Borosulfates—Synthesis and Structural Chemistry of Silicate Analogue Compounds

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Abstract: Borosulfates are oxoanionic compounds consisting of condensed sulfur- and boron-centered tetrahedra. Hitherto, they were mostly achieved from solvothermal syntheses in SO$_4$-enriched sulfuric acid, or from reactions with the superacid H[B(HSO$_4$)$_4$]. The crystal structures are very similar to those of the corresponding class of silicates and their substitution variants, especially regarding the typical structural motif of corner-sharing tetrahedra. However, the borosulfates are supposed to be even more versatile, because (BO$_4$) units might also be part of the anionic network. The following article deals with detailed reports on the different synthesis strategies, the crystal chemistry of borosulfates in comparison to silicates, and their hitherto identified properties.

Introduction

The anionic substructure of silicates consists of (SiO$_4$)$_4$ tetrahedra, which have the ability to cross-link by sharing common corners. Their structural diversity is almost inexhaustible and has been a fascinating field of research for reams of scientists, originating not only from mineralogy and geology, but also from chemistry and physics. Friedrich Liebau, one of the pioneers in silicate chemistry, established a crystal chemical classification.\[1\] Accordingly, the consensus is to distinguish between nesosilicates, sorosilicates, cyclosilicates, insosilicates, phyllosilicates, and tectosilicates, depending on the extent of cross-linking and expansion of the anionic network. Silicates are widely used in a number of different technical applications, where their function is mostly related to their respective crystal structure and the dimensionality of the anionic substructure.\[2\]

Thus, it is not astonishing that originating from the general structure of silicates, a number of substitutional variants occurred. Especially for aluminosilicates, aluminophosphates, and borophosphates, where aluminum, phosphorous, and boron reside on the position of silicon in the center of the tetrahedra, the correlation between syntheses, structures, and properties are well explored. For example, aluminosilicates are by now indispensable for the glass industry.\[3\]

Referring to Pauling’s rules, networks of corner-sharing tetrahedra are stable, if the respective central atoms are able to compensate the occurring charges, either by themselves or by extended crosslinking of the anionic network. In comparison to neat silicates, the formation of aluminosilicates is accompanied by the restriction of a maximum amount of aluminum atoms of less than 50% in the tetrahedra network, which is described by the Loewenstein rule.\[4\] Meanwhile several exceptions of this rule are known, for example, bicholite.\[5\]

Compared to neat silicates, it is not astonishing that aluminumphosphates and borophosphates are already known and able to form even 3D networks, despite significantly smaller boron and larger aluminum cations occupying the silicon positions. In these structures, phosphorous is able to compensate the degraded electrostatic bond strength (electrostatic valence rule) caused by boron and aluminum. In terms of Pauling’s rules, it is remarkable that polysulfates do exist. As expected, they do not tend to undergo crosslinking due to the large charge of the central sulfur atoms, resulting only in anionic chains with a hitherto maximum of six sulfur atoms within one anion.\[6\]

To branch sulfur-containing networks into further dimensions, the high charge of the sulfur atoms within the (SO$_4$)$_4$ tetrahedra can be compensated by a low charged tetrahedral homologue. Thus, the combination of (SO$_4$) and (BO$_4$) tetrahedra is not only possible but has already been confirmed by several examples, resulting in the formation of the so-called borosulfates. Up to now, the number of known borosulfates is comparably limited (see Table 1), but a remarkably wide variation of topologically different motifs has already been observed. Thus, this review has to be considered as a comprehensive overview, dealing with the definition of borosulfates, synthetic strategies, the structural chemistry of borosulfates, also in comparison to silicates, and their hitherto identified properties illustrated for selected examples.

Synthesis

Generally, there are two different synthetic approaches to achieve borosulfates: solvent driven reactions with oleum or conc. sulfuric acid as solvent and reactant, as well as solid-state reac-
tions with suitable sulfate species like disulfates as source for the \( \text{SO}_3 \) fragment. The latter start with grinding together a stoichiometric amount of the alkali metal hydrogensulfates or disulfates, and boron sources like the boron oxide \( \text{B}_2\text{O}_3 \), metaboric acid \( \text{HBO}_2 \), or boric acid \( \text{H}_3\text{BO}_3 \). According to the general concept of Lux and Flood, reactions at elevated temperatures result in the formation of the alkali borosulfates, exemplarily depicted in the following for the synthesis of \( \text{K}_2[\text{B(SO}_4)_3] \) as phase-pure crystalline, colorless, and hygroscopic powder [Eq. 1] [27]

\[
3 \text{K}_2(\text{SO}_3) + \text{B}_2\text{O}_3 \rightarrow 2 \text{K}_2[\text{B(SO}_4)_3]
\]

(1)

Corresponding to the following reaction, borosulfates like \( \text{K}_2[\text{B(SO}_4)_3] \) can also be thermally decomposed to \( \text{K}_2[\text{B(SO}_4)_3] \) under release of \( \text{SO}_3 \) [Eq. 2] [28]

\[
5 \text{K}_2[\text{B(SO}_4)_3] \rightarrow 3 \text{K}_2[\text{B(SO}_4)_3] + \text{B}_2\text{O}_3 + 3 \text{SO}_3
\]

(2)

Most of the known borosulfates were synthesized from reactions of suitable boron species with conc. or \( \text{SO}_3 \)-enriched sulfuric acid (oleum) as solvent and reaction partner. Especially approved are three approaches, which generally can be classified as reactions according to the concept of Lux and Flood, or to the Lewis concept of acids and bases. In both cases, condensation reactions accompany the formation of the products.

1. One-pot synthesis in a vessel with a large excess of sulfuric acid (approx. 10 mL).

2. One-pot synthesis with oleum (1 mL) and \( \text{H}_2\text{BO}_3 \) in evacuated and torch sealed soda lime or silica glass ampoules (solvothermal).

3. Synthesis with the a priori prepared complex superacid \( \text{H}[\text{B(HSO}_4)_4] \) in sulfuric acid and torch sealed soda lime or silica glass ampoules (solvothermal). \( \text{H}[\text{B(HSO}_4)_4] \) can be obtained from the reaction of \( \text{H}_2\text{BO}_3 \) with a slight excess of conc. sulfuric acid [10,25].

Due to a frequently observed sensitivity towards moisture, all further characterizations of the solid-state products are strictly proceeded and prepared under inert conditions utiliz-

Hubert Huppertz studied chemistry at the University of Bayreuth, Germany. In 1997, he finished his doctorate with a fundamental work on the structural extension of nitridosilicates in the group of Prof. W. Schnick. Changing to the Ludwig-Maximilians University in Munich, he conducted his habilitation from 1998–2003 with a chemical focus on high-pressure/high-temperature syntheses. In 2008, he was appointed as full professor for General and Inorganic Chemistry at the University of Innsbruck, Austria. His main research interests are dedicated to the explorative synthetic discovery of new compounds in solid state chemistry, for example, in the syntheses of novel borates and luminescent materials. Since 2013, he also fills the position of a Dean of the Faculty of Chemistry and Pharmacy at the University of Innsbruck.

Michael Daub studied chemistry at the Albert-Ludwigs-Universität Freiburg, Germany and finished his diploma in 2010. He obtained his Ph.D. with a work on synthesis and crystal chemistry of borosulfates at the Albert-Ludwigs-Universität Freiburg under the supervision of Prof. Dr. Harald Hillebrecht in 2015. He stayed at the group of Harald Hillebrecht as a PostDoc working in the field of halide-based perovskites with regards to optoelectronic applications.

Harold Hillebrecht studied chemistry at the University of Freiburg, Germany. In 1991, he finished his doctorate with a work on metal-metal interactions in halogenometallates of transition metals in the group of Prof. Thiele. From 1991-1993 he was PostDoc in the Group of von Schnering at MPI-FKF, Stuttgart. Returning to Freiburg he finished his habilitation in 1997. In 1997, he was appointed as assistant professor for Inorganic Chemistry at the University of Bonn, followed in 1999 by an appointment as full professor at the University of Bayreuth. In 2002 he returned to the University of Freiburg as full professor. His main research interests are the synthesis and characterization of new compounds in combination with structure-property relations in solid-state chemistry. Substance classes of interest are high-temperature materials, intermetallics, borides, and perovskites.
| Compound       | Space Group |
|----------------|-------------|
| Na₂[B(SO₄)₂]   | P2₁/a       |
| Na₂[B(SO₄)₂]   | P2₁2₁2₁     |
| K₂[B(SO₄)₂]   | P2₁         |
| Li₂[B(SO₄)₂]   | P2₁/c       |
| K₂[B₂(SO₄)₂(OH)] | D₂/a     |
| Rb₂[B(SO₄)₂]  | P4₂2₂       |
| Cs₂K[B₂(SO₄)₂] | P4₂2       |
| Cs₂Na₂[B₂(SO₄)₂] | P2₁/c    |
| Cs₂Li₂[B₂(SO₄)₂] | P2₁/n     |

**Table 1. Literature known borosulfates, sorted by dimensionality of the anionic network.**

| Compound       | Space Group |
|----------------|-------------|
| Cu[B₂(SO₄)₂(HSO₄)] | P1         |
| Gd₂[B₂(SO₄)₆]  | C2/c       |
| Y₂[B₂(SO₄)₆]   | C2/c       |
| La₂[B₂(SO₄)₆]  | C2/c       |
| Ce₂[B₂(SO₄)₆]  | C2/c       |
| Pr₂[B₂(SO₄)₆]  | C2/c       |
| Nd₂[B₂(SO₄)₆]  | C2/c       |
| Sm₂[B₂(SO₄)₆]  | C2/c       |
| Eu₂[B₂(SO₄)₆]  | C2/c       |
| Tb₂[B₂(SO₄)₆]  | C2/c       |
| Dy₂[B₂(SO₄)₆]  | C2/c       |
| Ho₂[B₂(SO₄)₆]  | C2/c       |
| Er₂[B₂(SO₄)₆]  | C2/c       |
| Tm₂[B₂(SO₄)₆]  | C2/c       |
| Yb₂[B₂(SO₄)₆]  | C2/c       |
| Lu₂[B₂(SO₄)₆]  | C2/c       |

**Anionic Chains**

| Compound       | Space Group |
|----------------|-------------|
| H₂O[B₂(SO₄)₄]  | P4/ncc     |
| NH₄[B₂(SO₄)₄]  | P4/ncc     |
| Na[B₂(SO₄)₄]   | P2/c       |
| K[B₂(SO₄)₄]    | P4/ncc     |
| K[B₂(SO₄)₄]    | Ibaa       |
| Rb[B₂(SO₄)₄]   | Ibaa       |
| Ag[B₂(SO₄)₄]   | P4/ncc     |
| Cu[B₂(SO₄)₄]   | P1         |
| Pb[B₂(SO₄)₄]   | Pnna       |

**2D Borosulfates**

| Compound       | Space Group |
|----------------|-------------|
| Ca₂[B₂SO₄]    | P2₁/c       |
| Mg₂[B₂SO₄]    | C2/c       |

**3D Borosulfates**

| Compound       | Space Group |
|----------------|-------------|
| Li₂[B₂SO₄]    | Pc         |

**"Unconventional" Borosulfates**

| Compound       | Space Group |
|----------------|-------------|
| B₃O₁₀       | C2         |
| Rb₂B₃O₁₀    | Pnna       |
| Cs₂B₃O₁₀    | P2/c       |
| Sr₂[B₂O₅(SO₄)] | Pnna    |
| Ba₂[B₂O₅(SO₄)] | Pnma   |
| Pb₂[O₅(B₂O₅)] | P2/m      |
| α-Mg₂[B₂O₅(SO₄)] | P3     |
| β-Mg₂[B₂O₅(SO₄)] | P3      |
| Mn₂[B₂O₅(SO₄)] | P3        |
| Co₂[B₂O₅(SO₄)] | P3        |
| Ni₂[B₂O₅(SO₄)] | P3        |
| Zn₂[B₂O₅(SO₄)] | P3        |

**5-O-S Bridges**

| Compound       | Space Group |
|----------------|-------------|
| Li[B₂O₅]    | P2₁2₁2₁     |
| Na[B₂O₅]    | P2₁/c       |

**Review**

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ing Schlenk technique or a glovebox. To avoid undesirable side reactions, the glovebox or reaction containers need to be equipped adequately, meaning for example, that the specimen should be treated exclusively with a glass spatula or that the Schlenk flasks are sealed with PTFE greased taps.

In the context of a mechanistic view, the described syntheses of conventional borosulfates can be understood as a formal condensation reaction between the corresponding „B-O-H“ and „H-O-S“ functionalities of the starting materials. Furthermore, „S–O–“ and „B–O–“ can also formally be inserted in existing „B-O-B“ and „S-O-S“ moieties, respectively. This is a striking difference in comparison with the reaction mechanisms during the formation of silicates, where in most cases and without any differentiation a formal insertion of „M–O“ into the „Si–O“ entities occurs. With the exception of the area of hydrothermal syntheses, the condensation reaction plays an underpart role in the syntheses of silicates.

Definition

Borosulfates are inorganic metal or non-metal salts with an oxoanionic substructure consisting of corner-sharing boron and sulfur-centered polyhedra (Figure 1). The most basic borosulfate anion consists of only one central boron atom coordinated by four (SO₃) units, forming the [B(SO₃)₄]²⁻ anion, which can be regarded as a molecular anion (0D). Additional vertex-sharing of the different tetrahedra results in the formation of cyclic [B₄(SO₃)₁₂]⁶⁺ anions (1D), one-dimensional infinite chains according to [B(SO₃)₃]⁻ (1D), anionic layers (2D), and 3D network structures. The dimensionality of unbranched borosulfates can be even better understood considering the connectivities of the underlying supertetrahedra [B(SO₃)₄] basic building units as TX₄ (T= B, X= SO₃). According to Liebau, the TX ratio determines the dimensionality of an anion; 1:4 yields 0D, 1:3 1D, 1:2 3D frameworks and between 1:3 and 1:2 more or less 2D band and layer structures are summarized.

In course of this review, we call compounds, which comply with the afore introduced definition and reveal exclusively B-O-S bridges, classical borosulfates. Unconventional borosulfates are compounds with a non-continuous alternating network of (BO₄) and (SO₄) units, like samples with B-O-B and S-O-S bridges as well as compounds with electronically uncharged B-O-S subunits. Clearly, heteroleptic compounds with borate and sulfate anions without covalent inter-anion connection are not counted to the class of borosulfates. Moreover, we like to point out that borosulfates reveal no discrete sulfate and borate anions, but (SO₄) and (BO₄) subunits, building up the more or less extended anionic network (0D–3D).

The designation borosulfates is a trivial name for the class of compounds, which is in scope of this review. Whether the term borosulfate is correct or the respective salts should better be denoted as sulfatoborates or boron-sulfur oxides depends on the Lewis acidic nature of the central sulfur and boron atoms as well as the charge of the oxido network and has to be elucidated independently for each single representative. However, they are always intermediate compounds of the system MₓOᵧ–BₓOᵧ–SOₓ (H₂O) (M= main-group/transition metal, ammonium, oxonium). A correct nomenclature of the oxoanionic substructures, adding the sequences of bridging ligands and potential acidic hydrogen atoms connected to the anionic network, would rapidly become very complicated. According to the IUPAC rules of nomenclature, other notations than borosulfates would be formally correct, but would in most cases not contribute to a better understanding. As also preferred for other heteropolyanions like borophosphates, where also (BO₄) units have been found in several structures,
trivial names are also used and meanwhile accepted by the IUPAC. Thus, we use the term borosulfates for all afore and further mentioned representatives. Liebau presented a comprehensive description and classification of silicate structures.[25] Kniep adopted and expanded these rules for the class of borophosphates.[26] Due to the close structural relationship of the borosulfates to borophosphates and silicates, the rules are also adopted for the description and classification of borosulfates.

**Discrete Molecular Anionic Borosulfates (0D)**

As mentioned before, borosulfates are classified by the dimensionality of the anionic substructure. The most basic anionic subunit found is the $[\text{BSO}_4]^{3-}$ anion (Figure 1, left), which is described as molecular anion (0D). This anion occurs for example in the first ever presented borosulfate $\text{K}_2[\text{BSO}_4]$. The finding of boron atoms in the center of exclusively four $(\text{SO}_4)$ units is unique. In the structure of $\text{K}_2[\text{BSO}_4]$, the boron atoms adopt a slightly distorted body-centered packing with the apices of the $(\text{BO}_4)$ units almost perfectly arranged parallel to the crystallographic c-axis, resulting in a polar structure.

The closest related species can be found in the mineral Zunyite, which formally reveals an open-branched silicate anion $[\text{Si(SiO}_4)]^{12-}$, adopting $T_d$ symmetry and being connected to $\text{AlO}_6$ octahedra. As expected, the terminal $\text{Si}-\text{O}$ bonds in $\text{K}_2[\text{BSO}_4]$ are significantly shorter (139.4(6)–145.4(5) pm) than the bridging $\text{Si}-\text{O}$ bonds (154.7(4)–157.1(4) pm). According to the method suggested by Balic-Žunić and Makovicky, the $\text{BO}_4$ and $\text{SO}_4$ tetrahedra can be classified as regular (deviations of the tetrahedra from the ideal symmetry $-\text{BO}_4$: 0.43 % and $\text{SO}_4$: 0.08–0.23 %) compared to an ideal tetrahedron.[27] The $[\text{BSO}_4]^{3-}$ anion has also been found for the following seven homologues $\text{Li}_2[\text{BSO}_4]$, $\text{Na}_2[\text{BSO}_4]$, $\text{K}_2[\text{BSO}_4]$ and $\text{Rb}_2[\text{BSO}_4]$[11] as well as for the mixed alkali borosulfates $\text{CsLi}[\text{BSO}_4]$ and $\text{CsNa}[\text{BSO}_4]$. In detail, the anionic substructures are similar but not identical.

To understand structure property relationships, geometry optimization of the $[\text{BSO}_4]^{3-}$ anion from an infinite anionic chain found for $\text{Cu}[\text{BSO}_4]$ can be regarded as a cut-out by protonation from an infinite anionic chain found for $\text{Cu}[\text{BSO}_4]$ and can be obtained coexistent from a solution of a CuO, boric acid, and SO$_4$-enriched sulfuric acid. Hirshfeld analysis of $\text{Cu}[\text{BSO}_4]$ revealed positively charged Cu ions, whereas sulfur, boron, and hydrogen atoms were also positively charged. All oxygen atoms are negatively charged. According to a Hirshfeld spin density analysis, the spin density is almost exclusively located on Cu, corroborating the d$^9$ configuration of copper and a paramagnetic behavior. Obviously, the protonation of the $[\text{BSO}_4]^{3-}$ anion causes no drastic changes in the crystal structure and stability of the crystalline compound. To understand structure property relationships, geometry optimizations for different protonated and non-protonated conformations of the $[\text{BSO}_4]^{3-}$ anion were performed (Figure 4).

The structures of Gd$_2[\text{BS}_6\text{O}_{14}]^{10-}$ and Cu$[\text{BSO}_4]$($\text{H}_2\text{SO}_4$)$^{18-}$ are closely related to each other, exhibiting two central boron atoms bridged by two $(\text{SO}_4)$ units and terminated by four $(\text{SO}_4)$ tetrahedra in the case of Gd$_2[\text{BS}_6\text{O}_{14}]$, and by two $(\text{SO}_4)$ as well as two $(\text{H}_2\text{SO}_4)$ tetrahedra in the case of Cu$[\text{BSO}_4]$($\text{H}_2\text{SO}_4$) (Figure 3). Both anionic substructures are classified as cyclic anions (1D).

The superacid $\text{H}[\text{BS}_6\text{O}_{14}(\text{OH})]$ was synthesized a priori and additionally reacted in an appropriate stoichiometry with the alkali metal chloride, particularly in a closed system to inhibit the deprotonation of $\text{H}[\text{BS}_6\text{O}_{14}]$. The central structural motif of $\text{K}_2[\text{BS}_6\text{O}_{14}(\text{OH})]$ is the unprecedented non-condensed molecular...
Infinite Anionic Borosulfate Chains (1D)

Borosulfates in form of infinite anionic chains are known with mono- and divalent counter cations, main group and transition metals as well as hydronium and ammonium cations. Even coinage and precious metals can function for charge compensation. Taking all literature known borosulfates into account, chains are the most prominent anionic substructure. To date, only two basically different modifications are known, the open and loop-branched chains (Figure 5). Open-branched chains are only scarcely realized. One example is $K_3[B(SO_4)_3]$, exhibiting $(BO_4)$ tetrahedra coordinated by four $(SO_4)$ tetrahedra, two bridging ones, and two in monodentate terminal fashion.$^{[7]}$

The loop-branched chains are more dominant and always very similar to each other. They do mostly differ in terms of their torsion angles between the tetrahedra. In this context, the four compounds with the general formula $A[B(SO_4)_2]$ ($A=K, NH_4, H_3O$, and Ag) are special.$^{[9, 17]}$ All of them crystallize in the centrosymmetric space group $P4/ncc$. Ag$[B(SO_4)_2]$ and $K[B(SO_4)_2]$ are isotypic, whereas $(H_3O)[B(SO_4)_2]'^{[18]}$ and $(NH_4)[B(SO_4)_2]'^{[17]}$ and are isotypic, whereas $(H_3O)[B(SO_4)_2]'^{[18]}$ and $(NH_4)[B(SO_4)_2]'^{[17]}$ are homeotypic to the silver and potassium borosulfates. These anionic chains consist of central boron atoms, which are coordinated by four $(SO_4)$ tetrahedra and can be regarded exemplarily for infinite anionic borosulfate chains.

Each $(SO_4)$ unit bridges two boron atoms, resulting in an infinite anionic chain according to the Niggli formula $\frac{1}{n}\{B(SO_4)_2\}^-$. In terms of the close relationship between borosulfates and silicates, criteria for building and bonding of the anionic substructures are comparable. Thus, utilization of Loe-

**Figure 3.** Protonated and non-protonated borosulfate anions in Gd$_2[B_2S_3O_6]$ (left) and Cu$[B(SO_4)_2]_2$ (right).

**Figure 4.** Calculated free energy differences $\Delta G$ of the complex anion $[B_2(SO_4)_3(SO_4H)]^{4+}$ between the hypothetical chair conformation (left) and the experimentally found twist conformation (right) as well as $pK_a$ values for the deprotonation to $[B_2(SO_4)_3HSO_4]^{3+}$ and to $[B_2(SO_4)_3]^{5+}$. Color code: blue—oxygen, yellow—sulfur, red—boron, and white—hydrogen.$^{[15]}$

**Figure 5.** Cutout from the open-branched chain $\frac{1}{n}\{B(SO_4)_2\}^-$ and the infinite loop-branched chain $\frac{1}{n}\{B(SO_4)_2(SO_4H)\}^-$. 

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Borosulfates with Layer-like Topology (2D)

The number of classic borosulfates with layer-like topology is very limited. To the best of our knowledge, only Mg[B(SO$_4$)$_2$]$_2$[7] and CaB$_2$S$_4$O$_6$[29] are the exclusive examples (besides B$_2$S$_3$O$_4$ with uncharged layers[22]—see Unconventional borosulfates with B-O-B bridges below), which have been reported in literature, so far. They were obtained from solvothermal reactions in oleum. Starting materials for CaB$_2$S$_4$O$_6$ were CaCO$_3$ and boric acid, whereas Mg[B$_2$(SO$_4$)$_4$] represents the first compound synthesized from a boride, namely MgB$_2$. Both compounds crystallize with a new structure type and reveal open-branched single layers of corner-sharing (BO$_4$) and (SO$_4$) tetrahedra: Each of the four oxygen atoms of the (BO$_4$) tetrahedra coordinates to an adjacent sulfur atom and each sulfur atom shares two of four coordinating oxygen atoms with (BO$_4$) tetrahedra, whereas two oxygen atoms remain terminal, resulting in the formation of 2D infinite layers, which are always terminated by (SO$_4$) units. No B-O-B and S-O-S bridges are found, thus Loewenstein’s rule is obeyed. According to Liebau’s formalism, both compounds are analogous to phyllosilicates. The anionic borosulfate substructures are closely related, revealing directly adjacent twelve-membered (zwölfer) and four-membered (vierer) rings, however with a different arrangement of the rings to each other. Generally, both are built up by six alternating, corner-sharing (SO$_4$) and (BO$_4$) tetrahedra forming a zwölfer ring, and six further zwölfer rings are in direct coordination. Furthermore, four vierer rings branch-off the central zwölfer ring, realized for two via a bridging (BO$_4$) tetrahedron and for two via a free (BO$_4$)(SO$_4$)($BO_6$) edge. In the case of CaB$_2$S$_4$O$_6$ the zwölfer rings are centrally capped by a charge compensating Ca$^{2+}$ cation. The Ca$^{2+}$ cations are eightfold coordinated by oxygen atoms (terminal oxygen atoms of the (SO$_4$) units), forming a distorted square antiprism. The Mg$^{2+}$ cations in Mg[B(SO$_4$)$_2$] are octahedrally coordinated by six oxygen atoms, belonging to terminal (SO$_4$) units.

Zwölfer rings are not unknown, however, they are uncommon for the structural chemistry of silicates. Originating from silicate chemistry, Traskite[18] and Megacyclite[30] are examples for structures with zwölfer rings of exclusively corner-sharing (SiO$_4$) tetrahedra. However, both are better assigned to the category of cyclosilicates, revealing only unbranched rings with several charge-compensating cations nearby. Phyllosilicates with zwölfer rings are rather scarce. The anionic substructures of [K$_2$F$_2$][Ln$_5$Si$_9$O$_{24}$] (Ln = Sm, Eu, Gd) are some of the rare examples.[31] However, the combination of directly adjacent rings of zwölfer and vierer rings remains elusive for silicates.

In comparison to the silver borosulfate Ag[B(SO$_4$)$_2$], with infinite anionic chains and the astonishing result that the boron atom carries the most positive Lewis acidic character, also the layer like borosulfate CaB$_2$S$_4$O$_6$ has been investigated by means of quantum chemical analysis of the solid-state structure performed on DFT level. After full geometry optimization, the electrostatic potentials revealed to be as expected, the calcium cations, sulfur, and boron atoms are positive, whereas all (terminal and bridging) oxygen atoms are negatively charged. Mulliken partial charges of the sulfur atoms were found to be slightly more positive than for boron. These results suggest that in contrast to the silver borosulfate Ag[B(SO$_4$)$_2$] boron cannot be considered as the single Lewis center of the extended heteropolyanionic network. Thus, the non-complex notation of the sum formula, CaB$_2$S$_4$O$_6$, is favorable, indicating once more the close structural and electronic relationship of borosulfates to silicates, namely in this case a phyllosilicate.

Borosulfates with Maximum Off-branching (3D)

Hitherto, the number of borosulfates with a 3D network of corner sharing tetrahedra is extremely limited. So far, the only example is Li[B(SO$_4$)$_2$].[7] This unique compound was obtained by the thermal decomposition of Li[B(SO$_4$)$_2$] (see Unconventional Borosulfates below) according to [Eq. 3]:

$$\text{Li}[\text{B}(\text{S}_2\text{O}_7)_2] \rightarrow \text{Li}[\text{B}(\text{SO}_4)_2] + 2\text{SO}_3$$

(3)

The sum formula of the obtained lithium species is identical to the borosulfates $A[B(SO_4)_2]$ ($A$ = Na, K, NH$_4$, H$_2$O, Ag). However, the structure of the anionic subunit is different (Figure 6). Due to the identity of the (SO$_4$) units around the central boron atoms, the (BO$_4$) tetrahedra are highly symmetric. The S–O–
bond lengths within the \( \text{SO}_4 \) tetrahedra differ: \( \text{S} - \text{O} \) bonds with oxygen being the bridging atom are about 10 pm longer than the terminal \( \text{S} - \text{O} \) bonds with the oxygen atom being in coordination to the charge compensating lithium cations. Also, the lithium cations are tetrahedrally coordinated by oxygen atoms, which leads to an interesting similarity of \( \text{Li}[^{\text{B(SO}_4}_4]_2^- \) to the orthorhombic high temperature modification of \( \text{SiO}_4 \), namely [tridymite]. \( \text{Li}[^{\text{B(SO}_4}_4]_2^- \) represents an ordered variant with a fourfold enlarged unit cell. Obviously, the stability of the compound is due to the ideal volume ratio and thus electrostatic interaction of the anionic substructure with the charge compensating lithium cations.

Hitherto unknown are the reasons for the different dimensionalities of the anionic borosulfate substructures. Somewhat far-fetched, however in good agreement with Loewenstein’s rule, is the fact that the dimensionality of the anionic substructure increases by decreasing the content of the high-charged centers of the tetrahedra, as can be exemplarily seen by the loss of \( \text{SO}_3 \) during the thermal decomposition of \( \text{Li}[^{\text{B(SO}_4}_4]_2^- \) and formation of \( \text{Li}[\text{B(SO}_3]_2^- \). Or the other way around: The anionic substructure branches-off, when a low-charged center inside of the tetrahedra will be inserted, as can easily be seen from the comparison of the crystal structures of polysulfates and borosulfates (0D–3D).

Furthermore, the anionic part within all classical borosulfates can formally be regarded as \( TX_4 \) super-tetrahedral units, like \( \text{[B(SO}_4]_4}^- \). Within this view, the structural diversity arises through sharing common corners and/or edges of these \( TX_4 \) supertetrahedra (Figure 7). For the anion \( \text{[B(SO}_4]_4}^{3-} \), we found in analogy to \( \text{[SiO}_4]^{4-} \) isolated \( TX_4 \) supertetrahedra. In similarity to \( \text{[SiO}_4]^{5-} \), for \( \text{[B(SO}_4]_4}^{3-} \), 1D chains of corner-sharing \( \text{BS}_4 \text{S}_4^2^- \) tetrahedra are observed. The anion \( \text{[BS}_4\text{O}_6]^{8-} \) exhibits formally the same composition as \( \text{[B(SO}_4]_4}^{5-} \), but now two \( \text{BS}_4^2^- \) tetrahedra are sharing a common edge forming a 0D oligomeric structure. For the anion \( \text{[B(SO}_3]_4}^- \), there are different cases: In \( \text{Li}[^{\text{B(SO}_4}_4]_2^- \), the \( \text{BS}_4 \text{S}_2^- \) tetrahedra are forming in analogy to \( \text{SiO}_4 \) a 3D network through sharing common corners. For \( \text{A}[^{\text{B(SO}_3}_4]_4}^- \) (A = Na, K, NH\textsubscript{4}, H\textsubscript{2}O, and Ag), the super \( TX_4 \text{S}_2^- \) tetrahedra are connected via common edges resulting in 1D chains (as also found as \( \text{SiS}_4 \text{S}_2^- \) tetrahedra in \( \text{SiS}_3 \)). The anion \( \text{[B(SO}_3]_6}^{3-} \) is a third anion that formally exhibits the same composition but now both previous connectivity modes (corner-/edge-sharing) are realized, ending in a 2D anion.

**Unconventional Borosulfates**

According to our previously introduced definition, borosulfates reveal anionic networks of arbitrary dimensionality, built up by corner-sharing (\( \text{SO}_4 \)) and (BO\textsubscript{4}) tetrahedra. Compounds with no perfect alternation of (\( \text{SO}_4 \)) and (BO\textsubscript{4}) tetrahedra are classified as unconventional borosulfates. They bear for example B-O-B or S-O-S bridges. In contrast, unchanged networks of (\( \text{SO}_4 \)) and (BO\textsubscript{4}) tetrahedra meet none of the aforementioned requirements. However, in course of this review we also like to consider these compounds, because they are the closest relatives and might help to understand the relationship between the synthesis parameters, the constitution, and thus the dimensionality of the crystal structures.

**Unconventional borosulfates with S-O-S bridges**

The number of borosulfates with S-O-S bridges is even more limited compared to those exhibiting B-O-B bridges. Hitherto,
only six representatives were published. Charge compensation of the anionic sub-structure is always achieved by monovalent cations and the dimensionality of the borosulfate anions is hitherto limited to 0D and 1D. For all compounds, the S-O-S bridges occur in (S\(_2\)O\(_7\))\(_2^−\) fragments formed by two (SO\(_4\)) tetrahedra, which are coordinated by one vertex oxygen atom. In each case, the (S\(_2\)O\(_7\)) subunits are in chelating coordination to the central boron atoms. The non-boron coordinating oxygen atoms remain terminal. Unconventional borosulfates with S-O-S bridges may play an important role for the formation of the polyhedral networks. For example, Li[B(S\(_2\)O\(_7\))] as a 3D representative of the conventional borosulfate is obtained by release of the leaving group SO\(_4\) from the unconventional 0D borosulfate Li[B(S\(_2\)O\(_7\))]\(_2^−\) (see below).

The molecular anion [B(S\(_2\)O\(_7\))]\(^{−}\) is found in the crystal structures of A[B(S\(_2\)O\(_7\))]\(_2^−\) (A = Li, Na, K, NH\(_4\))\(^{[7,9,17]}\). The anion is comparable to the borosulfate anion [B(S\(_2\)O\(_7\))]\(^{3−}\) in K[B(S\(_2\)O\(_7\))]. Both anions exhibit boron as a Lewis acid center of an isolated complex anion. Up to now, comparable arrangements were only obtained with metals and semi-metals on the boron site, for example, [Au(S\(_2\)O\(_7\))]\(^{2−}\) and [Si(S\(_2\)O\(_7\))]\(^{2−}\)\(^{[20]}\). In both cases, sulfates species act as ligands. In the case of K[B(S\(_2\)O\(_7\))], four monodentate anions coordinate to the central boron atom and for A[B(S\(_2\)O\(_7\))]\(_2^−\) (A = Li, Na, K, NH\(_4\)) two bidentate chelating disulfate anions are found (Figure 8). According to the crystal structure and the isolated complex anions, the charge distribution and thus a correct description as sulfato- or disulfatoborates is doubtless.

As also found for „free“ and metal-coordinated disulfates, the bond lengths differ in the (S\(_2\)O\(_7\)) subunits of A[B(S\(_2\)O\(_7\))]\(_2^−\) (A = Li, Na, K, NH\(_4\)). The shortest bond lengths with approx. 140 pm are the terminal S−O bonds. The coordinating S−O(B) bonds are slightly elongated to approximately 150 pm and the bridging S−O(S) bonds reveal values of about 160 pm. The (BO\(_4\)) tetrahedra are almost symmetric and reveal B−O bond lengths of approx. 140 pm. In the case of (NH\(_4\))[B(S\(_2\)O\(_7\))]\(_2^−\), two crystallographically different [B(S\(_2\)O\(_7\))]\(^{−}\) anions exhibit different conformation. One anion shows a boat conformation of the two six-membered dreier rings, whereas the other one exhibits a chair conformation. A comparable behavior has also been observed and investigated by means of quantum chemical calculations for the infinite anionic chains in Cu[B(S\(_2\)O\(_7\))]\(_2^−\).

Cs[B(S\(_2\)O\(_7\))(S\(_2\)O\(_4\))]\(^{[17]}\) and H[B(S\(_2\)O\(_7\))(S\(_2\)O\(_4\))]\(^{[17]}\) were the first borosulfates with Cs\(^+\) and H\(^+\) as counter cations and furthermore the first examples in which (SO\(_4\)) and (S\(_2\)O\(_7\)) occur in the same moiety. Compared to the structures of K[B(S\(_2\)O\(_7\))] and Rb[B(S\(_2\)O\(_7\))], the two terminal (SO\(_4\)) units are substituted by (S\(_2\)O\(_7\)) fragments. According to Liebau’s formalism for silicates, the resulting structures can be described as cyclo-branched vierer single chain, which run parallel to the crystallographic c-axis. According to the substitution, the charge of the extended heteropolyanion is reduced to −1. In contrast to Cs[B(S\(_2\)O\(_7\))(S\(_2\)O\(_4\))], hydrogen bridges interconnect the anionic chains in H[B(S\(_2\)O\(_7\))(S\(_2\)O\(_4\))] to layers perpendicular to the crystallographic b-axis (Figure 9). Two different hydrogen bridges
occur, which point towards the terminal atoms of \((\text{S}_2\text{O}_7\text{)}\) moieties. One hydrogen bridge can be classified as strong, the other as medium strong.\(^{[14]}\)

Besides the expected elongation of the \(\text{S}–\text{O}\) bonds participating in the hydrogen bridging, the more pronounced elongation of the bridging \(\text{S}–\text{O}\) bond in the \((\text{S}_2\text{O}_7\text{)}\) double tetrahedra (160.6 and 164.5 pm) compared to the non-protonated species in \(\text{Cs}[\text{B}(\text{SO}_4)\text{(S}_2\text{O}_7\text{)}]\) is remarkable. The hydrogen bonding system is very similar to that found for \(\text{H}_2\text{SO}_4\)\(^{[35]}\) and \(\text{H}_2\text{S}_2\text{O}_7\)\(^{[36]}\). According to this finding and the absence of any further charge compensating counter cation, \(\text{H}[\text{B}(\text{SO}_4)\text{(S}_2\text{O}_7\text{)}]\) can be classified as a one-dimensional heteropolysulfuric acid.

**Unconventional borosulfates with B-O-B bridges**

\(\text{B}_2\text{S}_3\text{O}_7\) was the second ever published and crystallographically characterized compound with corner sharing \((\text{S}_2\text{O}_7\text{)}\) and \((\text{BO}_3\text{)}\) tetrahedra.\(^{[22]}\) Due to the lack of a charged anionic substructure, \(\text{B}_2\text{S}_3\text{O}_7\) is no borosulfate, however obviously features the same structural fragments. This non-metal oxide was obtained from the reaction of boric acid with chlorosulfuric acid. The synthesis is accompanied by the release of \(\text{HCl}\), which is the reason for the formation of the first crystal structure with a network of \((\text{SO}_4\text{)}\) and \((\text{BO}_3\text{)}\) including B-O-B bridges, dubbed in the formulation \([\text{B}_2\text{O}(\text{SO}_4\text{)}]_\text{3}\). In \(\text{B}_2\text{S}_3\text{O}_7\), each boron atom is coordinated by three \((\text{SO}_4\text{)}\) tetrahedra and each \((\text{SO}_4\text{)}\) tetrahedron is bridged by, respectively one common oxygen atom to three \((\text{BO}_3\text{)}\) tetrahedra. Furthermore, all \((\text{BO}_3\text{)}\) tetrahedra are vertex-linked by the remaining oxygen atoms of the \((\text{BO}_3\text{)}\) tetrahedra, whereas one oxygen atom of each \((\text{SO}_4\text{)}\) tetrahedron remains uncoordinated, resulting in the formation of \((\text{B}_2\text{O}_3\text{)}\) centered double layers (Figure 10).

In contrast to the previously presented layered borosulfates, wherein zwölf er and vierer rings are the predominant motifs, \(\text{B}_2\text{S}_3\text{O}_7\) reveals sechser rings of alternating \((\text{SO}_4\text{)}\) and \((\text{BO}_3\text{)}\) tetrahedra within one single layer. Six-membered rings are a very common structural motif for a large number of phyllosilicates. In contrast to the most prominent examples from silicate chemistry, in \(\text{B}_2\text{S}_3\text{O}_7\), the apices of the \((\text{SO}_4\text{)}\) and \((\text{BO}_3\text{)}\) tetrahedra point into different directions.

Another borosulfate with layer-like topology of the anionic substructure is \(\text{Cs}_3\text{B}_2\text{S}_3\text{O}_{14}\), which was synthesized from the reaction of \(\text{B}_2\text{O}_3\), \(\text{CsCl}\), and oleum (65 % \(\text{SO}_3\)) in an open silica crucible at 300 °C.\(^{[23]}\) \(\text{Cs}_3\text{H}_2\text{B}_2\text{S}_3\text{O}_{14}\) is a side-product of this reaction. The layers of \(\text{Cs}_3\text{B}_2\text{S}_3\text{O}_{14}\) are composed of four \((\text{BO}_3\text{)}\) units, which are bridged by four \((\text{SO}_4\text{)}\) tetrahedra. Furthermore, each \((\text{BO}_3\text{)}\) unit is chelated by one \((\text{SO}_4\text{)}\) tetrahedron. Thus, heteropolyanionic monolayers with terminal \((\text{SO}_4\text{)}\) tetrahedra occur. However, in the case of \(\text{Cs}_3\text{B}_2\text{O}(\text{SO}_4\text{)}_{12}\), two oxygen atoms of the terminal \((\text{SO}_4\text{)}\) tetrahedra remain uncoordinated and point towards the faces of the layers (Figure 11). Referring to Liebau’s nomenclature of silicates, the anionic network can be described as loop-branched single layers. Interestingly, the charge compensating \(\text{Cs}\) cations reside on two very different sites within and between the anionic layers.

Reduced dimensionality, however, reveals another new structural motif in the borosulfates \(\text{Ba}[\text{B}_2\text{O}(\text{SO}_4\text{)}]_3\), \(\text{Sr}[\text{B}_2\text{O}(\text{SO}_4\text{)}]_3\) and \(\text{Pb}[\text{B}_2\text{O}(\text{SO}_4\text{)}]_3\). The heteropolyanionic substructure consists of borosulfate double chains, built up by alternating \((\text{SO}_4\text{)}\) and \((\text{BO}_3\text{)}\) tetrahedra, exhibiting also B-O-B bridges, which allow the formation of double chains (Figure 12). Furthermore, two boron atoms are chelated by one \((\text{SO}_4\text{)}\) tetrahedron. The obtained extended one-dimensional heteropolyanion obeys the topology of a ribbon silicate by maintaining B-O-B bridges. While \(\text{Ba}[\text{B}_2\text{O}(\text{SO}_4\text{)}]_3\) and \(\text{Sr}[\text{B}_2\text{O}(\text{SO}_4\text{)}]_3\) are isotypic, comprising alternating orientations of adjacent chains, the same chains occur in \(\text{Pb}[\text{B}_2\text{O}(\text{SO}_4\text{)}]_3\) with the same orientation leading to a monoclinic distortion.\(^{[24]}\)

Two different molecular anions were found for the alkaline earth subgroup metal borosulfates \(\text{Rb}_2\text{B}_3\text{S}_3\text{O}_{17}\) (\(\alpha\)-\(\text{Mg}, \text{Mn, Ni, Co, Zn}\))\(^{[23, 24]}\). Both contain \((\text{B}_2\text{O}_3\text{)}\) units. In the case of \(\alpha\)-\(\text{Mg}[\text{B}_2\text{O}(\text{SO}_4\text{)}]_3\) and \(\alpha\)-\(\text{Mg}[\text{B}_2\text{O}(\text{SO}_4\text{)}]_3\) (\(\alpha\)-\(\text{Mg, Mn, Ni, Co, Zn}\)), all terminal oxygen atoms of a central \((\text{B}_2\text{O}_3\text{)}\) unit are saturated by monodentate \((\text{SO}_4\text{)}\) tetrahedra. The latter remain without any further condensation, resulting in the molecular anion \([\text{B}_2\text{O}(\text{SO}_4\text{)})]^{3–}\). Referring to the formalism for silicates by Liebau, the anion \([\text{B}_2\text{O}(\text{SO}_4\text{)})]^{3–}\) can be explained as an open-branched quadruple tetrahedra chain. The \(\beta\)-polymorph of \(\text{Mg}[\text{B}_2\text{O}(\text{SO}_4\text{)}]_3\) shows another structure type, however with the same structural fragments (Figure 13). Merely, the B-O-B bridges partly differ. In two thirds of these bridges, the six terminal oxygen atoms reveal an eclipsed conformation, whereas for the remaining bridges the staggered conformation occurs, as it is exclusively found in the \(\alpha\)-polymorph. In addition, the molecular anion of \(\text{Rb}_2\text{B}_3\text{S}_3\text{O}_{17}\) features central \((\text{B}_2\text{O}_3\text{)}\) units. Herein, they are in trans-orientation coordinated by monodentate \((\text{SO}_4\text{)}\) tetrahedra and the remaining oxygen atoms of the \((\text{B}_2\text{O}_3\text{)}\) centers are saturated by means of two further bidentate chelating \((\text{SO}_4\text{)}\) tetrahedra. The

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**Figure 10.** Extended unit cell of \(\text{B}_2\text{S}_3\text{O}_7\) in projection on (010), exhibiting \((\text{B}_2\text{O}_3\text{)}\)-centered double layers.
anion resembles acut-out of the borax structure
with the monodentate \((\text{SO}_4)^{2-}\) tetrahedra being
anions and the chelating \((\text{SO}_4)^{2-}\) tetrahedra substituted by
bridging \((\text{BO}_3)^{-}\) groups.

**Optical Properties of Outer and Inner Transition Metal Borosulfates**

One of the main goals to explore the class of crystalline borosulfates was their presumably weak coordination behavior as \(\text{H}_2\left[\text{B}(_4\text{O})_5\right]\) was found to be a super acid.\(^{[27]}\) Due to the presence of optically active rare earth ions in \(RE_j\left[\text{B}_2\left(\text{SO}_4\right)_6\right]\) with \(RE = \text{Y}, \text{La}–\text{Nd}, \text{Sm}, \text{Eu}, \text{Tb}–\text{Lu}\),\(^{[16]}\) it was possible to measure reliable luminescence spectra for borosulfates for the very first time. The excitation and emission spectra of \(\text{Ce}^{3+}, \text{Eu}^{3+}\), and
Tb³⁺ revealed both consistence of the optical properties with respect to the crystal structure, and a weak coordination behavior of the borosulfate ligands. This is in accordance to the previous contribution on the optical properties of transition metal borosulfates \( \alpha\text{-M}_4[\text{B}_2\text{O}(\text{SO}_4)_6] \) \( (M = \text{Mg, Mn, Co, Ni, Zn}) \). Based on optical reflection spectra, weakly coordinating host structures, comparable to those of pure sulfates, were identified. Since borosulfates comprise higher condensed structures than sulfates, they should be better suited in comparable applications as vibrational losses during luminescence should be less relevant.

### Boroselenates and -tellurates

Whereas a relatively large number of borosulfates is meanwhile known, the number of representatives for the higher homologues such as boroselenates and borotellurates is quite limited. However, one has to consider that starting from \( \text{S}^\text{VI} \) via \( \text{Se}^\text{VI} \) to \( \text{Te}^\text{VI} \) the ionic radii as well as the „redox-lability” is increasing, while the electronegativity and the Brønsted acidity of the respective oxygen acid is decreasing.

The crystal structure of \( (\text{H}_2\text{O})\text{Na}_6[\text{B(SeO}_4\text{)}_4][\text{SeO}_4] \) is built up by „Zunyite-like” \([\text{B(SeO}_4\text{)}_4]\)_\( ^{1-} \) anions and additional isolated \( (\text{SeO}_4)^{2-} \) tetrahedra. The structure is closely related to the borophosphates \( \text{A}_n[\text{B(PO}_4\text{)}_4][\text{PO}_4] \) \( (A = \text{Sr, Pb}) \). The structure of \( \text{K}_4[\text{BSe}_4\text{O}_15(\text{OH})] \) is also built up by „Zunyite-like” anions, and therefore similar to the protonated borosulfate \( \text{K}_4[\text{BS}_2\text{O}_8(\text{OH})] \). The structures of \( \text{A}_3[\text{B(SeO}_4\text{)}_3] \) \( (A = \text{Rb, Cs}) \) are again closely related to borosulfates and borophosphates as the Rb-compound crystallizes isotypically to \( \text{Ba}[\text{B(PO}_4\text{)}_3] \) and \( \text{A}[\text{B(SO}_4\text{)}_3] \) \( (A = \text{K, Rb}) \).

The larger ionic radii of \( \text{Te}^\text{VI} \) prefers an octahedral arrangement of the surrounding oxygen atoms. This is also reflected on the respective oxygen acids: While \( \text{H}_2\text{SO}_4 \) and \( \text{H}_2\text{SeO}_4 \) are strong Brønsted acids with the chalcogens tetrahedrally coordinated by oxygen atoms, telluric acid \( \text{H}_6\text{TeO}_6 \) is octahedrally coordinated and a weak acid. It is therefore not surprising that the borotellurate anions exhibit also octahedrally surrounded tellurium atoms. Two types of borotellurate anions are known. In \( \text{Na}_2\text{RE}_2\text{TeO}_6(\text{BO}_3)_2 \) \( (\text{RE} = \text{Y, Dy–Lu}) \) there are isolated oligomers of \( \text{TeO}_6 \) octahedra that are trans-connected with two trigonal planar \( (\text{BO}_3) \) units by sharing common corners. In

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**Figure 14.** Ternary plot of borosulfates charge compensated by monovalent cations. The classical borosulfates are all located on a line between \( \text{A}_2\text{SO}_4 \) and the composition „\( \text{B}_2\text{O}_3\cdot3\text{SO}_3 \)”. The unconventional borosulfates with \( 3\)-\( \text{O} \)-\( 5 \)-\( \text{S} \) bridges are placed on a line between \( \text{SO}_3 \) and \( \text{AB}_2\text{O}_8 \), and the unconventional borosulfates with \( 3\)-\( \text{O} \)-\( 5 \)-\( \text{B} \) bridges are found on a line between \( \text{A}_2\text{SO}_4 \) and \( \text{B}_2\text{S}_2\text{O}_9 \).
Ba$_2$B$_4$TeO$_{19}$, the anionic borotellurate part forms a complex 3D framework that may be described as [(TeO$_4$)$_2$O$_2$]$^-$·6[BO$_4$]$^-$·2[BO$_3$]$^-$.[44]

A complete separation of the different polyhedra is observed in Bi$_2$B$_4$TeO$_9$ with isolated TeO$_6$ octahedra and trigonal planar BO$_3$ units.[44] Separated polyhedra are also present in A$_4$H$_2$S$_2$O$_6$ (A = Rb, Cs).[23] where planar sheets with the composition B$_2$O$_3$ are intercalated by $\text{A}^{+}$, $(\text{SO}_4)^{2-}$, and $(\text{HSO}_4)^{-}$ represented by the formula A$_4$H(SO$_4$)$_2$(B$_2$O$_3$)$_2$. Therefore, these compounds should not be classified as borosulfates.

**Conclusion and Outlook**

Borosulfates are an upcoming class of compounds. The synthesis and characterization is still an ongoing field of research. The hitherto explored and (in terms of this review) presented structural diversity is already immense. Corner-sharing networks of $(\text{SO}_4)$ and $(\text{BO}_4)$ tetrahedra dominate the crystal structures, which are closely related to silicates and the respective substitution variants. The anionic subunits range from molecular anions (OD) as found for K$_4$[B(SO$_4$)$_2$]$_2$ over one dimensional infinite anionic chains and layers up to 3D networks, all charge compensated by metal or non-metal cations. The structural diversity enlarges even more referring to compounds with S-O-S and B-O-B bridges, which formally violate Loewenstein’s rule, whereas in contrast to borophosphates a (BO$_4$) group has not been found as structural motif of borosulfates, yet. Figure 14 shows a ternary plot for the known (alkali) borosulfates. The classical borosulfates are all located on a line between A$_4$SO$_4$ and a hypothetical phase with the composition $\text{B}_2\text{O}_3$·3SO$_4$. The unconventional borosulfates with S-O-S bridges are placed on a line between SO$_4$ and A[B(SO$_4$)$_3$]$_2$, whereas the unconventional borosulfates with B-O-B bridges are found on a line between A$_5$SO$_4$ and B$_5$SO$_4$. Obviously, boron-rich borosulfates are still elusive, however currently under investigation. Besides the structural beauty and astonishing rationality, borosulfates are promising candidates for several applications like host lattices for luminescence materials, NLO, super acids, etc. However, the research in this field is at the beginning. To achieve tailored compounds for the desired applications, the relationship between synthesis, crystal structure, and properties needs to be investigated in more detail. Thus, we are sure, that this promising field of inorganic chemistry will rise rapidly.

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**Conflict of interest**

The authors declare no conflict of interest.

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