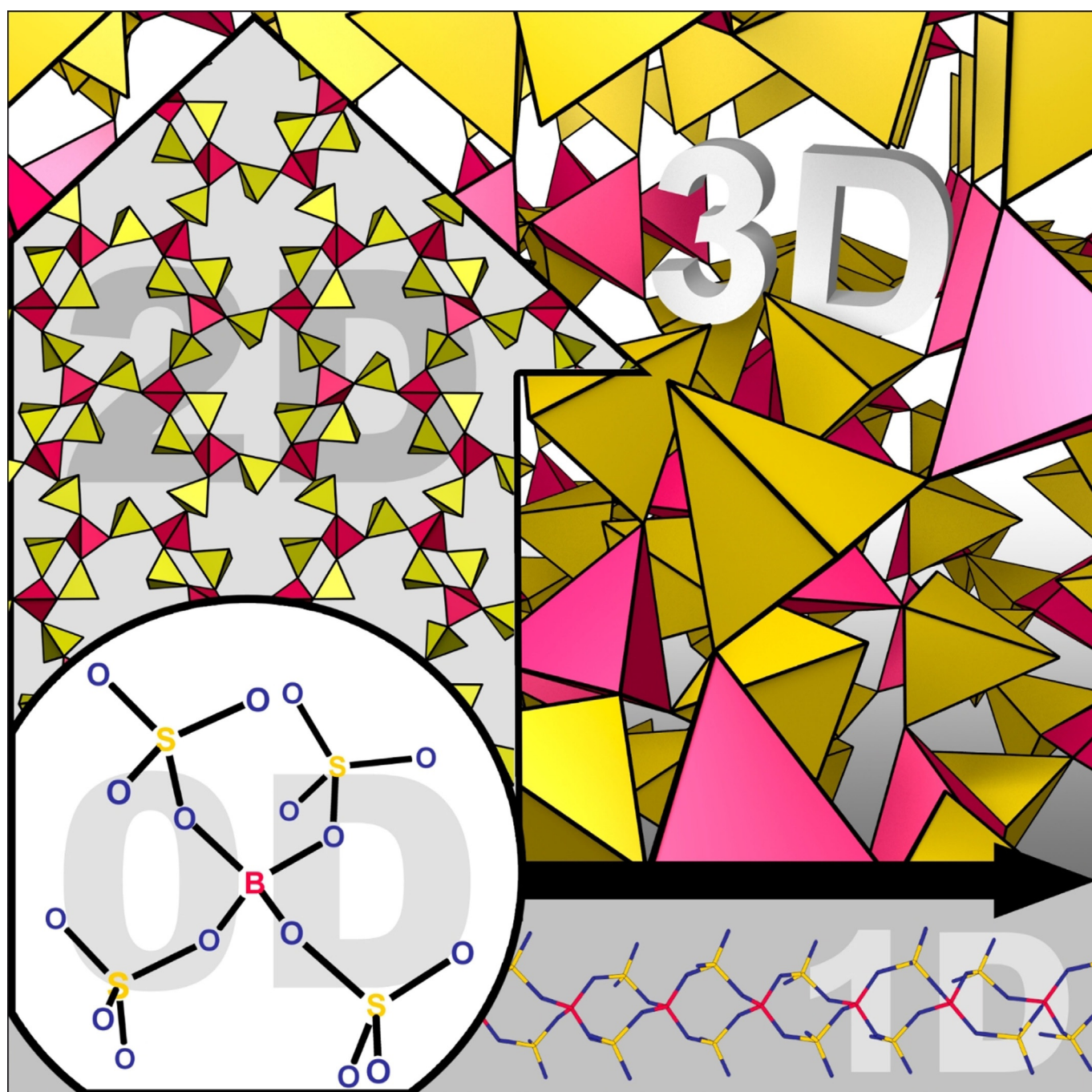Chemistry
Europe
European Chemical
Societies Publishing

▌ **Solid-State Structures** |*Reviews Showcase*|

Borosulfates—Synthesis and Structural Chemistry of Silicate Analogue Compounds

Jörn Bruns,*[a] Henning A. Höppe,*[b] Michael Daub,[c] Harald Hillebrecht,*[c] and Hubert Huppertz*[d]

Chemistry–A European Journal

Review

doi.org/10.1002/chem.201905449

Chemistry Europe
European Chemical
Societies Publishing

Abstract: Borosulfates are oxoanionic compounds consisting of condensed sulfur- and boron-centered tetrahedra. Hitherto, they were mostly achieved from solvothermal syntheses in SO_3-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_3) 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) 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*, *inosilicates*, *phyllosilicates*, and *tectosilicates*, depending on the extent of crosslinking 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, bicchulite.[5] Compared to neat silicates, it is not astonishing that aluminophosphates 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) 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-

[a] Dr. J. Bruns
Universität zu Köln
Institut für Anorganische Chemie
Greinstrasse 6, 50939 Köln (Germany)
E-mail: j.bruns@uni-koeln.de

[b] Prof. Dr. H. A. Höppe
Lehrstuhl für Festkörperchemie
Universität Augsburg
Universitätsstr. 1, 86159 Augsburg (Germany)
E-mail: henning@ak-hoeppe.de

[c] Dr. M. Daub, Prof. Dr. H. Hillebrecht
Universität Freiburg
Institut für Anorganische und Analytische Chemie
Albertstr. 21, 79104 Freiburg (Germany)
and Freiburger Materialforschungszentrum FMF
Stefan-Meier-Str. 21, 79104 Freiburg (Germany)
E-mail: harald.hillebrecht@ac.uni-freiburg.de

[d] Prof. Dr. H. Huppertz
Universität Innsbruck
Institut für Allgemeine, Anorganische und Theoretische Chemie
Innrain 80–82, 6020 Innsbruck (Austria)
E-mail: hubert.huppertz@uibk.ac.at

The ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/chem.201905449.

Chemistry–A European Journal

Review
doi.org/10.1002/chem.201905449

Chemistry Europe
European Chemical
Societies Publishing

tions with suitable sulfate species like disulfates as source for the (SO$_4$) fragment. The latter start with grinding together a stoichiometric amount of the alkali metal hydrogensulfates or disulfates, and boron sources like the boron oxide B$_2$O$_3$, metaboric acid HBO$_2$, or boric acid H$_3$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 K$_3$[B(SO$_4$)$_3$] as phase-pure crystalline, colorless, and hygroscopic powder [Eq. 1]:[7]

$$3\,K_2(S_2O_7) + B_2O_3 \rightarrow 2\,K_3[B(SO_4)_3] \tag{1}$$
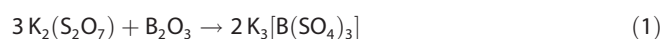
Corresponding to the following reaction, borosulfates like K$_3$[B(SO$_4$)$_3$] can also be thermally decomposed to K$_5$[B(SO$_4$)$_4$] under release of SO$_3$ [Eq. 2]:[8]

$$5\,K_3[B(SO_4)_3] \rightarrow 3\,K_5[B(SO_4)_4] + B_2O_3 + 3\,SO_3 \tag{2}$$
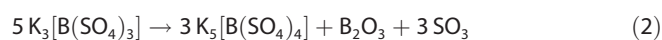
Most of the known borosulfates were synthesized from reactions of suitable boron species with conc. or SO$_3$-enriched sulfuric acid (oleum) as solvent and reaction partner. Especially approved are three approaches, which generally can be classified as reactions according to the concept of Lux and Flood, 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 H$_3$BO$_3$ in evacuated and torch sealed soda lime or silica glass ampoules (solvothermal).

3. Synthesis with the a priori prepared complex superacid H[B(HSO$_4$)$_4$] in sulfuric acid and torch sealed soda lime or silica glass ampoules (solvothermal). H[B(HSO$_4$)$_4$] can be obtained from the reaction of H$_3$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.

Jörn Bruns studied chemistry at the Carl-von-Ossietzky University Oldenburg (Germany), where he obtained his B.Sc. and M.Sc. Subsequently, he worked under the supervision of Prof. M. Wickleder on the synthesis and characterization of new solid-state materials from extreme oxidizing media and finished his doctorate in 2015. Afterwards he joined the Huppertz group at the University of Innsbruck (Austria) for a PostDoc and focused on high-pressure/high-temperature synthesis as well as silicate analogue materials. Recently, he moved to Cologne to build up his own working group. His research interests are unconventional inorganic synthesis, solid-state chemistry, and functional carbon-free materials.

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.

Henning Höppe was born in 1972 in Nürnberg (Nuremburg/Germany). He studied Chemistry at the University Bayreuth and obtained his Ph.D. in 2003 under the supervision of Prof. Dr. W. Schnick at Ludwig-Maximilians-University München. From 2003 till 2004 he worked as a PostDoc with Prof. M. L. H. Green FRS at the University of Oxford. After that he started his own group at the Albert-Ludwigs-University Freiburg, where he stayed until he was appointed a professor for solid-state chemistry and materials sciences at University Augsburg in 2010. His research group focusses on explorative solid-state chemistry on optical functional materials based on silicate-analogous compounds like borosulfates, fluorooxoborates, and phosphates.

Harald 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.

Chemistry–A European Journal

Review
doi.org/10.1002/chem.201905449

Chemistry
Europe
European Chemical
Societies Publishing

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

Compound	Space Group	a [pm]	b [pm]	c [pm]	α [°]	β [°]	γ [°]	Ref.
				0D Borosulfates				
$Na_5[B(SO_4)_4]$-I	$Pca2_1$	1073.0(2)	1389.1(3)	1819.7(4)				[7]
$Na_5[B(SO_4)_4]$-II	$P2_12_12_1$	862.39(17)	927.50(19)	1667.1(3)				[7]
$K_5[B(SO_4)_4]$	$P4_1$	990.23(5)		1618.7(1)				[8]
$Li_5[B(SO_4)_4]$	$P2_1/c$	801.91(1)	1021.11(1)	1504.01(2)		104.033(1)		[9]
$K_4[BS_4O_{15}(OH)]$	$I2/a$	1452.4(3)	739.16(10)	1578.57(19)		115.50(1)		[10]
$Rb_5[B(SO_4)_4]$	$P4_32_12$	1014.8(4)		1668.9(14)				[11]
$CsK_4[B(SO_4)_4]$	$P4_32_12$	994.33(14)		1688.1(3)				[12]
$Cs_3Na_2[B(SO_4)_4]$	$P2_1/c$	1364.04(8)	794.75(3)	1395.73(8)		90.781(4)		[13]
$Cs_3Li_2[B(SO_4)_4]$	$P2_1/n$	1376.98(14)	823.76(5)	1390.66(12)		91.778(8)		[14]
				1D Borosulfates				
				Cyclic anions				
$Cu[B(SO_4)_2(HSO_4)]$	$P\bar{1}$	530.96(7)	707.52(4)	1129.77(6)	81.154(1)	80.302(2)	80.897(4)	[15]
$Gd_2[B_2S_6O_{24}]$	$C2/c$	1356.97(7)	1144.26(6)	1102.71(6)				[10]
$Y_2[B_2(SO_4)_6]$	$C2/c$	1351.72(5)	1139.41(4)	1089.94(4)		93.4470(10)		[16]
$La_2[B_2(SO_4)_6]$	$C2/c$	1379.24(17)	1158.87(14)	1139.54(14)		93.611(4)		[16]
$Ce_2[B_2(SO_4)_6]$	$C2/c$	1374.00(5)	1153.71(4)	1130.57(4)		93.6606(12)		[16]
$Pr_2[B_2(SO_4)_6]$	$C2/c$	1371.14(11)	1153.05(9)	1126.43(9)		93.638(2)		[16]
$Nd_2[B_2(SO_4)_6]$	$C2/c$	1367.75(4)	1151.34(4)	1120.46(3)		93.5909(8)		[16]
$Sm_2[B_2(SO_4)_6]$	$C2/c$	1363.3(3)	1149.2(3)	1111.2(2)		93.567(6)		[16]
$Eu_2[B_2(SO_4)_6]$	$C2/c$	1360.2(6)	1147.0(5)	1105.0(5)		93.465(9)		[16]
$Tb_2[B_2(SO_4)_6]$	$C2/c$	1356.01(6)	1142.48(5)	1098.81(5)		93.5342(13)		[16]
$Dy_2[B_2(SO_4)_6]$	$C2/c$	1356.83(19)	1142.48(16)	1097.03(17)		93.450(4)		[16]
$Ho_2[B_2(SO_4)_6]$	$C2/c$	1350.53(14)	1140.95(11)	1092.10(11)		93.453(3)		[16]
$Er_2[B_2(SO_4)_6]$	$C2/c$	1355.1(5)	1141.1(4)	1088.2(4)		93.410(12)		[16]
$Tm_2[B_2(SO_4)_6]$	$C2/c$	1349.81(4)	1136.17(3)	1083.27(3)		93.4500(9)		[16]
$Yb_2[B_2(SO_4)_6]$	$C2/c$	1349.49(11)	1134.52(9)	1079.61(9)		93.390(2)		[16]
$Lu_2[B_2(SO_4)_6]$	$C2/c$	1346.9(3)	1136.4(3)	1079.9(3)		93.369(8)		[16]
				Anionic Chains				
$H_3O[B(SO_4)_2]$	$P4/ncc$	913.77(13)		734.23(15)				[17]
$NH_4[B(SO_4)_2]$	$P4/ncc$	919.80(1)		724.58(1)				[9]
$Na[B(SO_4)_2]$	$P2/c$	543.4(5)	757.0(7)	776.6(8)		99.74(2)		[9]
$K[B(SO_4)_2]$	$P4/ncc$	897.39(2)		741.14(3)				[9]
$K_3[B(SO_4)_3]$	$Ibca$	707.4(4)	1426.6(9)	2257.8(14)				[7]
$Rb_3[B(SO_4)_3]$	$Ibca$	727.59(11)	1479.36(11)	2263.7(2)				[7]
$Ag[B(SO_4)_2]$	$P4/ncc$	866.79(5)		728.97(5)				[18]
$Cu[B_2(SO_4)_4]$	$P\bar{1}$	524.70(3)	713.71(3)	792.22(5)	73.814(3)	70.692(2)	86.642(2)	[15]
$Pb[B_2(SO_4)_4]$	$Pnna$	1251.6(7)	1252.1(7)	730.2(4)				[19]
				2D Borosulfates				
$CaB_2S_4O_{16}$	$P2_1/c$	551.88(2)	1512.88(6)	1326.60(6)		92.88(1)		[20]
$Mg[B_2(SO_4)_4]$	$C2/c$	1744.28(10)	531.45(3)	1429.06(8)		126.323(2)		[21]
				3D Borosulfates				
$Li[B(SO_4)_2]$	Pc	763.53(15)	934.2(2)	843.2(2)		92.55(2)		[7]
				„Unconventional" Borosulfates				
				B-O-B Bridges				
$B_2S_2O_9$	$C2$	776.00(8)	416.64(4)	861.34(9)		94.785(2)		[22]
$Rb_4B_2S_4O_{17}$	$Pnna$	804.15(9)	1064.66(11)	2042.5(2)				[23]
$Cs_2B_2S_3O_{13}$	$P2/c$	1476.5(3)	671.0(1)	1252.8(3)		104.60(3)		[23]
$Sr[B_2O(SO_4)_3]$	$Pnma$	1657.38(27)	1203.68(19)	439.484(8)				[24]
$Ba[B_2O(SO_4)_3]$	$Pnma$	1718.48(7)	1238.05(4)	442.26(2)				[10]
$Pb[B_2O(SO_4)_3]$	$P2_1/m$	440.00(2)	1210.19(5)	860.43(4)		103.587(2)		[24]
α-$Mg_4[B_2O(SO_4)_6]$	$P\bar{3}$	801.65(9)		748.54(3)				[21]
β-$Mg_4[B_2O(SO_4)_6]$	$P\bar{3}$	1391.96(9)		748.54(3)				[21]
$Mn_4[B_2O(SO_4)_6]$	$P\bar{3}$	810.86(9)		775.09(9)				[21]
$Co_4[B_2O(SO_4)_6]$	$P\bar{3}$	799.1(3)		755.9(3)				[21]
$Ni_4[B_2O(SO_4)_6]$	$P\bar{3}$	793.59(4)		743.98(4)				[21]
$Zn_4[B_2O(SO_4)_6]$	$P\bar{3}$	799.71(7)		748.95(7)				[21]
				S-O-S Bridges				
$Li[B(S_2O_7)_2]$	$P2_12_12_1$	1086.3(2)	1087.7(2)	1776.9(4)				[7]
$Na[B(S_2O_7)_2]$	$P2_1/c$	1094.89(2)	854.91(2)	1270.13(3)		110.227(1)		[17]

Chemistry–A European Journal

Review
doi.org/10.1002/chem.201905449

Chemistry Europe
European Chemical
Societies Publishing

Compound	Space Group	a [pm]	b [pm]	c [pm]	α [°]	β [°]	γ [°]	Ref.
Table 1. (Continued)								
$K[B(S_2O_7)_2]$	Cc	1133.68(1)	814.6662(2)	1366.50(1)		94.235(1)		[17]
$Cs[B(SO_4)(S_2O_7)]$	$P2_1/c$	1045.25(2)	1131.91(2)	827.60(1)		103.206(1)		[17]
$H[B(SO_4)(S_2O_7)]$	$P2_1/c$	1569.74(10)	1143.62(7)	855.57(6)		90.334(3)		[17]
$NH_4[B(S_2O_7)_2]$	Cc	1144.03(2)	1494.39(2)	1386.93(2)		93.662(1)		[9]

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 been 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 (SO_4) units, forming the $[B(SO_4)_4]^{5-}$ anion, which can be regarded as a molecular anion (0D). Additional vertex-sharing of the different tetrahedra results in the formation of cyclic $[B_2(SO_4)_6]^{6-}$ anions (1D), one-dimensional infinite chains according to $\frac{1}{\infty}[B(SO_4)_{4/2}]^-$ (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 $[B(SO_4)_4]$ basic building units as TX_4 ($T=$ B, $X=$ SO_4). According to Liebau, the $T{:}X$

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 (BO_4) and (SO_4) 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 (SO_4) and (BO_4) 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 oxidic network and has to be elucidated independently for each single representative. However, they are always intermediate compounds of the system M_xO_y–B_2O_3–SO_3 (-H_2O) (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 (BO_3) units have been found in several structures,
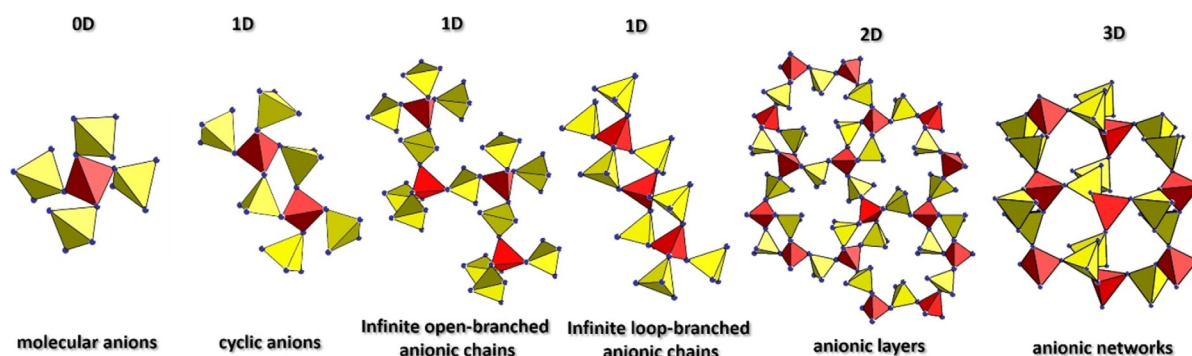

Figure 1. Schematic description of hitherto obtained borosulfate structures including a classification in different dimensions. Red polyhedra represent the (BO_4) units and yellow polyhedra the (SO_4) units.

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.[1] 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 $[B(SO_4)_4]^{5-}$ anion (Figure 1, left), which is described as molecular anion (0D). This anion occurs for example in the first ever presented borosulfate $K_5[B(SO_4)_4]$.[8] The finding of boron atoms in the center of exclusively four (SO_4) units is unique. In the structure of $K_5[B(SO_4)_4]$, the boron atoms adopt a slightly distorted body-centered packing with the apices of the (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 $[Si(SiO_4)_4]^{12-}$, adopting T_d symmetry and being connected to AlO_6 octahedra. As expected, the terminal S–O bonds in $K_5[B(SO_4)_4]$ are significantly shorter (139.4(6)–145.4(5) pm) than the bridging S–O bonds (154.7(4)–157.1(4) pm). According to the method suggested by Balic-Žunic and Makovicky, the BO_4 and SO_4 tetrahedra can be classified as regular (deviations of the tetrahedra from the ideal symmetry—BO_4: 0.43% and SO_4: 0.08–0.23%) compared to an ideal tetrahedron.[27] The $[B(SO_4)_4]^{5-}$ anion has also been found for the following seven homologues $Li_5[B(SO_4)_4]$,[9] the two polymorphs $Na_5[B(SO_4)_4]$-I and $Na_5[B(SO_4)_4]$-II,[7] $Rb_5[B(SO_4)_4]$[11] as well as for the mixed alkali borosulfates $CsK_4[B(SO_4)_4]$ and $Cs_3A_2[B(SO_4)_4]$ $A=Li$, Na.[12–14] In detail, the anionic substructures are similar but not identical. For a better comparison of the different $[B(SO_4)_4]^{5-}$ anions, the conformations can be described by the torsion angles of the terminal (SO_4) to the central (BO_4) units. For example, $Li_5[B(SO_4)_4]$ reveals a staggered arrangement with respect to the (BO_4) unit ($\tau = 160$–$172°$), which is in good agreement to the findings in $Na_5[B(SO_4)_4]$-I. The difference between the two polymorphs $Na_5[B(SO_4)_4]$-I and $Na_5[B(SO_4)_4]$-II manifests in the orientation of the molecular anions and the coordination spheres of the sodium counter cations, whereas the anions themselves are almost similar. Modification I reveals the $[B(SO_4)_4]^{5-}$ anions in a stacked manner parallel to (100), forming a hexagonal rod packing. In projection on (010), the anionic substructure can be described as corrugated layers. The anions in $Na_5[B(SO_4)_4]$-II are arranged more isotropically, in the manner of a bcc packing, as also found for $K_5[B(SO_4)_4]$.

To obtain the protonated borosulfate, $K_4[BS_4O_{15}(OH)]$,[10] the superacid $H[B(HSO_4)_4]$ 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 $H[B(HSO_4)_4]$. The central structural motif of $K_4[BS_4O_{15}(OH)]$ is the unprecedented non-condensed molecular

$[B(SO_4)_4]^{5-}$ $[B(SO_4)_3(HSO_4)]^{4-}$
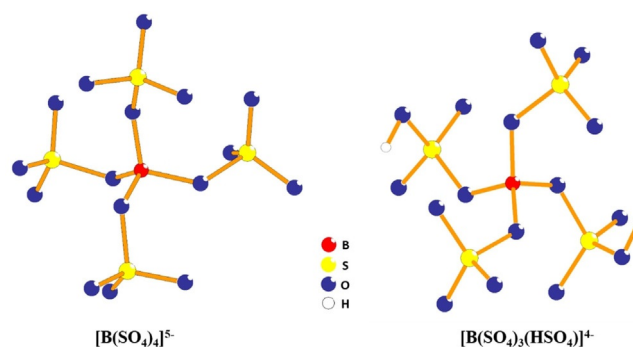
● B
● S
● O
○ H

Figure 2. Non-condensed complex anions $[B(SO_4)_4]^{5-}$ in $K_5[B(SO_4)_4]$ and $[B(SO_4)_3(HSO_4)]^{4-}$ in $K_4[BS_4O_{15}(OH)]$ with an occupancy factor of 0.5 for the protons.

$[B(SO_4)_3(HSO_4)]^{4-}$ anion (Figure 2, right), which resembles the topology of the anions in $A_5[B(SO_4)_4]$ ($A=$Li-Rb).

Cyclic Borosulfate Anions (1D)

The structures of $Gd_2[B_2S_6O_{24}]$[10] and $Cu[B(SO_4)_2(HSO_4)]$[15] are closely related to each other, exhibiting two central boron atoms bridged by two (SO_4) units and terminated by four (SO_4) tetrahedra in the case of $Gd_2[B_2S_6O_{24}]$, and by two (SO_4) as well as two (HSO_4) tetrahedra in the case of $Cu[B(SO_4)_2(HSO_4)]$ (Figure 3). Both anionic substructures are classified as cyclic anions (1D).

$Cu[B(SO_4)_2(HSO_4)]$ can be regarded as a cut-out by protonation from an infinite anionic chain found for $Cu[B_2(SO_4)_4]$ and can be obtained coexistent from a solution of a Cu_2O, boric acid, and SO_3-enriched sulfuric acid. Hirshfeld analysis of $Cu[B(SO_4)_2(HSO_4)]$ 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 $[B_2(SO_4)_6]^{6-}$ 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 $[B_2(SO_4)_6]^{6-}$ anion were performed (Figure 4).

The obtained datasets were compared to the structure of $Gd_2[B_2S_6O_{24}]$, wherefore no calculations have been reported, yet. pK_a values were calculated for different protonated and non-protonated conformations of the $[B_2(SO_4)_6]^{6-}$ anion and compared to those of H_2SO_4 and $Si(OH)_4$. For the chair and twist conformations of the complex anion $[B_2(SO_4)_4(SO_4H)_2]^{4-}$, pK_a values of 6.6 and 6.2 were calculated for the first deprotonation and pK_a values of 9.4 and 8.1, respectively, for the second deprotonation step. With the same methodology, pK_a values were calculated for sulfuric and silicic acid and turned out to be 5.3 for the first deprotonation of H_2SO_4 and 17.5 for $Si(OH)_4$, emphasizing that the borosulfate anion $[B_2(SO_4)_4(SO_4H)_2]^{4-}$ is obviously not a strong acid but behaves rather silicate-like.

Chemistry–A European Journal
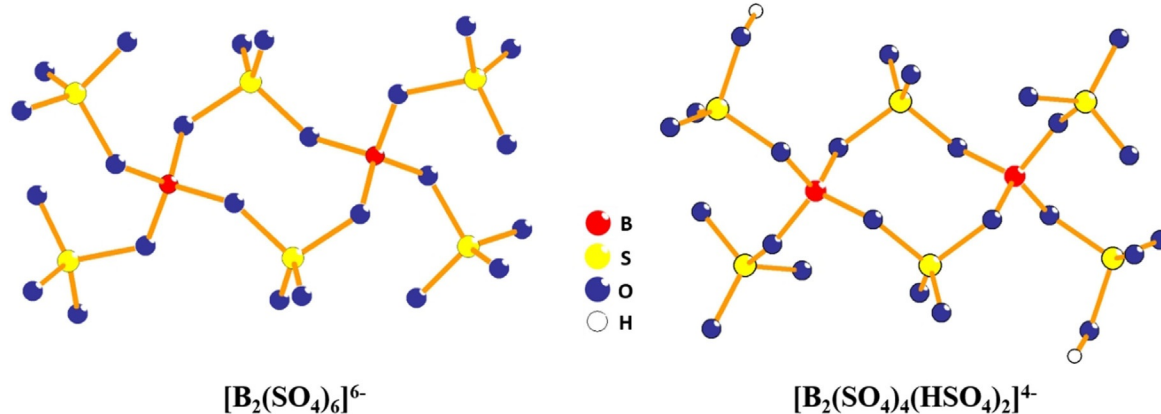
Review
doi.org/10.1002/chem.201905449

Chemistry Europe
European Chemical
Societies Publishing

Figure 3. Protonated and non-protonated borosulfate anions in $Gd_2[B_2S_6O_{24}]$ (left) and $Cu[B(SO_4)_2(HSO_4)]$ (right).

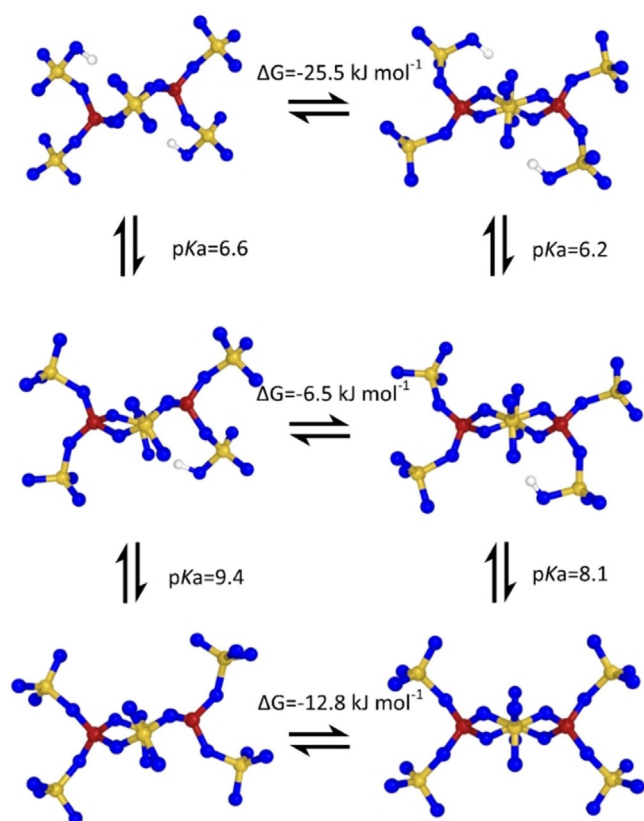**Figure 4.** Calculated free energy differences ΔG of the complex anion $[B_2(SO_4)_4(SO_4H)_2]^{4-}$ between the hypothetical chair conformation (left) and the experimentally found twist conformation (right) as well as pK_a values for the deprotonation to $[B_2(SO_4)_5(SO_4H)]^{5-}$ and to $[B_2(SO_4)_6]^{6-}$. Color code: blue—oxygen, yellow—sulfur, red—boron, and white—hydrogen.[15]

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 $P4/ncc$. $Ag[B(SO_4)_2]$[18] and $K[B(SO_4)_2]$[9] are isotypic, whereas $(H_3O)[B(SO_4)_2]$[17] and $(NH_4)[B(SO_4)_2]$[9] 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 $^1_\infty[B(SO_4)_{4/2}]^-$. 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-
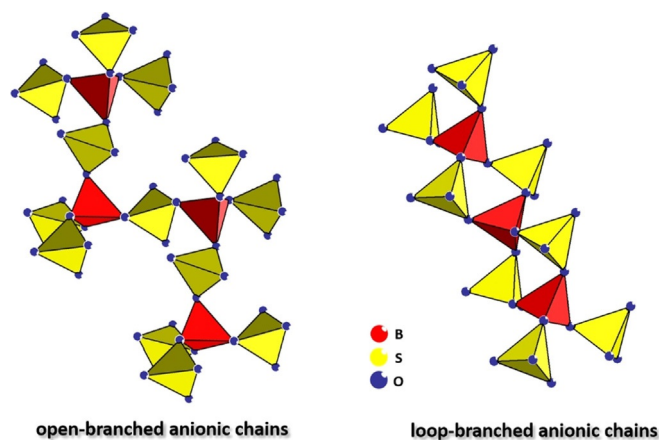

Figure 5. Cutout from the open-branched chain $^1_\infty[B(SO_4)_{4/2}]^-$ and the infinite loop-branched chain $^1_\infty[B(SO_4)_{2/2}(SO_4)_{2/1}]^{3-}$.

Chemistry–A European Journal

Review
doi.org/10.1002/chem.201905449

Chemistry Europe
European Chemical
Societies Publishing

wenstein's rule should be adequate.[4] Due to the absence of B-O-B bridges, Loewenstein's rule is obeyed for all afore mentioned anionic chains. A possible explanation of the preferred B-O-S bridges might be found in one of Pauling's rules,[28] which states that in a crystal structure with different highly charged cations and low coordination numbers no equal subunits tend to coordinate. Thus, with respect to the large concentration of sulfate anions during this and comparable reactions (excess of oleum with at least 20% SO_3 content) it was expected that (SO_4) units take terminal positions and form borosulfates of low dimensionality. Adopting also the classification rules of Liebau[1] and Kniep[26] for silicates and borophosphates, the infinite anionic chains $^1_\infty[B(SO_4)_{4/2}]^-$ can be described as loop-branched (lB) vierer-single chains with fundamental building units of unbranched (uB) trimers of double (SO_4) coordinated (BO_4) tetrahedra.

Referring to a clear definition, the designation „borosulfate" is an umbrella term. The Lewis acidity of the boron and sulfur centers is decisive for the correct nomenclature according to the IUPAC rules. Theoretical investigations can help to investigate this problem. Unfortunately, respective data are not known for all borosulfates. Definitely, this is a challenge for the future to better compare borosulfates with silicates and other multidimensional networks of tetrahedra. One of the few examples investigated by means of DFT calculations based on prior performed magnetochemical measurements is the silver borosulfate $Ag[B(SO_4)_2]$. Astonishingly, Mulliken partial charges and thus the expected Lewis acidity of the boron atoms are higher than the values obtained for the sulfur atoms. Accordingly, $Ag[B(SO_4)_2]$ has to be precisely designated as silver-*bis*sulfatoborate, because the boron atoms constitute the center of the complex anion.[18]

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 $Mg[B_2(SO_4)_4]$[21] and $CaB_2S_4O_{16}$[20] are the exclusive examples (besides $B_2S_2O_9$ 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 $CaB_2S_4O_{16}$ 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 $(BO_4)(SO_4)(BO_4)$ edge. In the case of $CaB_2S_4O_{16}$, 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 $Mg[B_2(SO_4)_4]$ 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[29] 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 $[K_9F_2][Ln_3Si_{12}O_{32}]$ ($Ln=Sm$, 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 $CaB_2S_4O_{16}$ 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, $CaB_2S_4O_{16}$, 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 $Li[B(S_2O_7)_2]$ (see Unconventional Borosulfates below) according to [Eq. 3]:

$$Li[B(S_2O_7)_2] \rightarrow Li[B(SO_4)_2] + 2\,SO_3 \tag{3}$$

The sum formula of the obtained lithium species is identical to the borosulfates $A[B(SO_4)_2]$ ($A=Na$, K, NH_4, H_3O, 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
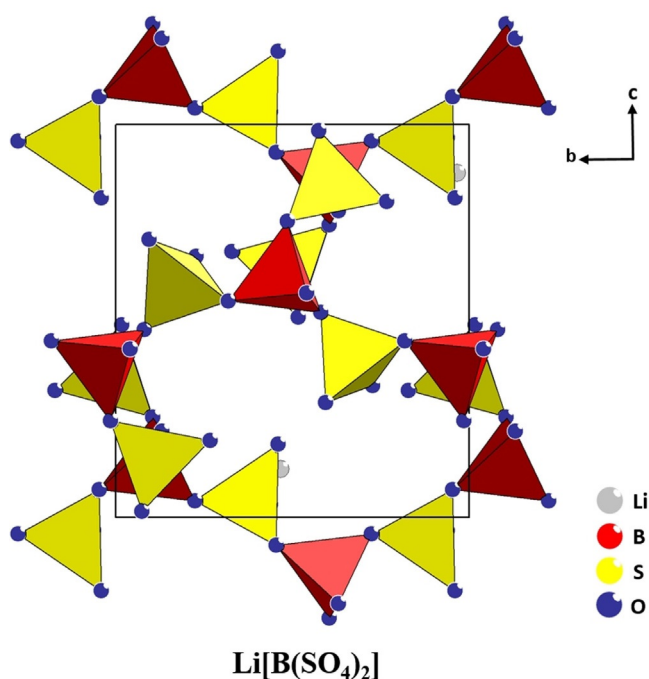
Chemistry–A European Journal

Review
doi.org/10.1002/chem.201905449

Chemistry Europe
European Chemical
Societies Publishing

Li[B(SO$_4$)$_2$]

Figure 6. Extended unit cell of Li[B(SO$_4$)$_2$] in projection on (1 0 0).

bond lengths within the (SO$_4$) tetrahedra differ: S–O bonds with oxygen being the bridging atom are about 10 pm longer than the terminal S–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 Li[B(SO$_4$)$_2$] to the orthorhombic high temperature modification of SiO$_2$, namely β-tridymite. Li[B(SO$_4$)$_2$] 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 SO$_3$ during the thermal decomposition of Li[B(S$_2$O$_7$)$_2$]

and formation of Li[B(SO$_4$)$_2$]. 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 [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 [B(SO$_4$)$_4$]$^{5-}$, we found in analogy to (SiO$_4$)$^{4-}$ isolated TX_4 supertetrahedra. In similarity to (SiO$_3$)$^{2-}$, for [B(SO$_4$)$_3$]$^{3-}$, 1D chains of corner-sharing „BS$_2$S$_{2/2}$" tetrahedra are observed. The anion [B$_2$S$_6$O$_{24}$]$^{6-}$ exhibits formally the same composition as [B(SO$_4$)$_3$]$^{3-}$, but now two „BS$_4$" tetrahedra are sharing a common edge forming a 0D oligomeric structure. For the anion [B(SO$_4$)$_2$]$^-$, there are different cases: In Li[B(SO$_4$)$_2$], the „BS$_{4/2}$" tetrahedra are forming in analogy to SiO$_2$ a 3D network through sharing common corners. For A[B(SO$_4$)$_2$] (A = Na, K, NH$_4$, H$_3$O, and Ag), the super $TX_{4/2}$ tetrahedra are connected via common edges resulting in 1D chains (as also found as SiS$_4$ tetrahedra in SiS$_2$). The anion [B$_2$(S$_4$O$_{16}$)]$^{2-}$ 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 (SO$_4$) and (BO$_4$) tetrahedra. Compounds with no perfect alternation of (SO$_4$) and (BO$_4$) tetrahedra are classified as unconventional borosulfates. They bear for example B-O-B or S-O-S bridges. In contrast, uncharged networks of (SO$_4$) and (BO$_4$) 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,
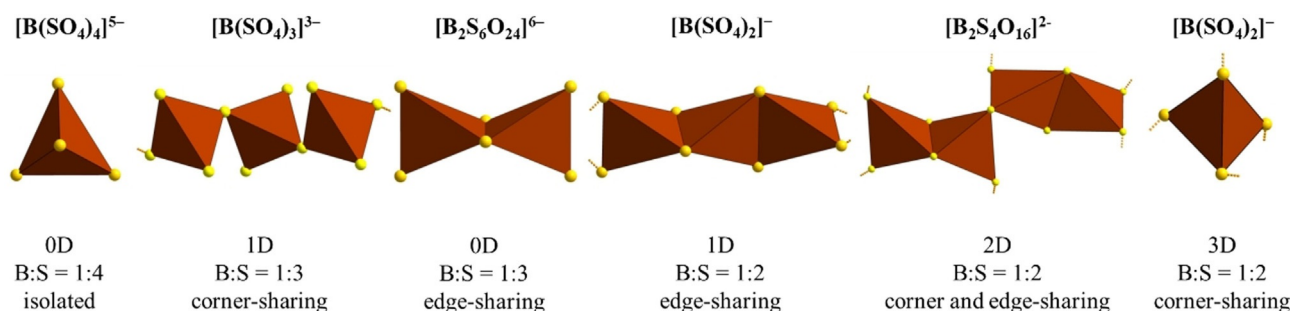

[B(SO$_4$)$_4$]$^{5-}$	[B(SO$_4$)$_3$]$^{3-}$	[B$_2$S$_6$O$_{24}$]$^{6-}$	[B(SO$_4$)$_2$]$^-$	[B$_2$S$_4$O$_{16}$]$^{2-}$	[B(SO$_4$)$_2$]$^-$
0D	1D	0D	1D	2D	3D
B:S = 1:4	B:S = 1:3	B:S = 1:3	B:S = 1:2	B:S = 1:2	B:S = 1:2
isolated	corner-sharing	edge-sharing	edge-sharing	corner and edge-sharing	corner-sharing

Figure 7. TX_4 super-tetrahedral units and the different observed connection modes for the known classical borosulfates.

Chemistry–A European Journal

Review
doi.org/10.1002/chem.201905449

Chemistry Europe
European Chemical
Societies Publishing

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_2O_7) fragments formed by two (SO_4) tetrahedra, which are coordinated by one vertex oxygen atom. In each case, the (S_2O_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, $Li[B(SO_4)_2)]$ as a 3D representative of the conventional borosulfate is obtained by release of the leaving group SO_3 from the unconventional 0D borosulfate $Li[B(S_2O_7)_2]$ (see below).

The molecular anion $[B(S_2O_7)_2]^-$ is found in the crystal structures of $A[B(S_2O_7)_2]$ ($A =$ Li, Na, K, NH_4).[7,9,17] The anion is comparable to the borosulfate anion $[B(SO_4)_4]^{5-}$ in $K_5[B(SO_4)_4]$. 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, $[Au(S_2O_7)_2]^{-[32]}$ and $[Si(S_2O_7)_3]^{2-}$.[33] In both cases, sulfate species act as ligands. In the case of $K_5[B(SO_4)_4]$, four monodentate anions coordinate to the central boron atom and for $A[B(S_2O_7)_2]$ ($A =$ 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_2O_7) subunits of $A[B(S_2O_7)_2]$ ($A =$ 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 $(NH_4)[B(S_2O_7)_2]$, two crystallographically different $[B(S_2O_7)_2]^-$ anions exhibit different
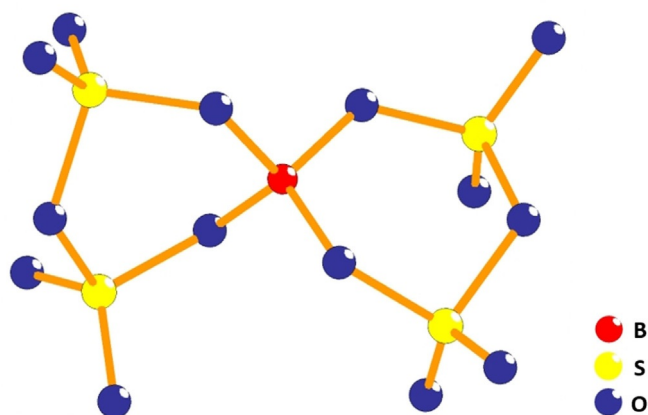

Figure 8. The molecular anion $[B(S_2O_7)_2]^-$ in the crystal structures of $A[B(S_2O_7)_2]$ ($A =$ Li, Na, K, NH_4).

conformations. 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 $Cu[B_2(SO_4)_4]$.

$Cs[B(SO_4)(S_2O_7)]^{[17]}$ and $H[B(SO_4)(S_2O_7)]^{[17]}$ were the first borosulfates with Cs^+ and H^+ as counter cations and furthermore the first examples in which (SO_4) and (S_2O_7) occur in the same moiety. Compared to the structures of $K_3[B(SO_4)_3]$ and $Rb[B(SO_4)_3]$, the two terminal (SO_4) units are substituted by (S_2O_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 $Cs[B(SO_4)(S_2O_7)]$, hydrogen bridges interconnect the anionic chains in $H[B(SO_4)(S_2O_7)]$ to layers perpendicular to the crystallographic b-axis (Figure 9). Two different hydrogen bridges
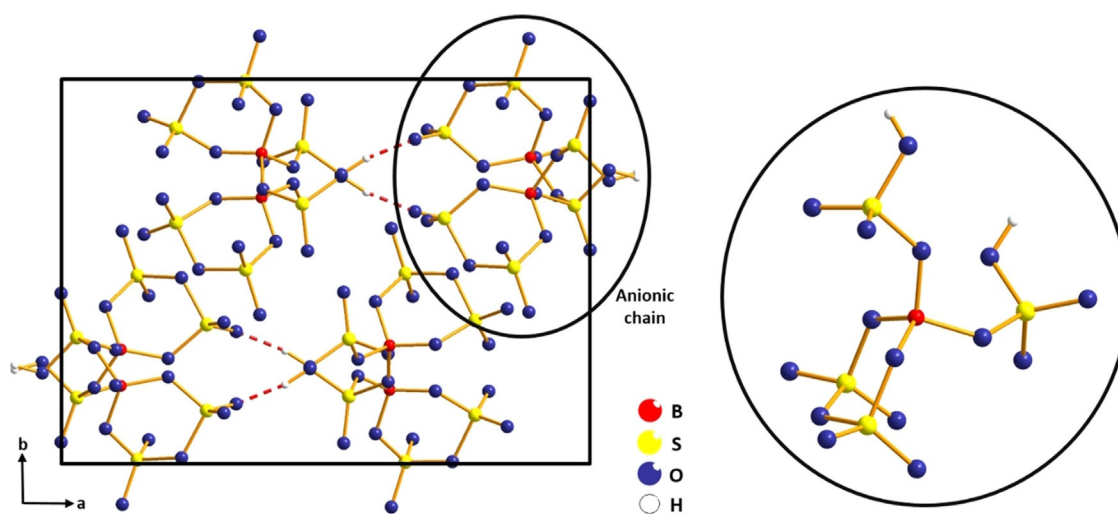

Figure 9. Left: Extended unit cell with hydrogen bridging of $H[B(SO_4)(S_2O_7)]$ and anionic chains running parallel to the crystallographic c-axis; right: Cut-out of one anionic chain in $H[B(SO_4)(S_2O_7)]$, emphasizing the repeating $\{B(HSO_4)_2(S_2O_7)\}$ units.

Chemistry–A European Journal

Review
doi.org/10.1002/chem.201905449

Chemistry Europe
European Chemical
Societies Publishing

occur, which point towards the terminal atoms of (S_2O_7) moieties. One hydrogen bridge can be classified as strong, the other as medium strong.[34]

Besides the expected elongation of the S–O bonds participating in the hydrogen bridging, the more pronounced elongation of the bridging S–O bond in the (S_2O_7) double tetrahedra (160.6 and 164.5 pm) compared to the non-protonated species in $Cs[B(SO_4)(S_2O_7)]$ is remarkable. The hydrogen bonding system is very similar to that found for H_2SO_4[35] and $H_2S_2O_7$.[36] According to this finding and the absence of any further charge compensating counter cation, $H[B(SO_4)(S_2O_7)]$ can be classified as a one-dimensional heteropolysulfuric acid.

Unconventional borosulfates with B-O-B bridges

$B_2S_2O_9$ was the second ever published and crystallographically characterized compound with corner sharing (SO_4) and (BO_4) tetrahedra.[22] Due to the lack of a charged anionic substructure, $B_2S_2O_9$ 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 HCl, which is the reason for the formation of the first crystal structure with a network of (SO_4) and (BO_4) including B-O-B bridges, dubbed in the formulation $[B_2O(SO_4)_2]$. In $B_2S_2O_9$, each boron atom is coordinated by three (SO_4) tetrahedra and each (SO_4) tetrahedron is bridged by, respectively one common oxygen atom to three (BO_4) tetrahedra. Furthermore, all (BO_4) tetrahedra are vertex-linked by the remaining oxygen atoms of the (BO_4) tetrahedra, whereas one oxygen atom of each (SO_4) tetrahedron remains uncoordinated, resulting in the formation of (B_2O_7) centered double layers (Figure 10).
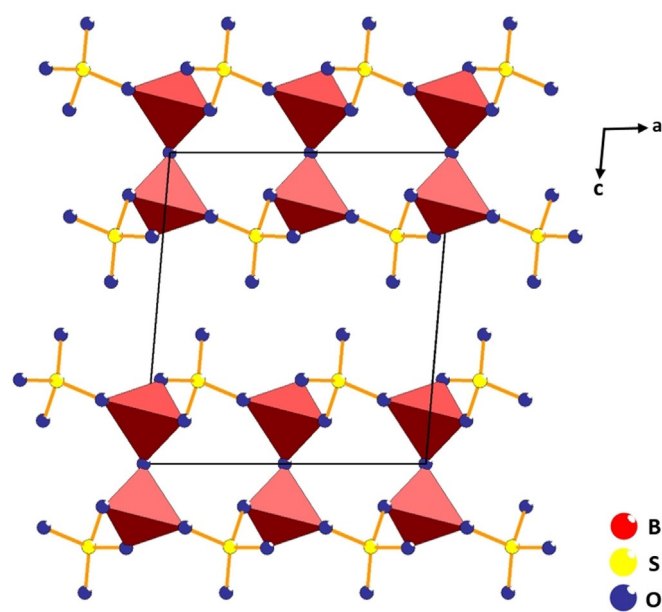

Figure 10. Extended unit cell of $B_2S_2O_9$ in projection on (0 1 0), exhibiting (B_2O_7)-centered double layers.

In contrast to the previously presented layered borosulfates, wherein zwölfer and vierer rings are the predominant motifs, $B_2S_2O_9$ reveals sechser rings of alternating (SO_4) and (BO_4) 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 $B_2S_2O_9$ the apices of the (SO_4) and (BO_4) tetrahedra point into different directions.

Another borosulfate with layer-like topology of the anionic substructure is $Cs_2B_2S_3O_{13}$, which was synthesized from the reaction of B_2O_3, CsCl, and oleum (65% SO_3) in an open silica crucible at 300 °C.[23] $Cs_3HB_4S_2O_{14}$ is a side-product of this reaction. The layers of $Cs_2B_2S_3O_{13}$ are composed of four (B_2O_7) units, which are bridged by four (SO_4) tetrahedra. Furthermore, each (B_2O_7) unit is chelated by one (SO_4) tetrahedron. Thus, heteropolyanionic monolayers with terminal (SO_4) tetrahedra occur. However, in the case of $Cs_2[B_2O(SO_4)_3]$ two oxygen atoms of the terminal (SO_4) 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 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 $Ba[B_2O(SO_4)_3]$, $Sr[B_2O(SO_4)_3]$ and $Pb[B_2O(SO_4)_3]$. The heteropolyanionic substructure consists of borosulfate double chains, built up by alternating (SO_4) and (BO_4) tetrahedra, exhibiting also B-O-B bridges, which allow the formation of double chains (Figure 12). Furthermore, two boron atoms are chelated by one (SO_4) tetrahedron. The obtained extended one-dimensional heteropolyanion obeys the topology of a ribbon silicate by maintaining B-O-B bridges. While $Ba[B_2O(SO_4)_3]$ and $Sr[B_2O(SO_4)_3]$ are isotypic, comprising alternating orientations of adjacent chains, the same chains occur in $Pb[B_2O(SO_4)_3]$ with the same orientation leading to a monoclinic distortion.[24]

Two different molecular anions were found for the alkali and alkaline earth subgroup metal borosulfates $Rb_4B_2S_4O_{17}$, α-$Mg[B_2O(SO_4)_6]$, and $A_4[B_2O(SO_4)_6]$ (A = Mg, Mn, Ni, Co, Zn).[23,24] Both contain (B_2O_7) units. In the case of α-$Mg[B_2O(SO_4)_6]$ and $A_4[B_2O(SO_4)_6]$ (A = Mg, Mn, Ni, Co, Zn), all terminal oxygen atoms of a central (B_2O_7) unit are saturated by monodentate (SO_4) tetrahedra. The latter remain without any further condensation, resulting in the molecular anion $[B_2O(SO_4)_6]^{8-}$. Referring to the formalism for silicates by Liebau, the anion $[B_2O(SO_4)_6]^{8-}$ can be explained as an open-branched quadruple tetrahedra chain. The β-polymorph of $Mg_4[B_2O(SO_4)_6]$ 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 α-polymorph. In addition, the molecular anion of $Rb_4B_2S_4O_{17}$ features central (B_2O_7) units. Herein, they are in *trans*-orientation coordinated by monodentate (SO_4) tetrahedra and the remaining oxygen atoms of the (B_2O_7) centers are saturated by means of two further bidentate chelating (SO_4) tetrahedra. The
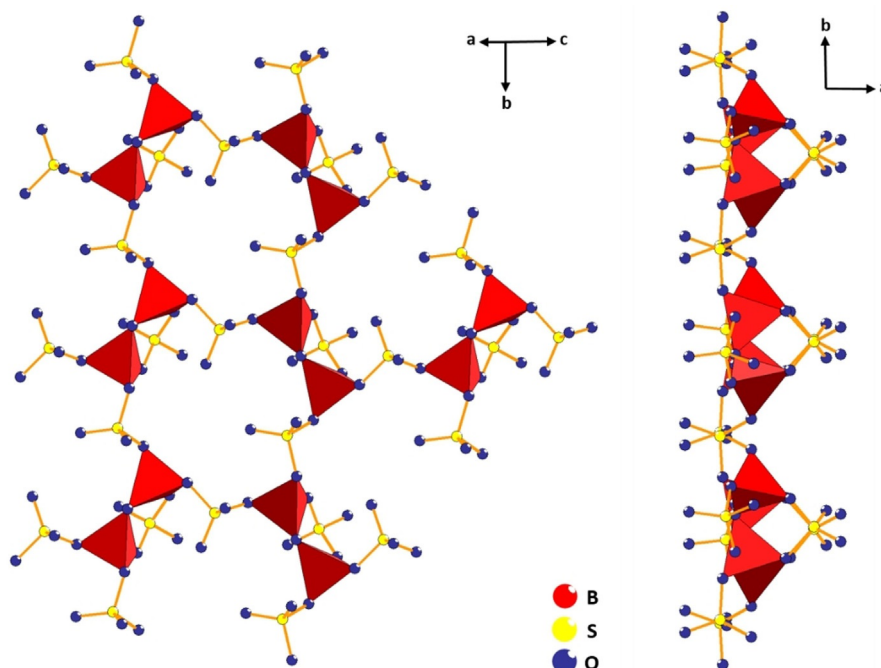
Chemistry–A European Journal

Review
doi.org/10.1002/chem.201905449

Chemistry Europe
European Chemical
Societies Publishing

Figure 11. Left: View on top of an anionic layer of $Cs_2B_2S_3O_{13}$; right: (SO$_4$) tetrahedra always pointing to the faces of the anionic layer in $Cs_2B_2S_3O_{13}$.
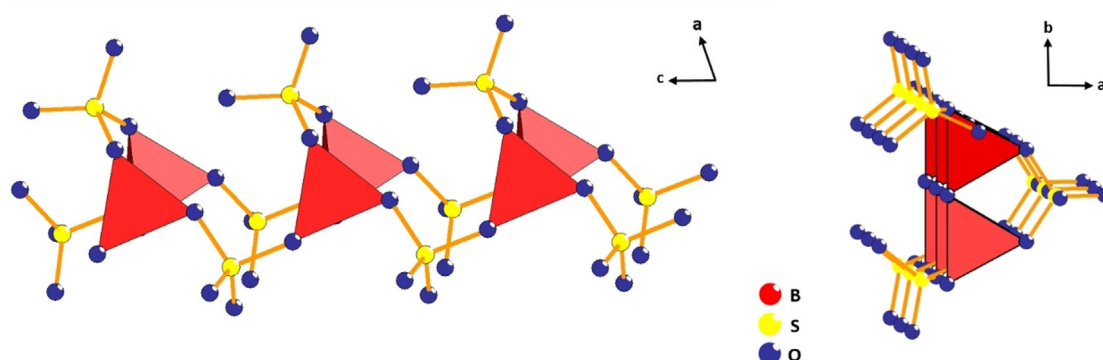
Figure 12. Left and right: Anionic chains with (B$_2$O$_7$) backbones in Ba[B$_2$S$_3$O$_{13}$]/ Ba[B$_2$O(SO$_4$)$_3$].
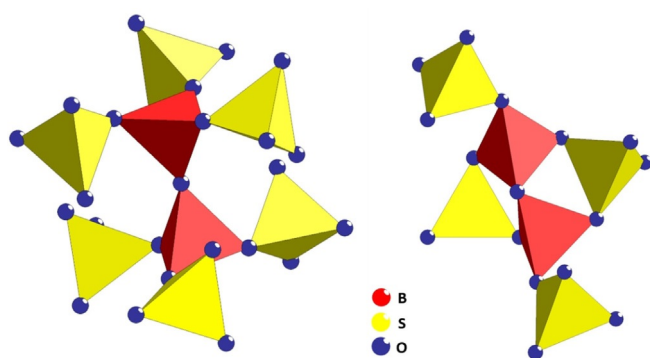
Figure 13. Left: molecular anion [B$_2$O(SO$_4$)$_6$]$^{8-}$ in α-Mg[B$_2$O(SO$_4$)$_6$] and A[B$_2$O(SO$_4$)$_6$] (A = Mn, Ni, Co, Zn); right: [B$_2$S$_4$O$_{17}$]$^{4-}$ anion in Rb$_4$B$_2$S$_4$O$_{17}$.

[B$_2$S$_4$O$_{17}$]$^{4-}$ anion resembles a cut-out of the borax structure [B$_4$O$_5$(OH)$_4$]$^{2-}$ with the monodentate (SO$_4$) tetrahedra being (OH)$^-$ anions and the chelating (SO$_4$) tetrahedra substituted by bridging (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 H$_5$[B(SO$_4$)$_4$] was found to be a super acid.[37] Due to the presence of optically active rare earth ions in RE_2[B$_2$(SO$_4$)$_6$] with RE = Y, La–Nd, Sm, Eu, Tb–Lu,[16] it was possible to measure reliable luminescence spectra for borosulfates for the very first time. The excitation and emission spectra of Ce^{3+}, Eu^{3+}, and

Chemistry–A European Journal

Review
doi.org/10.1002/chem.201905449

Chemistry Europe
European Chemical
Societies Publishing

Tb^{3+} 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 α-$M_4[B_2O(SO_4)_6]$ ($M=$ Mg, Mn, Co, Ni, Zn).[21] 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 S^{VI} via Se^{VI} to Te^{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.

Up to now, only a few boroselenates were characterized.[38] The crystal structure of $(H_3O)Na_6[B(SeO_4)_4](SeO_4)$ is built up by „Zunyite-like" $[B(SeO_4)_4]^{5-}$ anions and additional isolated $(SeO_4)^{2-}$ tetrahedra. The structure is closely related to the borophosphates $A_6[B(PO_4)_4](PO_4)$ ($A=$ Sr, Pb).[39,40] The structure of $K_4[BSe_4O_{15}(OH)]$ is also built up by „Zunyite-like" anions, and therefore similar to the protonated borosulfate $K_4[BS_4O_{15}(OH)]$. The structures of $A_3[B(SeO_4)_3]$ ($A=$ Rb, Cs) are again closely related to borosulfates and borophosphates as the Rb-compound crystallizes isotypically to $Ba[B(PO_4)_3]$[41] and $A[B(SO_4)_3]$ ($A=$ K, Rb).

The larger ionic radii of Te^{VI} prefers an octahedral arrangement of the surrounding oxygen atoms. This is also reflected on the respective oxygen acids: While H_2SO_4 and H_2SeO_4 are strong Brønsted acids with the chalcogens tetrahedrally coordinated by oxygen atoms, telluric acid H_6TeO_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 $Na_2RE_2TeO_4(BO_3)_2$ ($RE=$ Y, Dy–Lu),[42] there are isolated oligomers of TeO_6 octahedra that are *trans*-connected with two trigonal planar (BO_3) units by sharing common corners. In
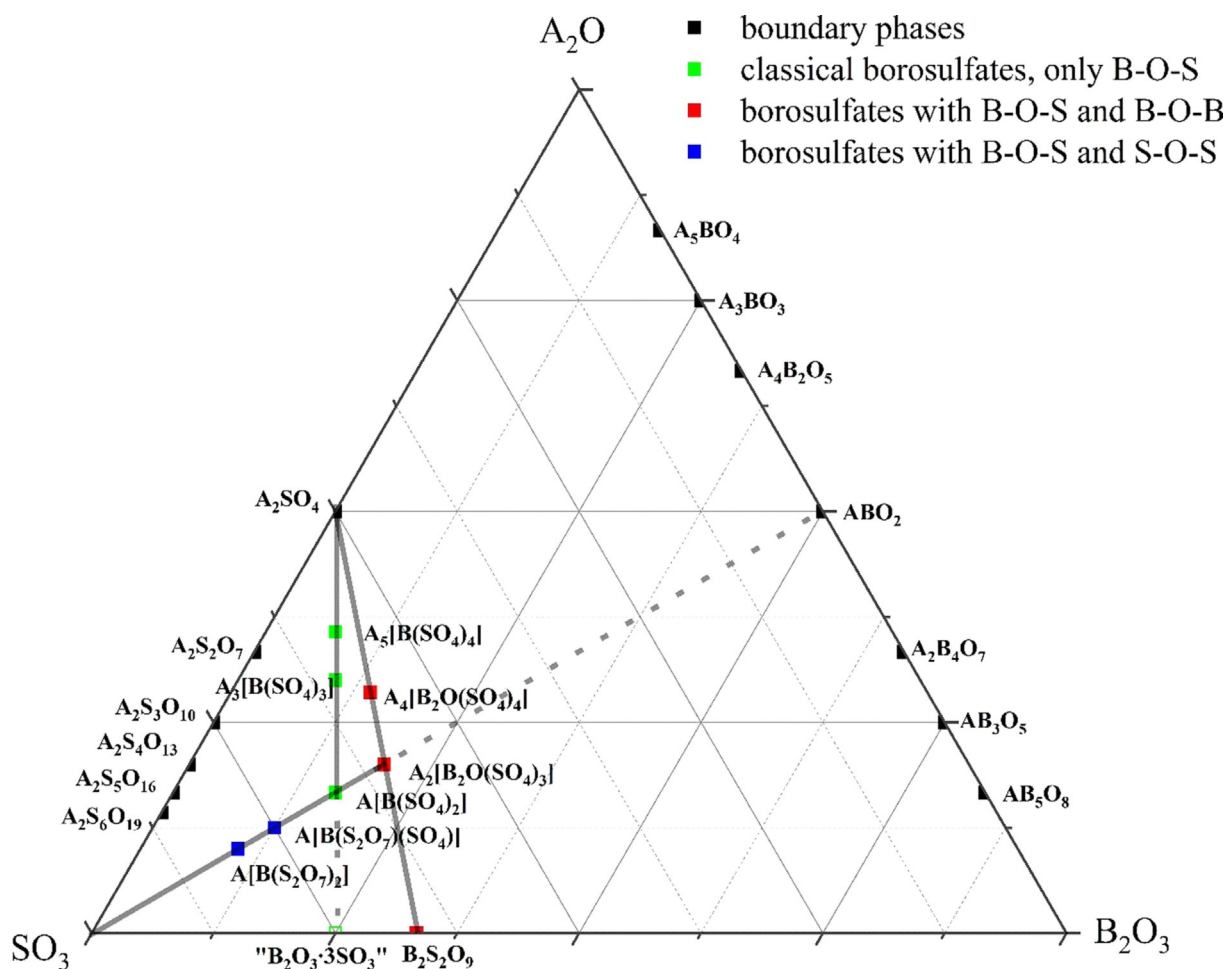

Figure 14. Ternary plot of borosulfates charge compensated by monovalent cations. The classical borosulfates are all located on a line between A_2SO_4 and the composition „$B_2O_3 \cdot 3SO_3$". The unconventional borosulfates with S-O-S bridges are placed on a line between SO_3 and ABS_2O_8 and the unconventional borosulfates with B-O-B bridges are found on a line between A_2SO_4 and $B_2S_2O_9$.

Chemistry–A European Journal

Review
doi.org/10.1002/chem.201905449

Chemistry Europe
European Chemical
Societies Publishing

$Ba_4B_8TeO_{19}$, the anionic borotellurate part forms a complex 3D framework that may be described as $\{[TeO_{4/2}O_2]^{2-}\ 6[BO_{4/2}]^-\ 2[BO_{3/2}]\}^{8-}$ [43].

A complete separation of the different polyhedra is observed in Bi_3BTeO_9 with isolated TeO_6 octahedra and trigonal planar BO_3 units.[44] Separated polyhedra are also present in $A_3HB_4S_2O_{14}$ (A = Rb, Cs),[23] where planar sheets with the composition B_2O_3 are intercalated by A^+, $(SO_4)^{2-}$, and $(HSO_4)^-$ represented by the formula $A_3H(SO_4)_2(B_2O_3)_2$. 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 (SO_4) and (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 (0D) as found for $K_5[B(SO_4)_4]$ 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_3) 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_2SO_4 and a hypothetic phase with the composition „$B_2O_3 \cdot 3\,SO_3$". The unconventional borosulfates with S-O-S bridges are placed on a line between SO_3 and $A[B(SO_4)_2]$, whereas the unconventional borosulfates with B-O-B bridges are found on a line between A_2SO_4 and $B_2S_2O_9$. 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, as well as intercalation of organic solvents, only to mention some. 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.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

[1] F. Liebau, *Structural Chemistry of Silicates*, Springer, Heidelberg, **1985**.
[2] a) W. A. Deer, R. A. Howie, J. Zussmann, *An Introduction to Rock-Forming Minerals*, Langmanns, London, **1966**; b) S. V. Krivovichev, *Minerals as Advanced Materials II*, Springer, Heidelberg, **2012**; c) J. Y. Ying, C. P. Mehnert, M. S. Wong, *Angew. Chem. Int. Ed.* **1999**, *38*, 56 – 77; *Angew. Chem.* **1999**, *111*, 58 – 82; d) W. Xun, Z. Jing, C. Jun, Z. Kebin, L. Yadong, *Angew. Chem. Int. Ed.* **2004**, *43*, 2017 – 2020; *Angew. Chem.* **2004**, *116*, 2051 – 2054.
[3] S. Oliver, A. Kupermann, G. A. Ozin, *Angew. Chem. Int. Ed.* **1998**, *37*, 46 – 62; *Angew. Chem.* **1998**, *110*, 48 – 64.
[4] W. Loewenstein, *Am. Mineral.* **1954**, *39*, 92 – 96.
[5] A. Gupta, N. Chatterjee, *Am. Mineral.* **1978**, *63*, 58 – 65.
[6] L. V. Schindler, A. Becker, M. Wieckhusen, T. Klüner, M. S. Wickleder, *Angew. Chem. Int. Ed.* **2016**, *55*, 16165 – 16167; *Angew. Chem.* **2016**, *128*, 16399 – 16401.
[7] M. Daub, K. Kazmierczak, P. Gross, H. Höppe, H. Hillebrecht, *Inorg. Chem.* **2013**, *52*, 6011 – 6020.
[8] H. A. Höppe, K. Kazmierczak, M. Daub, K. Förg, F. Fuchs, H. Hillebrecht, *Angew. Chem. Int. Ed.* **2012**, *51*, 6255 – 6257; *Angew. Chem.* **2012**, *124*, 6359 – 6362.
[9] M. Daub, H. A. Höppe, H. Hillebrecht, *Z. Anorg. Allg. Chem.* **2014**, *640*, 2914 – 2921.
[10] P. Gross, A. Kirchhain, H. A. Höppe, *Angew. Chem. Int. Ed.* **2016**, *55*, 4353 – 4355; *Angew. Chem.* **2016**, *128*, 4426 – 4428.
[11] L. Dong, S. Pan, Y. Wang, H. Yu, Y. Lin, S. Han, *Mater. Res. Bull.* **2015**, *63*, 93 – 98.
[12] CSD-1934713 at www.ccdc.cam.ac.uk/structures.
[13] CSD-1934712 at www.ccdc.cam.ac.uk/structures.
[14] CSD-1934711 at www.ccdc.cam.ac.uk/structures.
[15] J. Bruns, M. Podewitz, O. Janka, R. Pöttgen, K. Liedl, H. Huppertz, *Angew. Chem. Int. Ed.* **2018**, *130*, 9693 – 9697; *Angew. Chem.* **2018**, *57*, 9548 – 9552.
[16] P. Netzsch, M. Hämmer, P. Gross, H. Bariss, T. Block, L. Heletta, R. Pöttgen, J. Bruns, H. Huppertz, H. A. Höppe, *Dalton Trans.* **2019**, *48*, 4387 – 4397.
[17] M. Daub, K. Kazmierczak, H. A. Höppe, H. Hillebrecht, *Chem. Eur. J.* **2013**, *19*, 16954 – 16962.
[18] J. Bruns, M. Podewitz, M. Schauperl, K. Liedl, O. Janka, R. Pöttgen, H. Huppertz, *Eur. J. Inorg. Chem.* **2017**, 3981 – 3989.
[19] S. Schönegger, J. Bruns, B. Gartner, K. Wurst, K. Liedl, H. Huppertz, *Z. Anorg. Chem.* **2018**, *644*, 1702 – 1706.
[20] J. Bruns, M. Podewitz, M. Schauperl, B. Joachim, K. Liedl, H. Huppertz, *Chem. Eur. J.* **2017**, *23*, 16773 – 16781.
[21] P. Netzsch, P. Gross, H. Takahashi, H. A. Höppe, *Inorg. Chem.* **2018**, *57*, 8530 – 8539.
[22] C. Logemann, M. S. Wickleder, *Angew. Chem. Int. Ed.* **2013**, *52*, 14229 – 14232; *Angew. Chem.* **2013**, *125*, 14479 – 14482.
[23] M. Daub, H. Hillebrecht, *Eur. J. Inorg. Chem.* **2015**, 4176 – 4181.
[24] P. Netzsch, P. Gross, H. Takahashi, S. Lotfi, J. Brgoch, H. A. Höppe, *Eur. J. Inorg. Chem.* **2019**, 3975 – 3981.
[25] W. A. Herrmann, G. P. Albanese, R. B. Manetsberger, P. Lappe, H. Bahrmann, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 811 – 813; *Angew. Chem.* **1995**, *107*, 893 – 895.
[26] B. Ewald, Y.-X. Huang, R. Kniep, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1517 – 1540.
[27] a) T. Balic-Žunic, E. Makovicky, *Acta Crystallogr. Sect. B* **1996**, *52*, 78 – 81; b) E. Makovicky, T. Balic-Žunic, *Acta Crystallogr. Sect. B* **1998**, *54*, 766 – 773.
[28] L. Pauling, *J. Am. Chem. Soc.* **1929**, *51*, 1010 – 1026.
[29] Y. A. Malinovskii, E. A. Pobedimskaya, *Dokl. Akad. Nauk SSSR* **1976**, *229*, 1101 – 1104.

[30] N. A. Yamnova, R. K. Rastsvetaeva, D. Y. Pushcharovskii, T. Mernaf, M. G. Mikheeva, A. P. Homyakov, *Kristallografiya* **1992**, *37*, 334–343.

[31] a) M.-F. Tang, P.-Y. Chiang, Y.-H. Su, G.-Y. Hou, B.-C. Chang, K. H. Lii, *Inorg. Chem.* **2008**, *47*, 8985–8989.

[32] C. Logemann, M. S. Wickleder, *Inorg. Chem.* **2011**, *50*, 11111–11116.

[33] a) C. Logemann, T. Klüner, M. S. Wickleder, *Chem. Eur. J.* **2011**, *17*, 758–760; b) C. Logemann, D. Gunzelmann, T. Klüner, J. Senker, M. S. Wickleder, *Chem. Eur. J.* **2012**, *18*, 15495–15503; c) C. Logemann, K. Rieß, M. S. Wickleder, *Chem. Asian J.* **2012**, *7*, 2912–2920.

[34] T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48–76; *Angew. Chem.* **2002**, *114*, 50–80.

[35] E. Kemnitz, C. Werner, S. Trojanov, *Acta Crystallogr. Sect. C* **1996**, *52*, 2665–2668.

[36] W. Hönle, *Z. Kristallogr.* **1991**, *196*, 279–288.

[37] R. J. Gillespie, T. E. Peel, E. A. Robinson, *J. Am. Chem. Soc.* **1971**, *93*, 5083–5087.

[38] M. Daub, H. Hillebrecht, *Chem. Eur. J.* **2015**, *21*, 298–304.

[39] N. Shin, J. Kim, D. Ahn, K.-S. Sohn, *Acta Crystallogr. Sect. C* **2005**, *61*, i54–56.

[40] E. L. Belokoneva, E. A. Ruchkina, O. V. Dimitrova, S. Yu. Stefanovich, *Russ. J. Inorg. Chem.* **2001**, *46*, 179–185.

[41] R. Kniep, G. Goezel, B. Eisenmann, C. Roehr, M. Asbrand, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 749–751; *Angew. Chem.* **1994**, *106*, 791–793.

[42] J.-H. Feng, C.-L. Hu, X. Xu, F. Kong, J.-G. Mao, *Inorg. Chem.* **2015**, *54*, 2447–2454.

[43] L. Liu, J. Young, M. Smeu, P. S. Halasyamani, *Inorg. Chem.* **2018**, *57*, 4771–4776.

[44] M. Daub, M. Krummer, A. Hoffmann, L. Bayarjargal, H. Hillebrecht, *Chem. Eur. J.* **2017**, *23*, 1331–1337.