A Boron Sulfate

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$B_2S_2O_9$: A Boron Sulfate with Phyllosilicate Topology**

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The structural chemistry of silicates is dominated by the tendency of [SiO_4] tetrahedra to condense to higher aggregates by sharing common vertices. The great number of different possibilities for the tetrahedra linkage leads to the plethora of known silicates and their structural beauty and richness.[1] The structural versatility of silicates gives rise for special properties of this class of compounds and many of them play an important role in both geochemical processes and technical applications.[2] Thus, it is not surprising that chemical modification of silicate frameworks is an important issue for solid-state and material chemists. A typical modification is the incorporation of aluminum into the framework yielding so-called alumosilicates, which consist of vertex-connected [SiO_4] and [AlO_4] tetrahedra.[3] Anionic derivatization is also possible, for example, the formation of nitridosilicates.[4] In addition to of such alterations, the linkage of other tetrahedral building units should also lead to frameworks related to typical silicate type topologies. This has been nicely illustrated, for example, for the borophosphates joining [PO_4] and [BO_4] tetrahedra,[5] but also other combinations can be imagined. Some years ago we started to investigate the introduction of [SO_4] groups into polytetrahedral frameworks. As a result of the much lower tendency of sulfate tetrahedra to condense to large arrays we usually used SO_3-rich oleum or even neat SO_3 as reaction media under harsh conditions.[6] Surprisingly, under these conditions reactions with silicon compounds, aimed at forming tetrahedral networks built from [SiO_4] and [SO_4] moieties, a number of tris(disulfato)silicates, $[Si(S_2O_7)_3]^{2-}$, and tetrakis(disulfato)silicates, $[Si(S_2O_7)_4]^{4-}$, were obtained, exhibiting octahedrally coordinated silicon atoms.[7] Subsequently other groups were able to prepare a number of boron compounds that indeed show different linking of [BO_4] and [SO_4] tetrahedra.[8] However, in these compounds a linking of [BO_4] tetrahedra, that is, the formation of B-O-B bridges was never observed. Instead the condensation of [SO_4] tetrahedra, that is, the formation of disulfate groups, sometimes occurs which can be attributed to the excess of oleum used in the synthesis. To allow the preparation of compounds with higher boron contents and thus forcing the [BO_4] tetrahedra to condense we developed a synthesis method that avoids oleum as a reactant. Instead we choose chlorosulfonic acid, HSO_3Cl, as a source of sulfate ions which should form upon reaction with $B(OH)_3$. We present herein the first binary boron sulfate $B_2S_2O_9$ exhibiting a structure analogous to a typical layer-type silicate.

$B_2S_2O_9$ forms in the reaction of $B(OH)_3$ with HSO_3Cl in a sealed glass ampoule at 200 °C as colorless plate-shaped crystals (see Experimental Section). The structure consists of vertex-linked [BO_4] and [SO_4] tetrahedra (Figure 1). Each of the [BO_4] tetrahedra has three common vertices with [SO_4] tetrahedra and vice versa each sulfate group is connected to three [BO_4] moieties (Figure 2). In this way, layers of formula ${}^2_\infty[MO_{4/3}]$ (M = B, S) are formed which are further connected to double layers by vertex sharing of adjacent [BO_4] tetrahedra (Figure 3). In this way, each boron-centered tetrahedron is connected through all of its oxygen atoms while for each sulfate tetrahedron one oxygen atom remains uncoordinated.

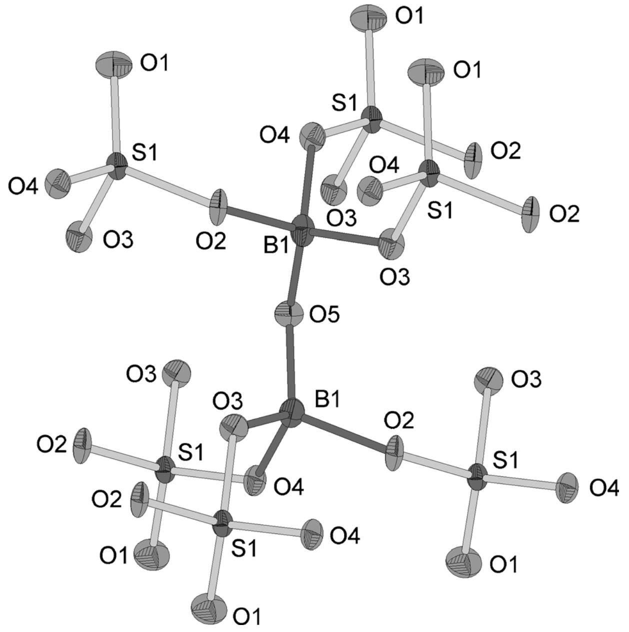

Figure 1. Structure and atom labeling for $B_2S_2O_9$. The Figure shows a section from the layered crystal structure (see Figure 2). The thermal ellipsoids are set at 90% probability. In the crystal structure there are two crystallographically different tetrahedra, [BO_4] and [SO_4], respectively. The [BO_4] moieties are linked by all their vertices, for the [SO_4] groups, one oxygen atom (O1) remains uncoordinated. Selected bond lengths [pm] and angles [°]: S1–O1: 140.36(8), S1–O2 150.67(7), S1–O3 151.67(8), S1–O4 150.37(8), B1–O2 151.7(1), B1–O3 150.0(2), B1–O4 150.0(2), B1–O5 137.9(1); S1-O2-B1 127.73(8), S1-O3-B1 127.62(6), S1-O4-B1 129.28(7), B1-O5-B1 128.8(1). A detailed list of all data can be found in the Supporting Information.

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Supporting information (including crystallographic data for $B_2S_2O_9$, further figures, the TG curve, and a Raman spectrum of the mother liquor) for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201307056.

The distances within the tetrahedra are almost independent of the atom at the center of the tetrahedron and show values around 150 pm. One exception is the bond length S1–O1 which is only 140.3 pm, in accordance with the terminal and uncoordinated situation of the O1 atom. This short distance is also reflected by high energy bands in the IR spectrum which are found between 1332 and 1436 cm^{-1}, that is, at positions which have been established by experiment and theory for S–O vibrations involving terminal oxygen atoms.[6b,d,e] Also, other stretching and deformation vibrations within the [SO_4] moieties could be assigned (cf. Supporting Information, Table S5). Furthermore, the typical vibrations of the [BO_4] tetrahedra are seen in the spectrum between 983 and 1039 cm^{-1}.[9] A special feature of the structure of $B_2S_2O_9$ is the occurrence of a B-O-B bridge which is symmetric, as confirmed by the equal distances B1–O5 of 137.9 pm. This value is at the lower side of typical ranges reported for borophosphates that contain such bridges.[5] As $B_2S_2O_9$ is the first sulfate containing a B-O-B bridge we do not know if such a short distance is typical for this type of compounds. For all of the oxygen-linked tetrahedra in $B_2S_2O_9$, the angles T-O-T (T = B, S) fall in a narrow range from 127.6 to 129.3°, independent of the nature of the atom at the center of the tetrahedron.

The condensation of the tetrahedral building units to layers occurs in a way that six-membered rings are formed (Figure 2, top). This kind of linkage is observed in a large number of different layered-structure silicates, the so-called phyllosilicates. The most prominent example is the mineral *muscovite*, that occurs in a number of varieties.[10] However, in typical silicates such as *muscovite*, the non-coordinating oxygen atom of each tetrahedron points in the same direction whereas in $B_2S_2O_9$ the apices of the sulfate and borate tetrahedra point in opposite directions (Figure 2, top). This arrangement leads to the non-planarity of the tetrahedral centers, which becomes especially clear if connection lines between the boron and the sulfur atoms are drawn (Figure 2). The resulting topology is a two-dimensional linkage of cyclohexane-type chairs to infinite layers, that is, a two-dimensional cut-out from the diamond-type of structure. This feature and the orientation of [BO_4] and [SO_4] tetrahedra with respect to each other also excludes a hexagonal (or trigonal) symmetry for the compound.[11] The layers are further connected by the free apices of the [BO_4] tetrahedra to form double layers (Figure 3). This type of double-layer formation is frequently found in the structural chemistry of silicates. However, owing to the different orientation of the [BO_4] and [SO_4] tetrahedra with respect to each other compared to layered silicates there is no directly related silicate analogue of $B_2S_2O_9$. The structure of the hexagonal modification of celsian, the so-called hexacelsian ($BaAl_2Si_2O_8$) comes quite close, but in hexacelsian all of the tetrahedra of the six-membered rings connect to the adjacent layers (for details see Supporting Information).[12] The double layers in $B_2S_2O_9$ are stacked essentially in the *c*-direction of the unit cell. They are remarkably off-set with respect to each other allowing for a closer packing density (Figure 3).

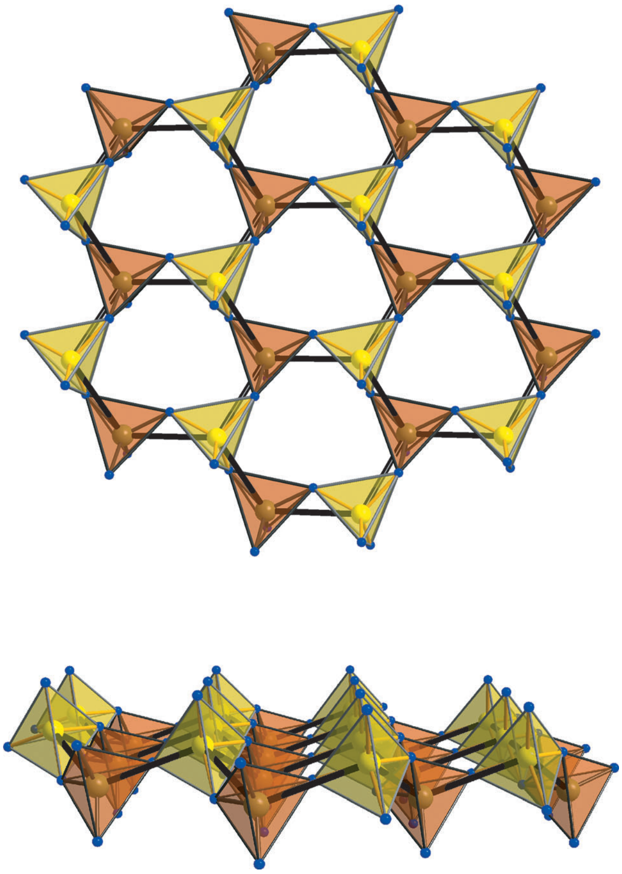

Figure 2. Connection of [SO_4] (yellow) and [BO_4] (orange) tetrahedra in $B_2S_2O_9$. The tetrahedra are linked to layers consisting of six-membered rings (top, viewed approximately along the *c*-direction). The non-coordinating oxygen atoms of the tetrahedra point alternatingly up and down. The centers of the tetrahedra (B and S) are arranged like cyclohexane rings with chair conformation, emphasized by black connection lines and especially clear in the bottom part of the Figure (viewed along the *b*-axis). The layers are further connected to double layers (see Figure 3). According to Liebau's systematics for silicates the following parameters can be given for $B_2S_2O_9$: linkedness, L = 1; connectedness, Q = $B^{4/4}$, $S^{4/3}$; branchedness, B = unbranched; dimensionality, D = 2; multiplicity, M = 2; Periodicity, P = 2.[1,12]

The close relationship of $B_2S_2O_9$ to typical layered silicates suggests some interesting options for further investigations. First intercalation chemistry should be fruitful. This kind of chemistry is well established for layered silicates, but there are new possibilities with respect to the presence of neutral layers in $B_2S_2O_9$. In this structure molecular complexes or even organic molecules should be able to enter the interlayer spacings. We have performed initial experiments trying to intercalate organic solvent molecules between the layers. It turned out that alcohols (CH_3OH, C_2H_5OH) react rapidly with $B_2S_2O_9$ causing its decomposition. Reactions of $B_2S_2O_9$ crystals with non-polar solvents (benzene, toluene) the crystals turn cloudy but do obviously not decompose. To date we could not confirm if intercalation had really occurred. Further investigations of these reactions are currently in progress. Moreover, the sophisticated synthesis procedure characterized by a defined hydrolysis of HSO_3Cl should allow for the preparation of other compositions with new silicate-related compositions, for example, the 1:1 composition of B_2O_3 and SO_3 ("B_2SO_6") which should form a three-dimen-

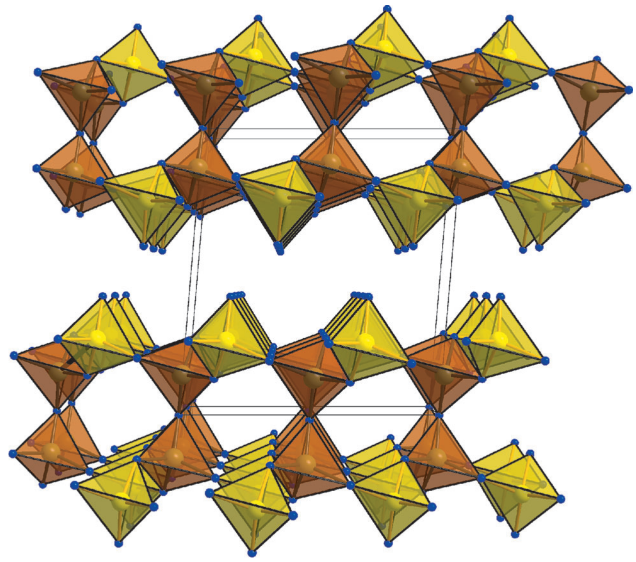

Figure 3. Stacking of the layers shown in Figure 2 along the crystallographic *c*-axis. Note that the layers are shifted with respect to each other to allow for a higher density. The shortest distances O–O between the layers are 289 and 291 pm.

sional structure adopting one of the SiO_2 modifications and have interesting new properties.

Experimental Section

Synthesis of $B_2S_2O_9$: $B(OH)_3$ (136 mg) and chlorosulfonic acid (1.5 mL) were filled in a glass tube ($d = 16$ mm, $l = 300$ mm). Mixing of $B(OH)_3$ and HSO_3Cl results in an immediate evolution of HCl gas, giving a colorless solution. The tube was then torch-sealed under vacuum, placed in a resistance furnace, and heated to 200 °C. The temperature was maintained for 24 h. Upon slow cooling (1.4 °C h^{-1}) a number of colorless and highly moisture sensitive single crystals were obtained. ***Caution!*** During the reaction and even after cooling to room temperature the glass tubes might be under pressure. The tubes have to be protected with an explosion shield during reaction and should be cooled with liquid nitrogen before they are opened. To determine the yield of the reaction, a glass ampoule was opened after reaction, the mother liquor was decanted, and adhering residual chlorosulfonic acid was removed in vacuum at 140 °C. According to the weight of the residual compound the reaction is quantitative.

Elemental analysis: For the elemental analysis a Euro EA-CHNS analyzer (HEKAtech) was used which allowed for the exact determination of the sulfur content. Sulfur content for $B_2S_2O_9$ (229.74 g mol^{-1}): calcd: 27.915 %; found: 27.594 %.

X-ray Crystallography: Several single crystals of $B_2S_2O_9$ were selected under protecting oil with the help of a polarization microscope and directly transferred into the cool nitrogen stream (120 K) of a single-crystal diffractometer (BRUKER APEX II). After unit-cell determination, the reflection intensities were collected. $B_2S_2O_9$: Colorless plates ($0.02 \times 0.11 \times 0.31$ mm), monoclinic, $C2$, $Z = 2$, $a = 776.00(8)$, $b = 416.64(4)$, $c = 861.34(9)$ pm, $\beta = 94.785(2)°$, $V = 0.27751(5)$ nm^3, Flack-X $= -0.04(6)$, $\rho = 2.749$ g cm^{-3}, $2\theta_{max} = 72.64°$, λ(Mo Kα) $= 71.073$ pm, 120 K, 6221 reflections, 1347 unique reflections ($R_{int} = 0.0327$, $R_{\sigma} = 0.0245$), numerical absorption correction ($\mu = 9.87$ cm^{-1}, min./max. transmission $= 0.7462/0.9825$, programs X-RED32 1.31 and X-Shape 1.06: Stoe, Darmstadt 2005 and 1999), structure solution by direct methods, full-matrix-least-square refinement (60 parameters) on $|F^2|$, (programs SHELXS-97 and SHELXL-97: G. M. Sheldrick, Programs for the solution and refinement of crystal structures, Göttingen 1997), $R_1 = 0.0173$, $wR_2 = 0.0449$ for 1312 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0181$, $wR_2 = 0.0451$ for all 1347 reflections, max./min. residual electron density $= 0.376/-0.409$ $e^- Å^{-3}$. 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-426544.

IR-spectroscopy: The sample was prepared in a glove box in a closed sample holder. Spectra were collected within a range of 6500 to 550 cm^{-1} with a Bruker Tensor 27 Spectrometer using the ATR-method (attenuated total reflection). The IR-data were processed with the OPUS 2.0.5 program.[14] Important IR energies: 1436 m, 1404 st, 1332 st, 1184 st, 1039 sh, 1018 m, 983 st, 833 st, 775 st, 657 m, 626 m, 603 sh, 549 m cm^{-1}(for assignment see Supporting Information, Table S5).

Raman spectroscopy: A Raman spectrum of the mother liquor after reaction was measured in a sealed glass tube was measured using a spectrometer RFS 100/S, (Bruker, Karlsruhe, Germany). Comparison with literature data shows the mother liquor to be in good agreement with that of chlorosulfonic acid. Important selected Raman intensities [cm^{-1}] (exp./lit.[15]): 1406/1408, 1196/1209, 1154/1150, 908/920, 621/625, 566, 512/513, 417/416, 314/312, 217/200. A Figure of the Raman measurement shown in Figure S3.

Thermal analyses: The investigation of the thermal behavior of $B_2S_2O_9$ was performed using a TGA/DSC apparatus (TGA/DSC1, Mettler-ToledoGmbH, Schwerzenbach, Switzerland). In a flow of dry nitrogen, 12 mg of $B_2S_2O_9$ were placed in a corundum crucible and heated at a rate of 10 K min^{-1} to 600 °C. The data were processed using the software of the analyzer (Mettler-Toledo STARe V9.2).[16] After a small amount of adhering HSO_3Cl was driven off, $B_2S_2O_9$ decomposes between 200 and 400 °C in at least three steps. The intermediates are not yet known, the final residue is (X-ray amorphous) B_2O_3 according the observed mass loss: 68.8 % (calcd: 69.7 %).

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[11] Note that the monoclinic angle which is relatively close to 90° ($\beta = 94.78°$) and the ratio a/b which is relatively close to $\sqrt{3}$ ($a/b = 1.86$; $\sqrt{3} = 1.73$) indeed reveals a relationship to a hexagonal metric. Accordingly a transformation using the appropriate matrix (0.5, −0.5, 0; 0, 1, 0; 0, 0, 1) leads to a pseudo-hexagonal cell with the parameters: $a = 440.4$, $b = 416.6$, $c = 861.3$ pm; $\alpha = 90$, $\beta = 94.22$, $\gamma = 118.23°$.

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