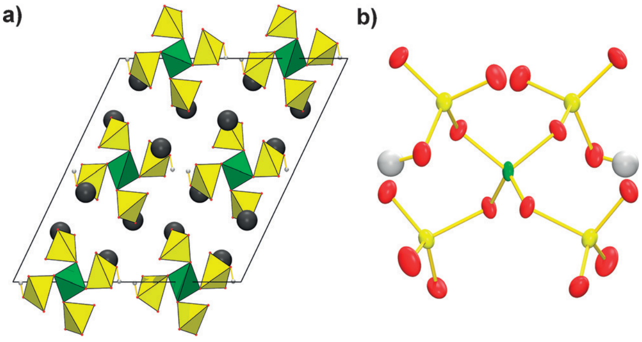

Figure 1. a) The unit cell of $K_4[BS_4O_{15}(OH)]$ (borate tetrahedra green, sulfate tetrahedra yellow, K atoms gray) viewed along [010]; b) the protonated borosulfate anion $[B(HSO_4)(SO_4)_3]^{4-}$ (B atoms green, S atoms yellow, H atoms white, O atoms red), ellipsoids are set at 70% probability.

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201510612.

valence calculations[18] (Supporting Information, Tables S16 and S19). The occupancy of the hydrogen sites was freely refined and yielded 0.49(5), which corresponds to the value expected due to charge balance. For the analogous compound $HK_4[(B(SeO_4)_4]$, this could not be clarified owing to disorder.[14] The $[B(HSO_4)(SO_4)_3]^{4-}$ super-tetrahedra build chains along [100] via strong hydrogen bonds.[19] The potassium atoms are situated on two crystallographically distinct sites in the vacancies of the resulting tetragonal body-centered rod packing. They are both coordinated by eight terminal oxygen atoms (one of them protonated) and one bridging oxygen atom, forming distorted, monocapped tetragonal prisms. The K−O distances range between 248 pm and 347 pm and match on average (295 pm) very well with the sum of ionic radii (291 pm[20]). Further details regarding the crystal structure of $K_4[BS_4O_{15}(OH)]$ are discussed in the Supporting Information. Coordination numbers as well as the electrostatic consistency of the structural model were checked by MAPLE and bond-valence calculations[15–18] (Supporting Information, Tables S15–S19).

$Ba[B_2S_3O_{13}]$ crystallizes in a new structure type in space group *Pnma* and represents the first borosulfate of a divalent cation (Figure 2). The anion features a novel connection pattern of borosulfate double chains. Alternate BO_4- and SO_4-tetrahedra are condensed to chains; an open-branched connection between two BO_4 tetrahedra of adjacent chains yields the aforementioned double chains. The BO_4 tetrahedra are additionally loop-branched vertically to the chain direction by a SO_4 unit. The connection pattern evolves from the condensation of two single borosulfate chains (known from the borosulfates $A_3[BS_3O_{12}]$, A = K, Rb) by formal elimination of three SO_3 molecules. Hence, $Ba[B_2S_3O_{13}]$ is the first ionic borosulfate with ribbon silicate topology and furthermore displays a B-O-B-bridge. Such bridges were hitherto only described for the purely covalent boron sulfate $B_2S_2O_9$ and very recently also for $Cs[B_2S_3O_{13}]$.[10] The barium ions are located on the special position 4*c* and coordinated by nine terminal O atoms belonging to the SO_4 tetrahedra and the B-O-B-bridging O atom forming a distorted Johnson solid J_{17}[21] (gyroelongated square bipyramid). The Ba−O distances range between 268 pm and 295 pm and correspond on average (282 pm) well with the sum of the ionic radii (287 pm[20]). Further details regarding the crystal structure of $Ba[B_2S_3O_{13}]$ are discussed in the Supporting Information. Coordination numbers as well as the electrostatic consistency of the structural model were checked via MAPLE and bond-valence calculations[15–18] (Supporting Information, Tables S18 and S19).

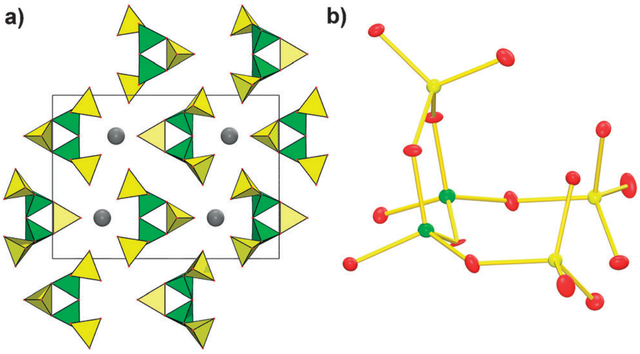

Figure 2. a) The unit cell of $Ba[B_2S_3O_{13}]$ (borate tetrahedra green, sulfate tetrahedra yellow, Ba atoms gray) viewed along $[00\bar{1}]$; b) Repeating unit of the anion $^2_\infty[B_2S_3O_{13}]^{2-}$ (B atoms green, S atoms yellow, O atoms red), ellipsoids are set at 70% probability.

$Gd_2[B_2S_6O_{24}]$ is the first trivalent metal borosulfate and crystallizes in a new structure type in space group *C*2/*c* (Figure 3). Moreover, the compound with the $[B_2S_6O_{24}]^{6-}$ anion is the first cycloborosulfate. The four-membered ring comprises four alternating condensed BO_4 and SO_4 tetrahedra. Via each oxygen atom of the BO_4 tetrahedra, which is not part of the ring, it features additional open-branched connected SO_4 tetrahedra. The resulting complex anions are arranged in a slightly distorted, tetragonal rod packing along [010]. The Gd^{3+} cations are situated in the resulting vacancies coordinated solely by terminal oxygen atoms belonging to the SO_4 tetrahedra forming a tetragonal antiprism. The Gd−O distances range between 228 pm and 249 pm and on average (238 pm) correspond well to the sum of the ionic radii (243 pm[20]). Further details regarding the crystal structure of $Gd_2[B_2S_6O_{24}]$ are discussed in the Supporting Information. Coordination numbers as well as the electrostatic consistency of the structural model were checked bx MAPLE and bond-valence calculations[15–18] (Supporting Information, Tables S18 and S19).

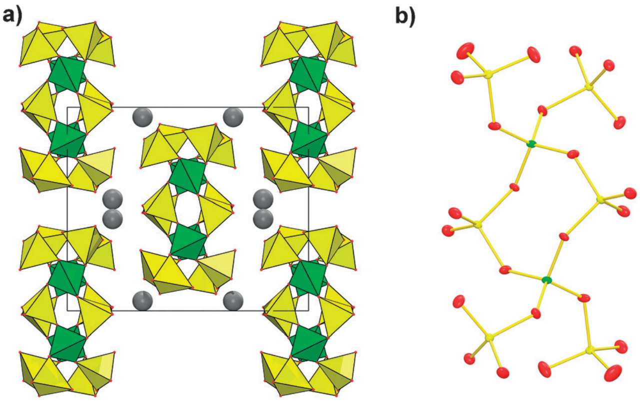

Figure 3. a) The unit cell of $Gd_2[B_2S_6O_{24}]$ (borate tetrahedra green, sulfate tetrahedra yellow, Gd atoms gray) viewed along $[00\bar{1}]$; b) The borosulfate anion $[B_2S_6O_{24}]^{6-}$ (B atoms green, S atoms yellow, O atoms red), ellipsoids are set 70% probability.

In summary, these three compounds demonstrate the extraordinary potential of borosulfates, suggesting a structural diversity as high as found for borophosphates or silicates. This can be fully exploited by foresightful and (if necessary) multi-stepped syntheses. By systematic development of protonated borosulfates potential applications as proton conductors or solid state acids might be established, while divalent and trivalent metal borosulfates remain interesting candidates for optical materials in general and especially as host structures for phosphors.

Experimental Section

Synthesis of $K_4[BS_4O_{15}(OH)]$: A mixture of HBO_2 (35.0 mg, 0.799 mmol) and $K_2S_2O_7$ (406.3 mg, 1.60 mmol) was pulverized in an agate mortar and transferred into a soda-lime glass ampoule (length: 60 mm, inner diameter: 5 mm, wall thickness: 1 mm). The ampoule was fused using a propane/butane burner; the mixture was compacted at one end of the ampoule by knocking. Subsequently, it was jacked up on the empty end to a height of ca. 1 cm inside a muffle furnace and heated to 300 °C with a heating rate of 100 °Ch^{-1}, held at at this temperature for 60 h and afterwards cooled to room temperature with a cooling rate of ca. 33 °Ch^{-1}. The ampoule was cooled with liquid N_2 for 5 min and opened at the product-free side with a hammer. 436.5 mg of product was isolated as a sintered, porous, white solid. The described unit cell was determined by single-crystal XRD for several crystals. The product was characterized by powder XRD as a mixture of $KHSO_4$ and one or several unknown phases (Supporting Information, Figure S1).

Synthesis of $Ba[B_2S_3O_{13}]$: Concentrated H_2SO_4 (1 mL, 17.7 mmol) was mixed with H_3BO_3 (273.6 mg, 4.43 mmol) in a porcelain crucible ($V = 15$ mL). The crucible was heated for 20 h in air inside a preheated muffle furnace at 280 °C. Subsequently, oleum (ca. 0.2 mL, 65 %) and $BaCl_2{\cdot}2H_2O$ (520.4 mg, 2.13 mmol) were promptly added, which resulted in a vigorous reaction with gas evolution. The hot crucible was immediately heated for another 60 h inside the muffle furnace at 280 °C, until the product was formed as fine, very hygroscopic, colorless, crystalline needles at the rim of the crucible and the complete liquid was evaporated. The powder diffraction pattern (Supporting Information, Figure S2) showed that the synthesis yielded $Ba[B_2S_3O_{13}]$ with $BaSO_4$ as the secondary phase. The mass fraction of the secondary phase was determined by TGA and amounted to ca. 10 % (Supporting Information, Figure S3).

Synthesis of $Gd_2[B_2S_6O_{24}]$: Anhydrous $GdCl_3$ was prepared from $GdCl_3{\cdot}6H_2O$.[22] H_3BO_3 (99.8 mg, 1.61 mmol) was dissolved within 75 min at 210 °C in concentrated H_2SO_4 (40 mL, 0.73 mol) in a separate Schlenk flask under a N_2 atmosphere for the synthesis of a solution of $H[B(HSO_4)_4]$ in sulfuric acid. Subsequently, oleum (1 mL, 65 %) was added to react remaining traces of water to H_2SO_4. Freshly prepared $GdCl_3$ was added in a N_2 counterflow under stirring at 210 °C, which was followed by a vigorous reaction with evolution of HCl, yielding a colorless hygroscopic precipitate. A portion (0.3 mL) of this suspension was treated under solvothermal conditions in a soda-lime glass ampoule (length: 60 mm, inner diameter: 5 mm, wall thickness: 1 mm) inside a muffle furnace for 60 h at 250 °C (heating rate: 50 °Ch^{-1}). The obtained colorless crystals (intergrown cubes and cuboctahedra, respectively) are relatively stable to moisture, as long as they are not pulverized. The crystals for single-crystal XRD measurements were fixed in a fused Lindemann glass capillary with a drop of mother liquor.

Single-crystal X-Ray diffraction data of all compounds were collected on a Bruker D8 Venture diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 70.93$ pm) and corrected for absorption by the multi-scan method. All of the structures were solved by direct methods and refined with anisotropic displacement parameters by full-matrix least-squares refinement against F^2: $K_4[BS_4O_{15}(OH)]$: $I2/a$, $Z = 4$, $a = 1452.4$ (3) pm, $b = 739.16$ (10) pm, $c = 1578.57$ (19) pm, $V = 1529.6$ (4)$\cdot 10^6$ pm^3, $\rho_{\mathrm{diff.}} = 2.399$, $2\theta_{\max} = 58°$, $T = 293$ (2) K, 16 092 reflections, 1600 unique reflections, 1223 observed reflections, $R_{\mathrm{int}} = 0.085$, $R_\sigma = 0.039$, min./max. transmission factor 0.6715/0.7454, $R_1 = 0.058$ and $wR_2 = 0.076$ for 1600 reflections, $R_1 = 0.035$ and $wR_2 = 0.070$ for 1223 reflections with $I > 2s(I)$, 116 parameters; $Ba[B_2S_3O_{13}]$: $Pnma$, $Z = 4$, $a = 1718.48$ (7) pm, $b = 1238.05$ (4) pm, $c = 44.226$ (2) pm, $V = 940.94$ (6)$\cdot 10^6$ pm^3, $\rho_{\mathrm{diff.}} = 3.269$, $2\theta_{\max} = 50°$, $T = 200$ (2) K, 16 105 reflections, 873 unique reflections, 823 observed reflections, $R_{\mathrm{int}} = 0.038$, $R_\sigma = 0.012$, min./max. transmission factor 0.6469/0.7458, $R_1 = 0.025$ and $wR_2 = 0.053$ for 873 reflections, $R_1 = 0.0228$ and $wR_2 = 0.0528$ for 823 reflections with $I > 2s(I)$, 95 parameters; $Gd_2[B_2S_6O_{24}]$: $C2/c$, $Z = 3$, $a = 1356.97$ (7) pm, $b = 1144.26$ (6) pm, $c = 1102.71$ (6) pm, $V = 1709.01$ (16)$\cdot 10^6$ pm^3, $\rho_{\mathrm{diff.}} = 3.546$, $2\theta_{\max} = 50°$, $T = 300$ (2) K, 21 746 reflections, 1510 unique reflections, 1415 observed reflections, $R_{\mathrm{int}} = 0.044$, $R_\sigma = 0.017$, min./max. transmission factor 0.3588/0.7471, $R_1 = 0.016$ and $wR_2 = 0.035$ for 1510 reflections, $R_1 = 0.014$ and $wR_2 = 0.034$ for 1415 reflections with $I > 2s(I)$, 154 parameters. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49) 7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-430383 ($K_4[BS_4O_{15}(OH)]$), CSD-430393 ($Ba[B_2S_3O_{13}]$) and CSD-430394 ($Gd_2[B_2S_6O_{24}]$).

Keywords: barium · borosulfates · gadolinium · potassium · sulfatoborates

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 4353–4355
Angew. Chem. **2016**, *128*, 4426–4428

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Received: November 16, 2015