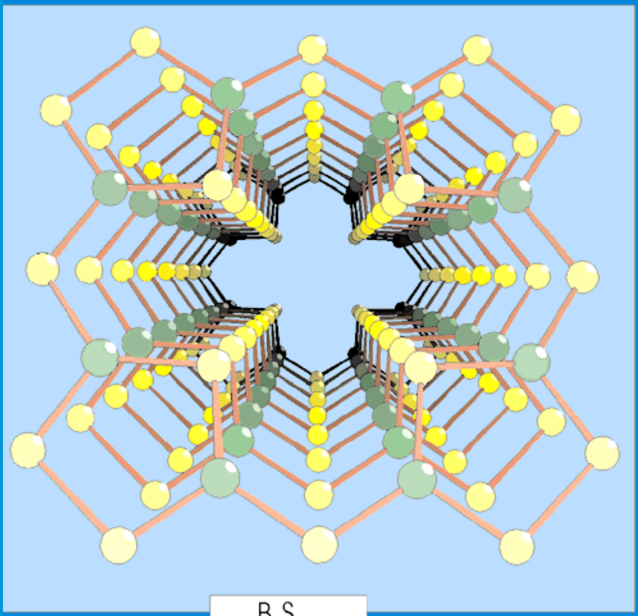
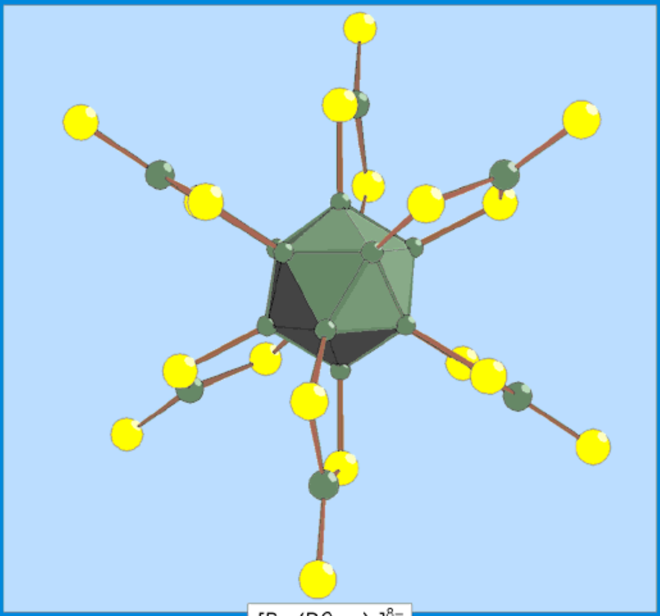
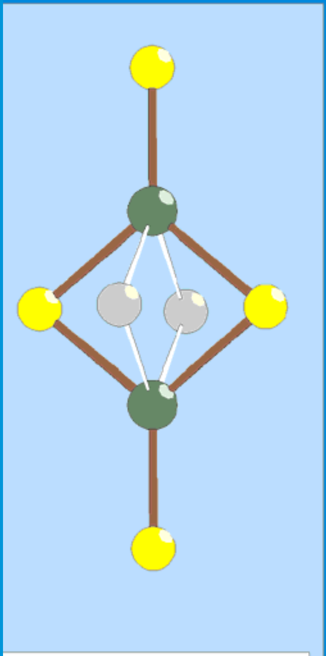


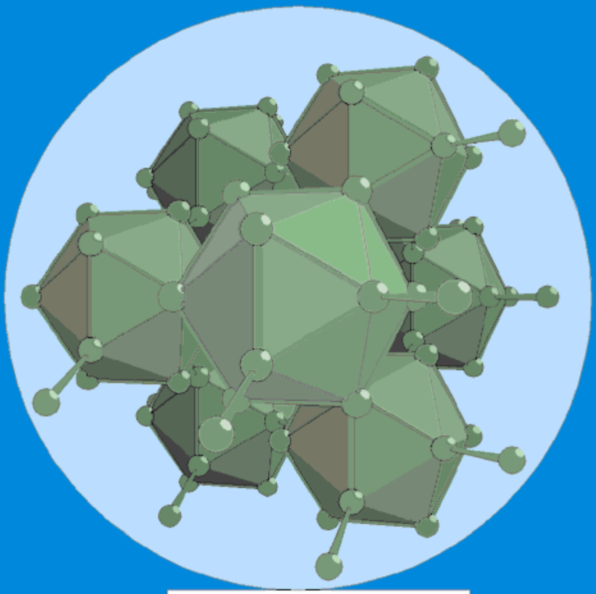
B_8S_{16}



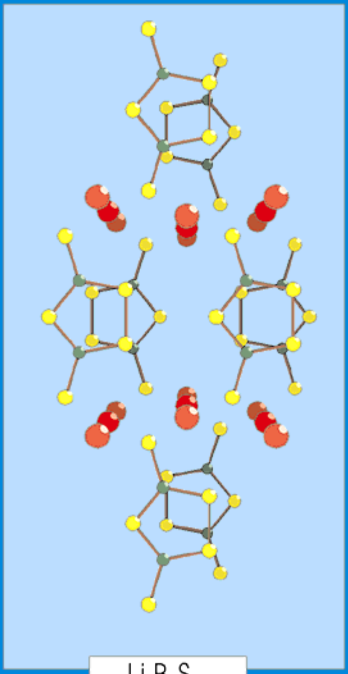
$[B_{12}(BSe_3)_6]^{8-}$



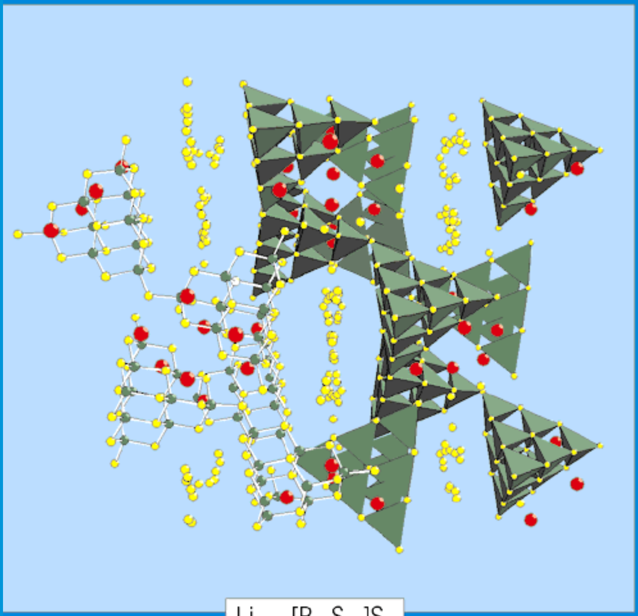
disordered $[B_2S_4]^{2-}$ anion



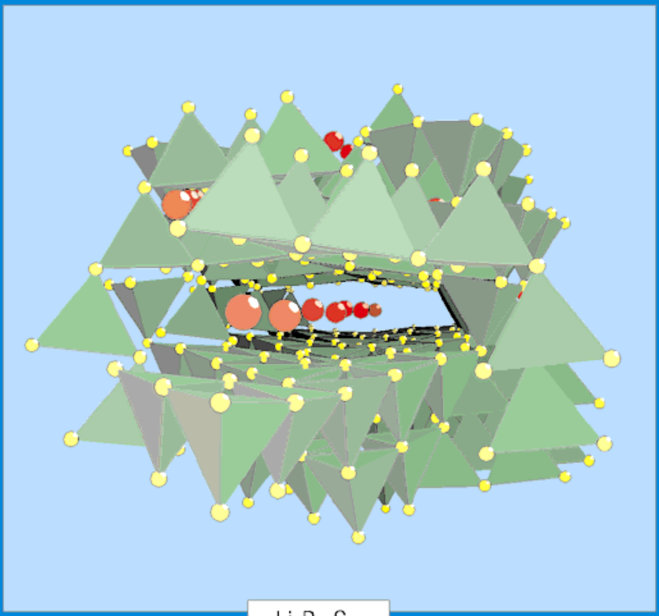
rhombohedral boron



$Li_2B_2S_5$



$Li_{6+2x}[B_{10}S_{18}]S_x$



$Li_9B_{19}S_{33}$

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Boron – Sulfur and Boron – Selenium Compounds—From Unique Molecular Structural Principles to Novel Polymeric Materials

Olaf Conrad, Christoph Jansen, and Bernt Krebs*

Dedicated to Professor Dr. Walter Siebert

Boron is known to exhibit an unusual chemistry in all of its compounds. In addition, it shows a high tendency to form amorphous products over a wide range of temperatures. In the compounds with the heavier chalcogens, sulfur and selenium, both features are combined to open an intriguing field to the preparative chemist as well as to the crystallographer, the physicist, and the theoretician. In the past 15 years modern preparative methods have led to novel and often unexpected boron – sulfur and boron – selenium compounds, for example the persubstituted B_{12} icosahedron in the $[B_{12}(BSe_3)_6]^{8-}$ ionic molecule that features a planar B_3Se_2 ring at the chelating ligand, and the thioborate macromolecular anions that combine adamantanoid and superadamantanoid units in fascinating frameworks with a quasi-amorphous distribution of highly mobile lithium ions. An overwhelming number of different structures—not yet covered under one rule for all—has to be sorted and classified. Technical application of amorphous lithium thioborates call for an understanding of the mechanisms of ionic conduction in order to find rules for tailoring both crystalline and amorphous materials for intense physicochemical and theoretical examination. Preparation techniques have to be developed and refined to produce high-purity material in glassy, microcrystalline, and single crystalline aggregation at will.

Keywords: boron · selenium · solid-state structures · sulfur

1. Introduction

In medieval times amorphous alkaline oxoborates already played a significant role in daily life,[1] but the first preparation of elemental boron is attributed to the works of F. von Crell,[2] H. Davy,[3] and J. L. Gay-Lussac and L.-J. Thenard[4] in the early 19th century. In 1824 J. J. Berzelius[5] published the first reported boron chalcogenide,[6] “threefold sulfur boron” (“Dreifachschwefelbor”). Nevertheless, the knowledge about boron – sulfur and boron – selenium compounds remained very sparse for almost another 150 years. Problems of various kinds contributed to the reasons that made this class of compounds resist its examination:

- High-purity elemental boron was very difficult to get access to.
- The choice of reaction container material remained difficult for several years, because quartz glass is attacked by boron and results in a quantitative exchange of silicon with boron with formation of B_2O_3 and SiQ_2 ($Q = S$, Se), whereas the chalcogenophilicity of most metals excluded the common metal containers.
- The reaction products and often even the starting materials are readily oxidized and/or hydrolyzed by moist air.
- Chalcogenoborates tend to remain in an amorphous rather than a crystalline state.

Over the past 25 years the overcoming of these problems by improved high-temperature solid- and molten-state syntheses led to a better and deeper insight into the structural diversity, the chemistry, the bonding character, and some physical properties of binary, ternary, and quaternary chalcogenoborates. This review will give a comprehensive overview of the structurally characterized boron chalcogenides, molecular boron – chalcogen heterocycles, Lewis acid – base complexes of boron halides and chalcogenic electron donors, and thio- and selenoborates. This review will also cover their preparation, structural principles, and some of their physical properties.

2. Synthetic Principles

The electron-deficient element boron is a more or less strong Lewis acid depending on its neighbors. In particular

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boron with an empty or partially occupied p_z orbital, that is a sp^2-hybridized boron atom, is readily attacked by Lewis bases. Therefore any high-temperature solid-state or molten-state synthesis must be carried out in vacuo or in an inert gas atmosphere. The choice of container material is crucial for the success of the synthesis. Sealed, evacuated silica or quartz glass tubes with several layers of glassy carbon on the inner walls have proven best for daily use and for routine purposes. However, very long annealing periods at elevated temperatures ($t > 5$ d, $T > 750$ K) or reactions at very high temperatures ($T > 1100$ K) necessitate the use of tantalum pipe that is sealed under argon at atmospheric pressure and incorporated into an evacuated quartz glass ampoule. Alternatively, the use of graphite, boron nitride, or silicon-free aluminium oxide crucibles in stainless steel cylinders, and of evacuated quartz-glass tubes has also shown satisfactory results. Regular Schlenk techniques in dried aprotic solvents are sufficient for the synthesis of planar molecular boron–chalcogen ring compounds as well as for their further reactions.

3. Boron in Trigonal-planar Coordination

3.1. Binary Boron Chalcogenides

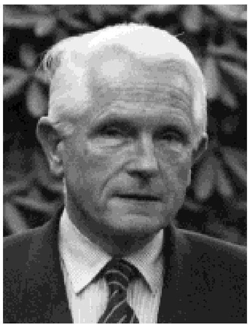
Aluminium shows coordination numbers not smaller than four in its binary chalcogenides, whereas in the case of boron chalcogenides the only exception to a trigonal-planar coordination is the metastable high-pressure phase B_2O_3-II which has boron distributed in the tetrahedral voids of a hexagonal close-packing arrangement of oxygen atoms.[7, 8] Although the ambient pressure modification B_2O_3-I exhibits boron along with trigonal-planar coordination, its three-dimensional interconnection differentiates the oxide from the sulfides and the selenide.[9] Despite a large number of publications on the existence of boron chalcogenides of different compositions[10–17] only B_2S_3,[18, 19] $(BS_2)_n$,[19, 20] B_8S_{16},[19, 20] and $(BSe_2)_n$[19, 20] have been characterized by means of single crystal X-ray structure determination (Figure 1). Suitable, but micro-twinned, colorless single crystals of B_2S_3 were prepared by controlled thermal decomposition of $Ag_6B_{10}S_{18}$ at about 1000 K. Colorless $(BS_2)_n$ and orange $(BSe_2)_n$ in amorphous and microcrystalline states can be prepared from the elements at temperatures of 1100 to 1300 K. Crystalline samples can be obtained by sublimation of the amorphous crude products in a temperature gradient of 670 to 400 K. Colorless B_8S_{16} is a by-product of the sublimation of $(BS_2)_n$ at the cooler end ($T < 373$ K) of the sublimator in only a few milligrams yield. Any attempt to produce larger quantities of pure B_8S_{16}, though very much desired, has so far failed.

B_2S_3, the “normal” boron sulfide according to the valencies, has a layer structure. Sheets of interconnected B_3S_3 and B_2S_2 rings extend throughout the crystal. Each of the B_3S_3 rings is connected by sulfur bridges to two B_3S_3 rings and one B_2S_2 ring. In the structure exocyclic B–S bond lengths are longer than endocyclic ones. A closer look shows that the average value is 1.817 Å, whereas the average B–S_{endo} bond length is 1.794 Å inside the six-membered ring and 1.811 Å in the

Olaf Conrad, born in 1967 in Berlin, Germany, studied chemistry at the University of Münster, where he received his Diplom in 1995. For his doctoral thesis he worked on the chemistry of aluminum chalcogenides and silver telluride and developed a further interest in the chemistry of thio- and selenoborates. He will spend a postdoctoral year in the group of Prof. Dr. R. S. Laitinen in Oulu/Finland, working on the chemistry of silicon sulfur and silicon selenium compounds.


O. Conrad


C. Jansen


B. Krebs

Christoph Jansen, born in 1964 in Billerbeck (Westfalen), Germany, started his career as a technician in chemistry (Chemielaborant) before he started his studies in 1988 at the University of Münster. He obtained his PhD in Chemistry in 1997 with a thesis on the synthesis and structures of thio- and selenoborates.

Bernt Krebs was born in 1938 in Gotha, Germany. He studied Chemistry at the University of Göttingen, Germany (1958–1963), and recieved his PhD in 1965 for studies on the crystal structure and chemistry of trithiocarbonic acid under supervision of G. Gattow. Thereafter followed postdoctoral research at Brookhaven National Laboratory (X-ray and neutron diffraction on biological macromolecules), Habilitation in Inorganic Chemistry in Göttingen, and faculty positions in Kiel (1971), Bielefeld (1974), and Münster, where he has been a Full Professor since 1977. He received the Max Planck Research Award in 1992 and the Wilhelm Klemm Award of the GDCh in 1997. He is a member of the Academy of Sciences and Literature in Mainz, Germany. His primary research interests include chemical and structural studies on thio and seleno compounds, chalcogen halides, chalcogenide solid-state compounds, transition metal oxygen compounds, cisplatin-A analogues, and metalloproteins as well as model complexes for these metalloproteins.

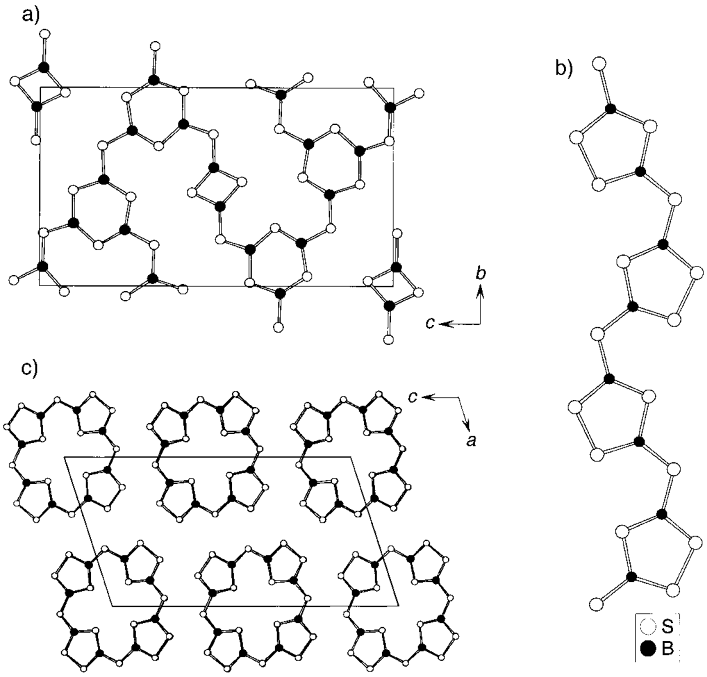


Figure 1. a) Crystal structure of B_2S_3; b) strand structure in $(BS_2)_n$ and $(BSe_2)_n$; c) crystal structure of B_8S_{16}.

strained four-membered ring. $(BQ_2)_n$ (Q = S, Se) exhibit layered structures, in which zigzag chains of interconnected 1,2,4-trithia(selena)-3,5-diborolane rings are oriented in a parallel manner within a plane and antiparallel to the strands of neighboring layers. In B_8S_{16} four of these B_2S_3 rings are connected to form a macrocycle that is topologically an analogue of porphin ($C_{20}H_{14}N_4$). The tetramers are stacked to form columns of parallel molecules. The plane vectors are tilted with respect to the columnar axis, which coincides with the crystallographic *b* axis. All rings are planar within experimental errors. The spacing between two layers is 3.48 Å in $(BS_2)_n$, which is significantly shorter than in B_2S_3 (3.81 Å) and the plane distance in B_8S_{16} (3.73 Å). The mean B–Q distance in the binary sulfides is 1.805 Å, in $(BSe_2)_n$ it is 1.934 Å. The transannular sulfur···sulfur distances of about 4.6 Å in B_8S_{16} suggest the capability of this molecule to incorporate Cu^{2+} ions in solutions. MO calculations indicate an energy gain comparable to that of cyclic thioether complexes of Cu^{2+} ions.[21]

3.2. Neutral Molecular Boron–Chalcogen Heterocycles

In 1955 E. Wiberg and W. Sturm found that $B_2S_3 \cdot BX_3$ (X = Cl, Br) in the early works of A. Stock at the beginning of the century[22] had to be rewritten as $(BSX)_3$,[23] a derivative of the hypothetical benzene analogue $H_3B_3S_3$. This initiated a broad research program on cyclic boron–chalcogen compounds in the following years. Four-membered 1.3.2.4-dithiadiboretanes,[24] five-membered 1.2.4.3.5-trithia(selena)diborolanes[25–27] and six-membered 1.3.5.2.4.6-trithia(selena)triborinanes[28–32] with several organic or halogen ligands were in most cases characterized by spectroscopic experiments. Structural information by electron diffraction experiments on gas phase molecules of $B_2S_3Cl_2$ and $B_2S_3(CH_3)_2$ proved these molecules to be exactly planar[33, 34] as was derived from the spectroscopic data and predicted from theoretical semiempirical calculations.[35] E. Wiberg and W. Sturm proposed the structure of $H_3B_3S_6$ to be a cyclic trimeric metathioboric acid,[29] which was proven in 1973 by single crystal X-ray structure determination.[36] The B_3S_6 entities deviate slightly from a perfectly planar arrangement. The average B–S distance is 1.803 Å. The proposed structure of $H_2B_2S_4$ by E. Wiberg and W. Sturm has not yet been verified, but J. A. Forstner and E. L. Muetterties reported the preparation of $B_2S_2(N(C_2H_5)_2)_2$,[24] the structure of which was verified later.[37] In 1974 W. Schwarz, H. D. Hausen, and H. Hess succeeded in the structure determination of $B_3S_3Br_3$.[38] The average B–S bond length of this planar molecule is 1.807 Å.

In recent years we were successful in several cases with systematic approaches to the preparation of suitable single crystals of molecular boron–chalcogen ring compounds, but a general method for this class of compounds is yet to be found. Selected data from the crystal structure determinations are shown in Table 1.[39, 40] In $B_3Q_3Ph_3$ (Q = S, Se) the six-membered heterocycle is planar within experimental errors.

Table 1. Structurally characterized molecular boron–chalcogen ring compounds and mean B–S(Se) distances [Å].

Compound	$\bar{d}$(B–Q)	Ref.	Compound	$\bar{d}$(B–Q)	Ref.
$B_2S_2[N(C_2H_5)_2]_2$	1.84	[37]	$B_3S_3Br_3$	1.807	[38]
$B_2S_3Cl_2$	1.794	[33, 34]	$B_3S_3Ph_3$	1.808	[39, 40]
$B_2S_3(CH_3)_2$	1.803	[33, 34]	$B_2Se_3I_2$	1.91	[39, 40]
$B_2S_3I_2$	1.795	[39, 40]	$B_2Se_3Ph_2$	1.93	[39, 40]
$B_2S_3Ph_2$	1.805	[39, 40]	$B_3Se_3Ph_3$	1.93	[39, 40]
$H_3B_3S_6$	1.803	[36]			

The B–Q bond lengths vary slightly and average to 1.808 and 1.93 Å for Q = S and Se, respectively. This is in excellent agreement to the bond lengths in the binary compounds and in $H_3B_3S_6$[36] and $B_3S_3Br_3$.[38] The three phenyl groups are rotated about the B–C bonds with different rotational angles. The B–C distances average to 1.55 Å in $B_3S_3Ph_3$ and 1.56 Å in $B_3Se_3Ph_3$, which are much longer than an average C(sp^2)–C(sp^2) bond length of about 1.42 Å. These data indicate that there is no, or very little, contribution of the π orbitals to the B–C bonds.

The five-membered ring in $B_2Q_3I_2$ (Q = S, Se) is planar within experimental error, whereas in $B_2S_3Ph_2$ and in $B_2Se_3Ph_2$ the bridging chalcogen atom is moved out of the plane. Figure 2 gives a representation of $B_2Se_3Ph_2$ and $B_2S_3I_2$. The angle between the normal vectors of planes B(1),Se(2),Se(2a),B(1a) and B(1),Se(1),B(1a) is 7.40°. The average B–Q bond lengths are 1.795 Å in $B_2S_3I_2$, 1.805 Å in $B_2S_3Ph_2$, 1.91 Å in $B_2Se_3I_2$, and 1.93 Å in $B_2Se_3Ph_2$.

3.3. Ternary Chalcogenoborates

Early works report on a variety of chalcogenoborates, often in contradiction to each other. These include the

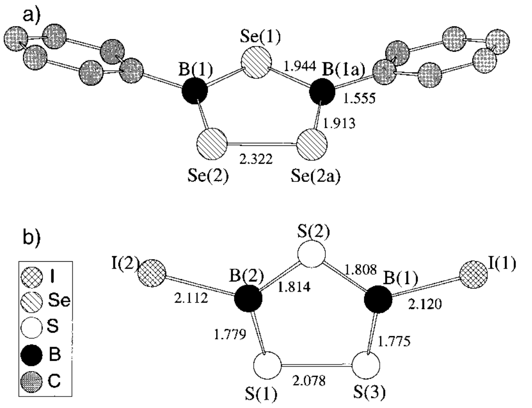


Figure 2. Crystal structures and bond lengths of a) $B_2Se_3Ph_2$ and b) $B_2S_3I_2$.

Table 2. Structurally characterized thio- and selenoborates and mean B–S(Se) distances [Å].

Compound	$\bar{d}(B_{tr}-S)$[a]	$\bar{d}(B_{tr}-S_{ex})$[b]	$\bar{d}(B_{tr}-S_{en})$[c]	$\bar{d}(B_{te}-S)$[d]	Ref.
Li_3BS_3	1.830				[56, 57]
Tl_3BS_3	1.833				[58]
$Sr_3[BS_3]_2$	1.826				[65]
$Ba_3[BS_3]_2$	1.814				[65]
Li_2CsBS_3	1.825				[60]
$LiSrBS_3$	1.824				[57]
$LiBaBS_3$	1.823				[59]
$KBa_4[BS_3]_3$	1.824				[61]
$K_4Ba_{11}[BS_3]_8S$	1.825				[60]
$Ba_{2.8}Sr_{4.2}[BS_3]_4S$	1.822				[60]
$Cs_2B_2S_4$	1.821	1.740	1.861		[62]
$Na_3B_3S_6$	1.805	1.768	1.824		[19, 64]
$K_3B_3S_6$	1.798	1.775	1.810		[19]
$Rb_3B_3S_6$	1.800	1.760	1.821		[65]
$Sr_3[B_3S_6]_2$	1.786	1.770	1.794		[65]
$LiSrB_3S_6$	1.804	1.778	1.817		[65]
$LiBaB_3S_6$	1.804	1.771	1.821		[59]
BaB_2S_4	1.808	1.786	1.821	1.926	[83]
SrB_2S_4				1.929	[69]
$TlBS_2$				1.930	[69, 70]
$Pb_4B_4S_{10}$				1.927	[19]
$Na_6B_{10}S_{18}$				1.922	[71]
$Ag_6B_{10}S_{18}$				1.915	[75]
$Li_{6+2x}[B_{10}S_{18}]S_x$	$(x \approx 2)$			1.920	[74]
$Li_5B_7S_{13}$				1.922	[74, 76]
$Li_9B_{19}S_{33}$				1.925	[76]
$Li_{4-2x}Sr_{2+x}B_{10}S_{19}$	$(x \approx 0.27)$			1.925	[71]
$Li_3Na_5B_{10}S_{19}$				1.925	[61]
Tl_3BSe_3	1.953				[58]

[a] Mean B–S(Se) distance with the boron center in a trigonal-planar coordination site; [b] mean exocyclic B_{tr}–S distance; [c] mean endocyclic B_{tr}–S distance; [d] mean B–S distance with the boron center in a tetrahedral coordination site.

classes of compounds M^IBS,[41, 42] M^IBS_2,[41, 43–48] M^IBSe_2,[41] $M^{II}(BS_2)_2$,[49, 50] $M^I_4B_2S_5$,[45, 48] $M^{II}_2B_2S_5$,[50–53] $M^I_3BS_3$,[45, 47] $M^I_8B_2S_7$,[45, 48] $M^I_5BS_4$,[54] $M^I_4B_6S_{11}$,[47] M^IBS_3,[47, 55] and $M^I_2B_2S_5$.[55] By using the isotypic nature of the well-known structure of sodium trimetaoxoborate Chopin derived the structures of $Na_3B_3S_6$ and $K_3B_3S_6$ from X-ray diffraction powder patterns,[43, 46] but apart from an approximate model of $Pb_2B_2S_5$[52] structural data of chalcogenoborates was not published until the mid seventies.

Figure 3 shows the four types of thioborate anions with boron in solely trigonal planar coordination sites. It should be mentioned that Tl_3BSe_3 represents the only selenoborate of this type. $[BS_3]^{3-}$, $[B_2S_4]^{2-}$, and $[B_3S_6]^{3-}$ formally represent charged fragments of the B_2S_3 structure, while $[B_2S_5]^{2-}$ shows the motif of $(BS_2)_n$. They can be considered as deprotonated thioboric acids, although H_3BS_3 and $H_2B_2S_5$ have not yet been reported. The structural nature of $H_2B_2S_4$ has not been determined by structure analysis but a cyclic structure was proposed.[23] Table 2 lists all thio- and selenoborates that are known today along with their degree of polymerization and some characteristic bond lenghts. The B–Q distances in BS_3^{3-} ions range from 1.814 to 1.830 Å and are remarkably unaffected by the nature of the counterion.[56–61] The average length of 1.823 Å is significantly longer than in the binary boron sulfides. This indicates less π interaction and is attributed to the high charge density of this small molecule. $Cs_2B_2S_4$ is the only known salt of the dimeric metathioboric acid.[62] It exhibits unusual bonding properties in the $B_2S_4^{2-}$ ion. The endocyclic B–S distances in this strained ring molecule are at 1.861 Å the longest reported for boron centers with trigonal planar coordination, the exocyclic distances are the shortest at 1.740 Å, whereas the average length of 1.821 Å corresponds to the BS_3^{3-} ions. The trigonal-planar coordination is highly distorted. The S_{endo}-B-S_{endo} angle in the ring is only 100.9°, the S_{endo}-B-S_{exo} angles are 129.5°. In addition, a nonbonding $B \cdots B$ distance of 2.37 Å is observed. This is, although very short, about 0.2 Å longer than in the four-membered ring of B_2S_3. This extreme situation can be attributed to repulsive forces between the boron atoms, which shift coplanarly from the center of the triangle towards the exocyclic sulfur atoms. The very short B–S_{exo} distance indicates the exocyclic sulfur atoms to be the main carriers of the charge. This explanation is supported by the fact that the bonding situation is reversed in B_2S_3, where the B–S_{endo} distance in the B_2S_2 ring averages to 1.801 Å and is shorter than the B–S_{exo} distance (1.819 Å).

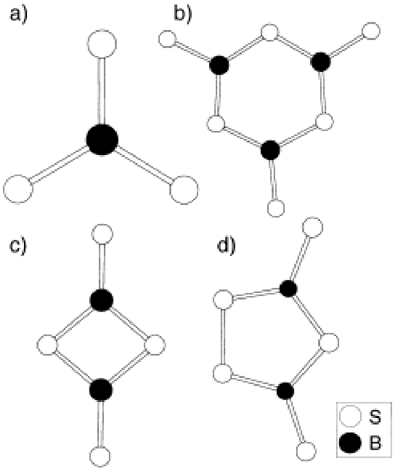


Figure 3. Types of thioborate anions with boron in trigonal-planar coordination, a) $[BS_3]^{3-}$, b) $[B_3S_6]^{3-}$, c) $[B_2S_4]^{2-}$, and d) $[B_2S_5]^{2-}$.

Alkali metal and alkaline earth salts of $H_3B_3S_6$ and thioborates with a $[B_2S_5]^{2-}$ ion exhibit a common structural feature: The average B–S distance of the anion ranges from

1.786 to 1.804 Å.[19, 43, 46, 63–65] Thus, the distance is about 0.02 Å shorter than in the other thioborates with boron in trigonal-planar coordination, and is close to the length of the B–S bonds in the binary compounds. Again, the bonding situation is reversed as compared to the binary sulfides. The $B-S_{exo}$ distances are shorter (ranging from 1.760 to 1.800 Å) than the $B-S_{endo}$ bond lengths (1.794 to 1.824 Å) in the thioborates. The B_3S_6 unit is crystallographically planar in $A_3B_3S_6$ (A = Na, K, Rb) but nonplanar in the cases of $Sr_3[B_3S_6]_2$ and $LiAB_3S_6$ (A = Sr, Ba), where the space group does not demand a planar molecule. The BS_3 subunits themselves are planar, so the distortion of the B_3S_6 entities is a consequence of packing forces in the crystal rather than coordinative interactions of p_z orbitals of boron to sulfur atoms of neighboring $[B_3S_6]^{3-}$ ions ($d(S\cdots S)_{min} = 3.590-3.793$ Å).

The $[B_2S_5]^{2-}$ ion is formally derived from $(BS_2)_n$ by thiolytic cleavage of the sulfur bridge. This anion has only been observed with the small alkali ions Li^+ and Na^+.[63] Because of the different coordination numbers of Li^+ (C.N. = 4) and Na^+ (C.N. = 8) these structures are not isotypic. The $B-S_{exo}$ distances of 1.768 Å are again significantly shorter than the $B-S_{endo}$ bond length of 1.818 Å in $Na_2B_2S_5$. But in the corresponding lithium salt they are at about the same length ($B-S_{exo}$ 1.800, $B-S_{endo}$ 1.807 Å). In both compounds the anions are crystallographically planar.

4. Boron with Tetrahedral Coordination

4.1. Coordinative Lewis Acid–Base Complexes

Trigonal-planarly coordinated boron close to sulfidic or disulfidic sulfur atoms may be subject to donor–acceptor complex formation. The strength of Lewis acidity and basicity can be modified by $p_\pi-p_\pi$ electron transfer from the sulfur to the boron in a B–S bond. Electron transfer can be increased by electron-withdrawing substituents (–I effect) on the boron atom or electron-donor substituents (+I-, +M effect) on the sulfur atom. It is known that the dihalogen(methylthio)boranes X_2BSCH_3 (X = Cl, Br) form cyclic trimers in the crystalline state.[66] This is an example of donor–acceptor complex formation. Boron is tetrahedrally coordinated, that is, it has been rehybridized from sp^2 to sp^3. The average $B(sp^3)-S$ bond length is 1.95 Å and is comparable to that found in chalcogenoborates with boron in a tetrahedral chalcogenic coordination. Table 3 summarizes the boron–sulfur donor–acceptor complexes with sp^3 boron centers. Crystal structure analyses of $(CH_3)_2Q\cdot BX_3$ and $(CH_2)_4S\cdot BX_3$ (Q = S, Se; X = Cl, Br, I)[67] showed the influence of the Lewis acidity on the strength of the complex formation. The molecules $(CH_3)_2S\cdot BX_3$ are shown in Figure 4. The S–B bond length decreases with increasing Lewis acidity of the boron trihalide ($BI_3 > BBr_3 > BCl_3$). An exception is $(CH_3)_2Se\cdot BI_3$ because intermolecular interaction of iodine and selenium (shortest Se ⋯ I distance: 4.112 Å) decreases the Lewis acidity of BI_3. The B–S bond length in these compounds ranges from 1.916 to 1.966 Å, while the B–Se bond length is between 2.065 and 2.101 Å. The products were synthesized from *n*-hexane (X = Cl) or CS_2 (X = Br, I).[68] Single crystals were grown by sublimation of the crude product in evacuated, sealed silica tubes in optimized temperature gradients. The crystals are colorless (X = Cl, Br) or pale yellow to pale red (X = I).

Table 3. B–S(Se) distances [Å] in donor–acceptor complexes of BX_3 and chalcogen donor ligands.[67]

Donor/acceptor	BCl_3	BBr_3	BI_3
$(CH_3)_2S$	1.963	1.934	1.923
thiophene	1.960	1.966	1.916
$(CH_3)_2Se$	2.101	2.065	2.079

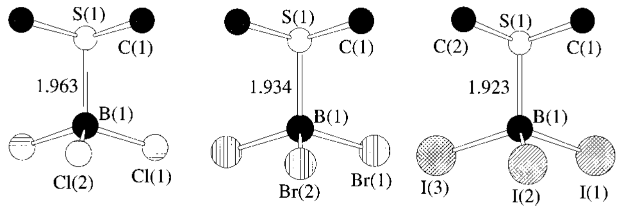


Figure 4. Crystal structure and B–S bond length [Å] of $(CH_3)_2S\cdot BX_3$ (X = Cl, Br, I).

4.2. Ternary and Quaternary Chalcogenoborates

The boron atoms in BS_3^{3-}, $B_2S_4^{2-}$ and $B_3S_6^{3-}$ are Lewis acidic. In the melt the sulfide, disulfide, and the sulfur atoms of the molecular anions are Lewis bases. In many thioborates and perchalcogenoborates that have been synthesized by high-temperature solid-state and molten-state techniques, anionic macromolecules and polymers are observed. This can be rationalized with the concept of donor–acceptor complex formation. The physical properties of the counterion seem to influence the strength of Lewis interaction. The counterions Li^+, Na^+, and Ag^+ favor extended, three-dimensional networks of macromolecular arrangements of adamantane- and "superadamantane"-type thioborate polymers.[51, 52, 69–77] On the other hand, isolated $[B_4S_{10}]^{8-}$ ions, or layered or chain-type polymers of BS_4 tetrahedra are found with soft ions like Pb^{2+}, Ba^{2+}, or Tl^+.[19, 51, 52, 69, 70] In planar boron–chalcogen ring compounds two cases of intermolecular Lewis-type interaction may be present:

- Interaction of exocyclic chalcogen atoms with boron atoms in a ring.
- Interaction of boron and chalcogen atoms between different rings.

In Figure 5 the formation of the polymeric $(BS_2)_n^{n-}$ ion in $TlBS_2$ is shown as interpreted on the basis of donor–acceptor complex formation between the exocyclic sulfur atoms and endocyclic boron atoms of $B_3S_6^{3-}$ units. In this case four-membered B_2S_2 rings are formed that, in contrast to B_2S_3, contain tetrahedrally coordinated boron centers. Consequently the formerly planar six-membered B_3S_3 ring is now in the chair conformation and is connected to three more B_3S_3 rings through B_2S_2 rings. A layered structure of polymerized B_3S_6 units is formed.[69, 70] A rehybridization of the boron center from sp^2 to sp^3 has taken place. Tetrahedral coordination enhances the flexibility of the boron atom to adjust to steric

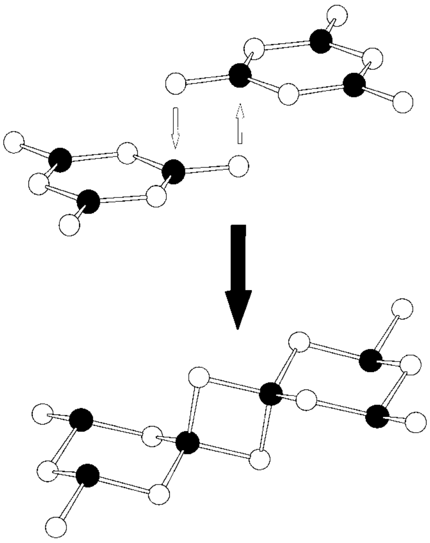


Figure 5. Donor–acceptor complex formation of $[BS_2]_n^{n-}$ in $TlBS_2$.

demands, as seen in the unusual bonding situation in the unfavoured four-membered ring: Two B–S bonds of 1.86 Å alternate with two contacts of 2.02 Å. The transannular B ⋯ B distance of 2.52 Å is larger than in $Cs_2B_2S_4$ (2.37 Å) as well as the transannular S ⋯ S distance of 2.930 Å ($Cs_2B_2S_4$: 2.871 Å). A similar donor–acceptor complex formation of $[B_3S_6]^{3-}$ and $[BS_2]^-$ fragments results in a layered arrangement of B_2S_2 and B_3S_3 rings in SrB_2S_4 (Figure 6).[69] The rather long B–S bond length in the four-membered ring of 1.968 Å leads to transannular B ⋯ B contacts of 2.604 Å and S ⋯ S distances of 2.950 Å. The weak interaction between the chains of BS_4 tetrahedra, which arise from the formation of the four-membered ring, is totally avoided by the use of Ba^{2+} ions instead of the smaller Sr^{2+} ions. In BaB_2S_4 the chains of corner-sharing BS_4 tetrahedra are not connected through B_2S_2 rings (Figure 6). Instead, the boron atoms remain in a trigonal-planar coordination bridging only the BS_4 tetrahedra within the chain. This principle is also found in $AgBO_2$ and $TlBO_2$.[78, 79] Trigonal-planar and tetrahedral coordination of boron atoms in the same compound is common for oxoborates, but BaB_2S_4 is the only known example of this feature in thioborates.

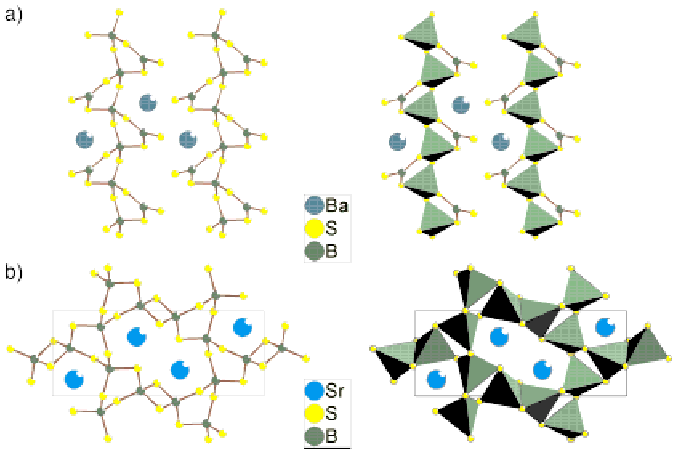


Figure 6. Crystal structures of a) BaB_2S_4 and b) SrB_2S_4.

Higher degrees of condensation to form even three-dimensional infinite networks of anionic macrotetrahedra is only found with small and medium-sized ions like Li^+, Na^+, Ag^+, and Sr^{2+}. In Figure 7 a possible interpretation of the formation of the adamantane-like $B_4S_{10}^{8-}$ ion is proposed. With just one additional sulfide group this macrotetrahedron can be built starting from planar boron–sulfur units. Each sulfur atom of a planar BS_3^{3-} unit coordinates to one of the boron atoms in a B_3S_3 ring, which needs to be rehybridized to sp^3. A sulfur atom on top of the remaining boron atom completes the $B_4S_{10}^{8-}$ entity. The "superadamantane" $B_{10}S_{20}$ unit is built in a similar way. The relatively highly charged fragment $[B_4S_{10}]^{8-}$, which is isostructural to P_4O_{10}, P_4S_{10}, and the $[Ge_4S_{10}]^{4-}$ ion,[80] and isoelectronic to $[Ga_4S_{10}]^{8-}$ and $[In_4S_{10}]^{8-}$,[19] is found only in $Pb_4B_4S_{10}$.[19, 51, 52] Covalent interactions between lead and terminal sulfur atoms are discussed as partially compensating for the charges. On the other hand, a wide variety of polymerized macrotetrahedra characterizes the class of compounds with small cations. In $Li_3Na_5B_{10}S_{19}$[61] and $Li_{4-2x}Sr_{2+x}B_{10}S_{19}$ ($x \approx 0.27$)[71] chains of $B_{10}S_{18}S_{2/2}$ are present (Figure 8), while in $Na_6B_{10}S_{18}$,[71] $Li_{6+2x}[B_{10}S_{18}]S_x$ ($x \approx 2$),[72, 74] and $Ag_6B_{10}S_{18}$[75] all the corners of a $B_{10}S_{16}S_{4/2}$ macrotetrahedron are connected to neighboring units and two independent, interpenetrating infinite three-dimensional networks are formed (Figure 8). The smallest possible unit of this kind, a BS_4^{5-} ion, has never been observed on account of its high charge. In $Li_9B_{19}S_{33}$[76] two $B_{10}S_{16}S_{4/2}$ entities share a BS_4 subunit to again form two independent, interpenetrating infinite three-dimensional networks of corner-sharing $B_{19}S_{30}S_{6/2}$ units. (Figure 9). Another example of this kind is found in $Li_5B_7S_{13}$,[74, 76, 77] where an alternation of $B_4S_6S_{4/2}$ tetrahedra and $B_{10}S_{16}S_{4/2}$ supertetrahedra forms the networks (Figure 9). Compounds with infinite networks of macrotetrahedra form very rigid three-dimensional anionic frameworks with fairly large voids and channels. These spaces have similar energetic environments so movement of cations is not

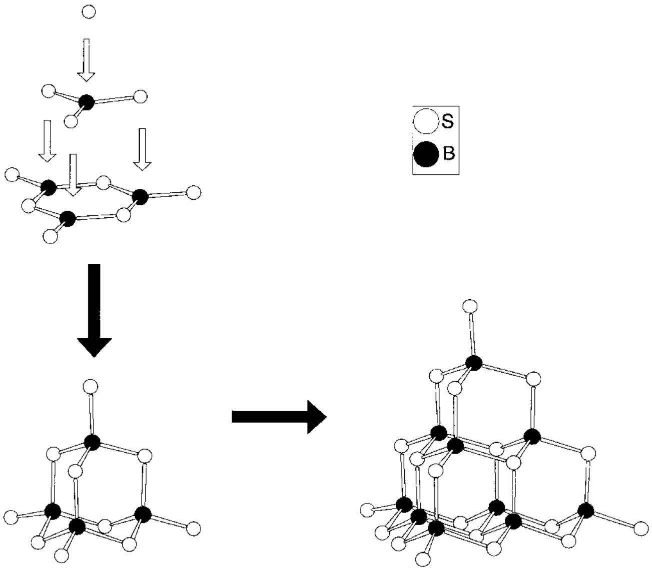


Figure 7. Donor–acceptor complex formation of adamantane- and "superadamantane"-type anionic fragments.

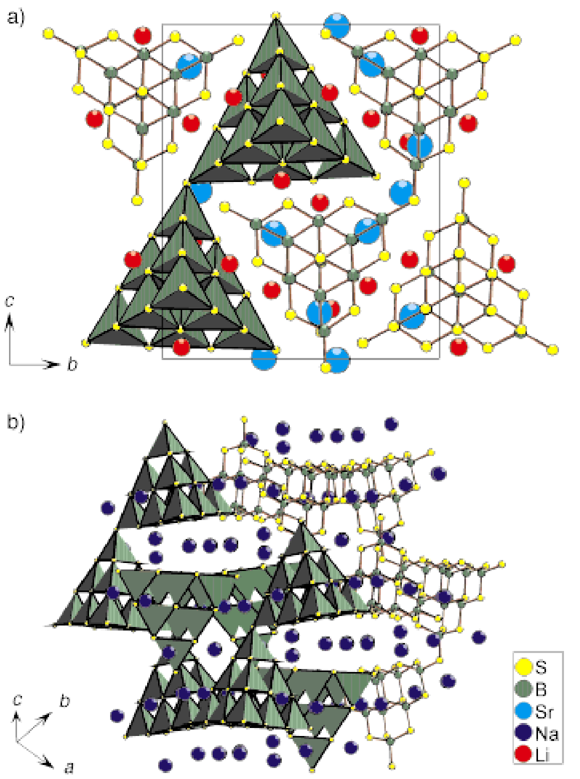


Figure 8. Crystal structure of a) $Li_{4-2x}Sr_{2+x}B_{10}S_{19}$ and b) $Na_6B_{10}S_{18}$.

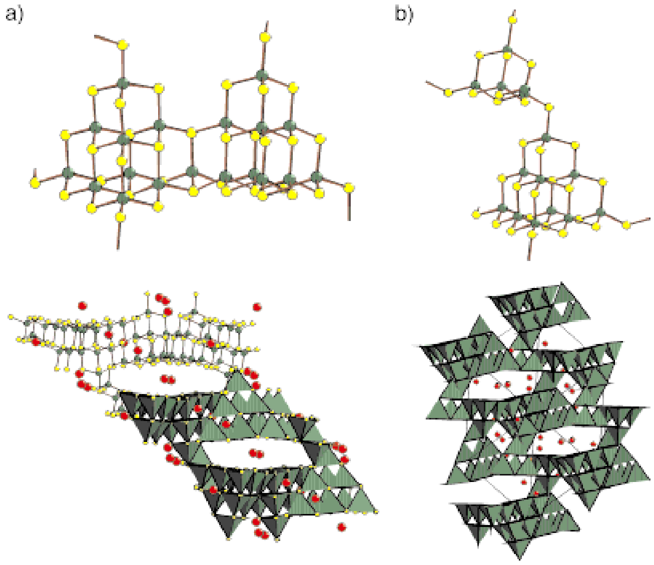


Figure 9. Crystal structure and building fragments of a) $Li_9B_{19}S_{33}$ and b) $Li_5B_7S_{13}$.

hindered. Solid-state NMR spectroscopy on ^7Li nuclei in $Li_5B_7S_{13}$, $Li_9B_{19}S_{33}$, $Li_{6+2x}[B_{10}S_{18}]S_x$, and $Li_{4-2x}Sr_{2+x}B_{10}S_{19}$ showed in some cases remarkable dynamics of the cations (see section 6).

4.3. Ternary and Quaternary Perchalcogenoborates

In recent times perthio- and perselenoborates have been the subject of intensive studies in our group. Their structures are dominated by chain-type polymeric anions that are based on the B_2Q_3 fragment ($Q = S$, Se) known from $(BQ_2)_n$. At least one example each of perthio- and perselenoborates has been synthesized with Li,[61, 63] Na,[63, 81] K,[81] Rb,[61, 82] Cs,[60] and monovalent Tl.[70, 82] Table 4 summarizes all known perchalcogenoborates. Only a small number of the thioborates with boron atoms with tetrahedral coordination contain a disulfide bridge, whereas all known selenoborates with tetrahedrally coordinated boron atoms contain diselenide units. Only two of these perchalcogenoborates, $Li_2B_2S_5$ and $Na_2B_2S_5$, contain boron atoms with trigonal-planar coordination. They represent the only discrete perchalcogenoborate anions. In all other perchalcogenoborates the structural elements are $[BQ_3]_n^{n-}$, $[B_2Q_7]_n^{2n-}$, and $[B_3Q_{10}]_n^{3n-}$ polymers. They are displayed in Figure 10a–c. Except for $Li_2B_2Se_7$ all of

Table 4. Structurally characterized perthio- and perselenoborates and mean B–S(Se) lengths [Å].

Compound	$\bar{d}$(B–S)	Ref.	Compound	$\bar{d}$(B–Se)	Ref.
$Li_2B_2S_5$	1.805	[63]	$Li_2B_2Se_7$	2.047	[61]
$Na_2B_2S_5$	1.802	[63]	$Na_2B_2Se_7$	2.044	[81]
$K_2B_2S_7$	1.919	[81]	$K_2B_2Se_7$	2.050	[81]
$RbBS_3$	1.927	[82]	$Rb_2B_2Se_7$	2.049	[61]
$CsBS_3$	1.930	[60]	$CsBSe_3$	2.064	[60]
$TlBS_3$	1.930	[70, 82]	$Cs_3B_3Se_{10}$	2.052	[60]
$Tl_3B_3S_{10}$	1.919	[70]	$TlBSe_3$	2.059	[83]

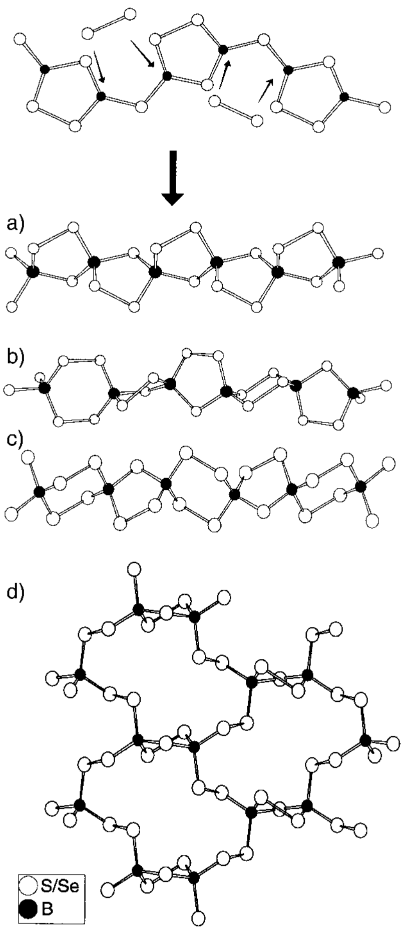


Figure 10. Donor–acceptor complex formation in perchalcogenoborates a) $[BQ_3]_n^{n-}$, b) $[B_3Q_{10}]_n^{3n-}$, c) $[B_2Q_7]_n^{2n-}$ and d) anion of $Li_2B_2Se_7$.

these are one-dimensional infinite polymers with a rising content of dichalcogenide in the order $[BQ_3]_n^{n-} < [B_3Q_{10}]_n^{3n-} < [B_2Q_7]_n^{2n-}$. The nucleophilic attack of diselenide to $(BSe_2)_n$ is also shown in Figure 10. As rehybridization of sp^2 to sp^3 is favored over oxidative cleavage of the B–Se bond, this again can be regarded as a donor–acceptor complex formation. This process results in an infinite chain of fused spirocyclic five-membered B_2Se_3 rings with boron centers in tetrahedral coordination. This motif is found in $RbBS_3$,[82] $CsBS_3$,[60] $TlBS_3$,[70, 82] $CsBSe_3$,[60] and $TlBSe_3$.[83] Insertion of a second diselenide bridge into every third ring results in the $[B_3Se_{10}]_n^{3n-}$ polymer, which is present in $Tl_3B_3S_{10}$[70] and $Cs_3B_3Se_{10}$.[60] A 1:1 ratio of spirocyclicly fused five-membered B_2Q_3 rings and six-membered B_2Q_4 rings is present in $[B_2Q_7]_n^{2n-}$ chains. These are found in $K_2B_2S_7$ and $A_2B_2Se_7$ (A = Na, K, Rb).[61, 81] In Figure 10d the anionic polymer in the compound $Li_2B_2Se_7$ is shown.[61] Here five-membered B_2Se_3 rings are connected by diselenide bridges into two dimensions. The four exocyclic diselenide bridges stretch out to four neighboring B_2Se_3 units to form a layered structure rather than to two entities to form a chain. In all perchalcogenoborates the B–Q bond lengths are within the range observed in other boron–chalcogen compounds. They range from 1.91 to 1.95 Å in perthioborates with sp^3 boron atoms and from 2.02 to 2.07 Å in perselenoborates.

5. Subvalent Chalcogenoborates

All syntheses of chalcogenoborates start from the corresponding metal chalcogenide, elemental chalcogen, and elemental boron. In the course of the reaction oxidation and fragmentation of the B_{12} icosahedra of elemental boron must occur to form the chalcogenoborates. The oxidant is clearly the chalcogen, but the steps of fragmentation of boron are as yet unknown. A hint, of course, could arise from crystallized intermediates, so a systematic search for subvalent chalcogenoborates must be undertaken. As the existence of $B_{12}S_{2-x}$[15] and $B_{12}SeB$[16] is proposed, a likely way of fragmentation proceeds via persubstitution of the B_{12} icosahedron. At the other end of the fragmentation path cyclic compounds with direct B–B contacts should be present. An example of this is found in B_4S_2 rings of 2.3.5.6-tetrakis(dimethylamino)1.4-dithiatetraborinane.[84]

The novel chalcogenoborate $Cs_8[B_{12}(BSe_3)_6]$[85] (Figure 11) contains the first B_{12} icosahedron completely saturated with chalcogen ligands. Six trigonal-planar selenoborate entities that function as bidentate ligands complete the B_{12} icosahedron to form a persubstituted *closo*-dodecaborate ion. This centrosymmetric molecule shows endocyclic B–Se bond lengths in the chelate-type B_3Se_2 ring of 1.952 to 2.011 Å, whereas the B–Se bonds to the exocyclic selenium atoms are significantly shorter (1.886 to 1.913 Å). This indicates that these atoms carry a large quantity of the charge of the $[B_{12}(BSe_3)_6]^{8-}$ ion. The *closo*-cluster contains 2n+2 binding electrons for the B_{12} unit and therefore obeys Wade's rules for cluster compounds. Six negative charges are located on the terminal selenium atoms, which leaves two negative charges on the central cluster. Additional interest for this compound comes from its preparation: It has been synthesized by the high temperature reaction of a stoichiometric mixture of Cs_2Se, Se, and B at 973 K and subsequent annealing (10 h at 873 K, 24 h at 673 K, 120 h at 473 K). The B_{12} icosahedron was preserved under these rather severe reaction conditions.

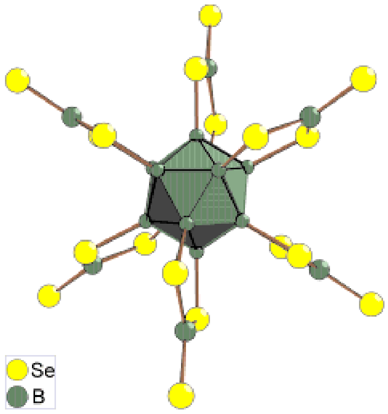


Figure 11. Structure of the $[B_{12}(BSe_3)_6]^{8-}$ ion in $Cs_8[B_{12}(BSe_3)_6]$

6. Solid-State ^{7}Li NMR Studies on Thioborates

Superionic conducting materials, that is solid compounds with ionic conductivity of about 1 S cm^{-1} with insignificant electronic conductivity, are of increasing interest for commercial applications like batteries, fuel cells, sensors, and electrochromic devices. As isotropic conductivity is wanted in most cases, amorphous materials are most commonly applied and therefore thoroughly investigated. But in the systematic search for new superionic conducting materials an understanding of the transport mechanisms of a charged mobile phase in an oppositely charged stationary phase is needed. Li^+- and Ag^+-containing thioborates with a rigid anionic framework are good candidates for high ionic conduction. In section 4.2. we presented the crystal structures of a number of these compounds that feature an anionic framework with a surplus of energetically similar sites along large voids and channels. The cations are distributed with high occupational disorder over a large number of these sites, which results in a quasi-amorphous distribution of the cations into a crystalline matrix. These compounds can serve as model systems for the study of transport mechanisms. In collaboration with the group of W. Müller-Warmuth ^{7}Li NMR spectroscopy experiments have been carried out with $Li_5B_7S_{13}$,[72] $Li_9B_{19}S_{33}$,[86] $Li_{4-2x}Sr_{2+x}B_{10}S_{19}$ ($x \approx 0.27$),[86] and $Li_{6+2x}[B_{10}S_{18}]S_x$ ($x \approx 2$).[72, 73] The spectra obtained are similar to those of glassy thioborates.[87–89] At low temperature (rigid lattice region), along with the dipolarly broadened central transition, an unstructured base of averaged quadrupole coupling signals is recorded, which can be attributed to the contribution of various energetically inequivalent lithium positions. Upon increased temperature a line narrowing caused by the motions of the lithium ions ("motional narrowing") is observed. An activation energy for the motion of about 20 to 30 kJ mol^{-1} is estimated according to Waugh and Fedin[90] from the temperature at which motional narrowing starts. In contrast to glassy lithium conductors, above a compound-specific temperature in crystalline thioborates one or two quadrupole coupling satellites evolve, which can be interpreted as anisotropic lithium motion over one or two energetically equivalent sites in the crystal lattice. From relaxation time measurements the double-exponential time dependency of the nuclear magnetization was extracted and interpreted on the basis of a contribution from the different mobilities of the ions in $Li_{6+2x}[B_{10}S_{18}]S_x$ as well as a contribution of different transport mechanisms in $Li_5B_7S_{13}$ and $Li_9B_{19}S_{33}$. In general, NMR studies on crystalline thioborates show good agreement to results from amorphous compounds and the same theory can be applied to describe the observations. Thus, as the structure is known from single-crystal analysis, structure–property relations can be examined and transferred to glassy ionic conductors.

7. Conclusions and Outlook

In the borderline field between molecular and solid-state chemistry the variable possibilities of preparative routes toward boron–sulfur and boron–selenium compounds have led to an ever growing number of different structural principles that are only in part fully understood and will definitely be the source of further surprise in future syntheses.

But tendencies can be named: Boron atoms in trigonal-planar coordination sites can be found mainly in sulfur reaction mixtures with a low boron sulfide content. If the ratio of M^I_2S (M^I = alkali metal, Ag, Tl):B_2S_3 is smaller than 1:1, the boron center is sp^3 hybridized, and the formation of three-dimensional networks of anionic macrotetrahedra is favored with smaller cations (Li^+, Na^+, Ag^+), whereas perthioborates are formed with K^+, Rb^+, Cs^+, and Tl^+. Perthioborates with Li^+ and Na^+ are known with a sp^2 hybridized boron center.

The size of selenium is incompatible to boron atoms to allow $\pi-\pi$ overlapping, so sp^2 hybridized boron centers cannot be stabilized. Perselenoborates with boron atoms with tetrahedral coordination are the by far most common boron–selenium compounds. Modifications in the selenium content as well as in the choice of counterions will be utilized to widen the range of possible interconnections of perselenoborate fragments. Much effort will be spent in the future on synthesizing macrotetrahedral networks in which sulfur is replaced by selenium, because there is no apparent reason why selenoborates shouldn't adopt this structural motif.

The discovery of $Cs_8[B_{12}(BSe_3)_6]$ opens the way to systematic research on subvalent chalcogenoborates. From this starting point the understanding of the steps involved in the reaction of boron with chalcogens will be a field of further very active research to try and bring light to the path from elemental boron at one end and the BQ_3^{3-} ion at the other.

As the research on ionic conductors for the use in battery systems and fuel cells goes on, and more and more interest is focussed on the understanding of the dynamics in solids, the crystal structure determination of materials that are ionic conductors in the glassy state becomes crucial. Lithium oxo-, thio- and selenoborates have proved to be good candidates for further investigation.

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