Triple-Vertex Linkage of (BO₄)-Tetrahedra in a Borosulfate: Synthesis, Crystal Structure, and Quantum-Chemical Investigation of Sr[B₃O(SO₄)₄(SO₄H)]

Leonard C. Pasqualini, Hubert Huppertz, Minyeong Je, Heechae Choi, and Jörn Bruns*

Abstract: Borosulfates are classified as silicate analogue materials. The number of crystallographically characterized compounds is still limited, whereas the structural diversity is already impressive. The anionic substructures of borosulfates exhibit vertex-connected (BO₄)- and (SO₄)-tetrahedra, whereas bridging between two (SO₄)- or even between two (BO₄)-tetrahedra is scarce. The herein presented compound Sr[B₂O-(SO₄)₂(SO₄H)] is the first borosulfate with a triple-vertex linkage of three (BO₄) tetrahedra via one common oxygen atom. DFT calculations complement the experimental studies. Bader charges (calculated for all atoms) as well as charge-density calculations give hint to the electron distribution within the anionic substructure and density-of-states calculations support the interpretation of the bonding situation.

Mainly, borosulfates are known as glasses.[1] However, elucidation of their crystal structures gained increasing interest for several applications like solid polyelectrolytes or NLO materials during the recent years.[2] Up to now, the number of structurally characterized borosulfates is low compared to silicates. Still, the structural diversity is already impressive. The anionic substructures of borosulfates are similar to silicates, exhibiting soro-, neso-, cyclo-, ino-, phyllo-, and tectosilicates like topologies of vertex connected (BO₄)- and (SO₄)-tetrahedra.[3] Even the formation of S-O-S[3b,c,e,4,5] and B-O-B[3i,6–9] bonds is not uncommon. This finding is in contrast to the structures of aluminosilicates, wherein Al-O-Al bonds are not to be expected according to Loewenstein’s rule.[10] However, also for borosulfates only vertex linkage of two (SO₄)- or (BO₄)-tetrahedra, resulting in the formation of (SO₄)₂⁻ and (B₂O₄)⁻subunits, is known.

Recently, Hörn and co-workers reported on Mg₉[H₂O→B(SO₄)₉]₂, exhibiting a Lewis-acid-base adduct of water to a [B(SO₄)₃]⁻ moiety.[11] The latter was obtained from a reaction of MgCO₃ and H₂BO₃ with sulfuric acid and low amounts of SO₃ at moderate temperature of 453 K. Accordingly, the reaction conditions play a crucial role for the constitution and topology of the anionic substructures. This has also been shown for the three different structurally characterized strontium borosulfates Sr[B₃(SO₄)₃][S₃O₄],[12] Sr[B₃(SO₄)₄],[13] and Sr[B₂O(SO₄)₃].[10] Especially the reaction temperature (T₃max) and time as well as the SO₃ content of the starting materials have a significant influence on the B:S ratio and the topology of the anionic network. Sr[B₂(SO₄)₃], exhibiting loop branched vierer single chains with S-O-B bridges exclusively, was synthesized from a 1:4 mixture of sulfuric acid and oleum (65 % SO₃) instead of a mixture with sulfuric acid. By reducing the time at T₃max from 24 h to 12 h for the same reaction Sr[B₂(SO₄)₃](SO₄H) reveals loop-branched vierer double chains and exhibits besides S-O-B also S-O-S bridges. The synthesis of Sr[B₂O(SO₄)₃] involves a pre-reaction of sulfuric acid with boric acid, followed by a long tempering period (96 h) at a high T₃max of 573 K of the mixture with oleum (65 % SO₃) and the strontium precursor. The anionic substructure of Sr[B₂O-(SO₄)₃] reveals a chain-like arrangement of the fundamental building block and B-O-B bridges. In our opinion, the increased temperature is the main reason for the formation of B-O-B bridges. By applying high temperatures, SO₃ can be released into the gaseous phase and is no longer available for the formation of S-O-B or even S-O-S bridges.

With the aim to synthesize a highly B-O-B enriched species and controlling the cation to boron ratio simultaneously, the title compound Sr[B₂O(SO₄)₃(SO₄H)] was synthesized at a high temperature of 523 K in a specially designed setup (Figure 1; for details see experimental section in the Supporting Information). Therefore, SrCO₃ and boric acid were ground together and filled into a glass vial, which was placed inside a glass ampoule filled with oleum (65 % SO₃) and a glass pin as spacer. By increasing the temperature, SO₃ is transferred to the gaseous phase and was allowed to react with the solid starting material. Due to this inventive setup, the amount of reacting SO₃ remains as low as possible. The product is a colorless crystalline solid (Figure S1) and is phase-pure according to powder X-ray diffraction (Figure S2).

The anionic substructure of Sr[B₂O(SO₄)₃(SO₄H)] is charge compensated by Sr⁺⁺ cations. The latter are coordi-
nated by nine oxygen atoms in form of a distorted single-capped square antiprism (Figures S3 and S4).

The borosulfate anions reveal an inosilicate like topology of \([\text{B}_2\text{O}(\text{SO}_4)_3(\text{HSO}_4)]\) aggregates bridged by two \((\text{SO}_4)\)-tetrahedra to form strongly corrugated chains (Figure 2) which run parallel to the crystallographic \(b\)-axis (Figure 3). Each aggregate exhibits one \((\text{SO}_4\text{H})\)-tetrahedron forming, according to Jeffrey’s classification,\(^{[13]}\) a medium strong hydrogen bridge with donor-acceptor distances of \(D-(\text{H})-A=2.539(2)\) \(\text{Å}\) to a bridging \((\text{SO}_4)\)-tetrahedron within the same chain. Three \((\text{SO}_4)\)-tetrahedra are vertex connected to the three central \((\text{BO}_3)\)-tetrahedra in a bidentate chelating manner, respectively. The terminal S–O bonds of the \([\text{B}_2\text{O}(\text{SO}_4)_3(\text{HSO}_4)]\) subunit and of the bridging \((\text{SO}_4)\)-tetrahedra reveal values of 1.42 \(\text{Å}\) in average. The average length of the terminal S–O bonds in the \((\text{HSO}_4)\)-tetrahedra is 1.43 \(\text{Å}\). Obviously, the single coordination of the \((\text{SO}_4)\) fragment has an influence on the S–O bond and causes an elongation for the S–O bond to 1.516(2) \(\text{Å}\). In the center of the \([\text{B}_2\text{O}(\text{SO}_4)_3(\text{HSO}_4)]\) aggregate resides one oxygen atom, which is the single vertex of three \((\text{BO}_3)\)-tetrahedra. The B–O bonds to the triple coordinated oxygen atom \(O111\) are elongated to values of 1.507(2), 1.508(2), and 1.524(2) \(\text{Å}\) compared to the B–O bonds of the B-O-S bridges with an average value of 1.46 \(\text{Å}\) (for a detailed list of bond lengths and angles see Tables S4 and S5). Compared to previous results on borosulfates,\(^{[3]}\) the reaction temperature of the herein presented synthesis is comparably high (523 \(\text{K}\)), which leads to a high B:S ratio of 3:5, making the formation of B-O-B bonds initially possible.

The fundamental building block (FBB), which describes the anionic substructure, shows a B:S ratio of 3:5 and can be written as 8\(\text{[FBB]}\) \(\times\) \(\text{[HSO}_4\text{]}\) \(\times\) \(\text{[OH]}\).\(^{[14]}\) These FBBs form the anionic chains with the Niggli formula \(\text{[}(\text{B}_3\text{O})/\text{SO}_4\text{]}_{1/2}(\text{SO}_4)_{1/2}(\text{HSO}_4)_{1/1}\) \(\times\) \(\text{[1]}\). A comparable \(\mu_1\) oxygen atom as vertex for three \((\text{BO}_3)\)-units is found in \(\text{Ag}_2(\text{NH}_4)_3[(\text{UO}_2)\text{B}_3\text{O}(\text{PO}_4)\text{H}_2)]\text{H}_2\text{O}\).\(^{[15]}\) The B–O bond lengths are similar to our findings and fall in the narrow range of 1.490(18) to 1.568(11) \(\text{Å}\). However, in this compound the charge compensation of the heteropolyanion is achieved by multiple, partially highly charged cations. For homopolyanions, a triple vertex connection around one oxygen atom is also uncommon but not unknown. Comparable arrangements are found in metal oxoborates \(\text{RE}(\text{BO}_3)\text{j}=(\text{RE}=(\text{Dy}-\text{Lu}))\)\(^{[16]}\), \(\text{Sr}[\text{BO}_{12}\text{OH}]\)\(^{[17]}\), the heptaborate anion \([\text{B}_7\text{O}_9(\text{OH})_5]\)\(^{[18]}\), and the nonaborate anion \([\text{B}_9\text{O}_{16}(\text{OH})_6]\)\(^{[19]}\).\(^{[20]}\)\(^{[21]}\) All mentioned examples, the B–O bond lengths fall in the same range (values around 1.5 \(\text{Å}\)). Even so, according to Pauling’s 4th rule\(^{[22]}\) the triple vertex connection remains unexpected. The latter assumption is also manifested by a recent study on around 5000 crystalline compounds, indicating that especially small main group elements fulfill Pauling’s 4th rule by \(\times\) 90\%.\(^{[23]}\)

Figure 1. Schematic drawing of the experimental setup. The torch sealed ampoule, in which the solid starting material is separated from the solvent by a glass tube, is placed inside a block shaped resistance furnace.

Figure 2. Left: Infinite anionic borosulfate chain in the structure of \(\text{Sr}[\text{B}_2\text{O}(\text{SO}_4)_3(\text{HSO}_4)]\). The chains run parallel to the crystallographic \(b\)-axis (Figure 3). Right: Cutout from the anionic chains in the structure of \(\text{Sr}[\text{B}_2\text{O}(\text{SO}_4)_3(\text{HSO}_4)]\) (FBB), emphasizing the central motif of three \((\text{BO}_3)\)-tetrahedra vertex-connected via one particular oxygen atom. B–O bond lengths \(\times\) \(\text{[A]}\): B1–O111 1.507(2), B2–O111 1.508(2), B3–O111 1.524(2).

Figure 3. Crystal structure of \(\text{Sr}[\text{B}_2\text{O}(\text{SO}_4)_3(\text{HSO}_4)]\). Infinite anionic chains run parallel to the crystallographic \(b\)-axis. The chains are separated by \(\text{Sr}^{2+}\) cations.

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1.18e, and the oxygen atoms bound to a sulfur atom and a boron atom (for example O12) have a Bader charge of 1.13e (Figure 5). The larger Bader charge of O111 (1.18e) than that of O12 (1.13e) can be explained with the small occupation of anti-bonding states below the Fermi energy, as shown in the calculated projected crystal orbital Hamiltonian population (-pCOHP) of Figure 6b. The slightly lower Bader charge on O12 is due to the more antibonding nature of the chemical bond leading to a higher degree of electron delocalization towards the S atom compared to the O–B bond in the case of the B-O unit containing the O111 atom.

The O12 atom has σ-bonds with boron and sulfur atoms as shown in the computed partial charge densities at the largest -pCOHP peaks (numbered 1 in Figure 6a). Furthermore, there is electron density located in p_s and p_σ-orbitals near the Fermi energy that contributes almost equally to bonding and antibonding (numbered 2 in Figure 6a). As can be seen from the calculated -pCOHP, the p_σ-orbital of O12 atom has major contribution to the antibonding among all the calculated electron orbitals (the largest peak is ~3.4 eV below the Fermi energy).

The partial charge densities of the atom O111 shows that it has σ-bonds with the surrounding boron atoms (numbered 1 in Figure 6b). Furthermore, this atom has significant amount of electron density near the Fermi level, as indicated by the localized p_σ-orbital (partial charge density in range 2 of Figure 6b), but nearly-zero bonding/antibonding state (see -pCOHP). Overall, the amount of antibonding is less pronounced for O111 than for O12.

The afore presented results shed new light on the structure family of borosulfates. Hitherto, borosulfates were often discussed in the context of silicates. Accordingly, the anionic substructure resembles a substitution variant like aluminosilicates. However, the formation of S–O–S and B–O–B bridges in some borosulfates is already contrary to the typical trends in silicate chemistry, like the Loewenstein rule.
triple vertex connection of three (BO$_3$) tetrahedra in the structure of Sr[B$_3$O(SO$_4$)$_4$(SO$_4$H)] outperforms this silicate untypically. Rather, the structure reflects a typical motif of borate chemistry. To the best of our knowledge, the formation of this unique compound is only possible via a smart synthesis strategy.

Since we have been able to describe the greatest similarity of a borosulfate to borates so far, the question now arises whether we can push it even further and possibly even realize such an arrangement under high-pressure conditions, we will also try to realize such an arrangement under high-pressure conditions, where the feasibility is much higher.

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Conflict of Interest

The authors declare no conflict of interest.

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