Thio- and Selenoborates: from Rings to Clusters and Networks

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Thio- and Selenoborates: from Rings to Clusters and Networks

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We herein present an overview on the structural diversity of thio- and selenoborates showing the development from molecular boron chalcogen compounds to layered and polymeric structures on one side and to boron cluster compounds on the other side.

Keywords: thioborates; perthioborates; selenoborates; perselenoborates; cluster compounds

INTRODUCTION

Improvement and optimization of appropriate methods for synthesis and crystallization along with systematic structural investigations brought about considerable progress in the chemistry and the structural characterization of binary and ternary boron sulfides and selenides. The synthesis of well-defined and highly pure boron chalcogen compounds is fairly difficult because of the high reactivity of in situ built boron chalcogenides towards a variety of container materials at elevated temperatures. The fused silica tubes usually employed for solid state reactions are attacked by boron chalcogenides at temperatures above 650 K forming silicon sulfur compounds by B-Si exchange at the surface of the ampoules finally leading to the destruction of the attacked

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ampoules. For the synthesis of pure samples the reaction vessel must either be made of boron nitride or graphite, or silica tubes coated with glassy carbon have to be used.

Besides the layered structured B_2S_3 [1] (Fig.1) boron sulfides and selenides with a boron : chalcogen ratio of 1 : 2 were prepared and identified as porphin-like molecular B_8S_{16} [2] and as chain polymers $(BQ_2)_n$ $(Q = S, Se)$ [3]. In these binary compounds boron is observed in a trigonal-planar BS_3 entity, in a B_2S_4 unit containing a strained four-membered B_2S_2 ring, in a B_3S_6 entity with a planar six-membered B_3S_3 ring, and the B_2Q_5 $(Q = S, Se)$ unit incorporating a planar five-membered $B_2(Q_2)Q$ ring with a Q-Q contact.

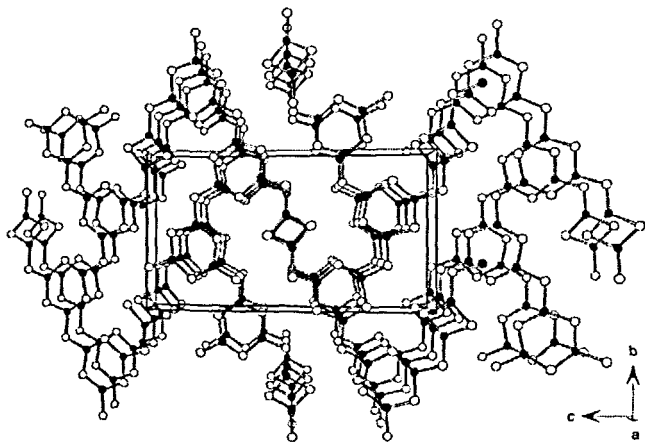Fig. 1:   Crystal structure of B_2S_3 [1]

The corresponding anions of these structural features are observed in a large number of thioborates and selenoborates which may be considered as salts of the hypothetical thioboric and selenoboric acid, respectively (Fig. 2). In this series the acid $B_3S_3(SH)_3$ has been sythesized and characterized [4], $B_2S_2(SH)_2$ was reported but later not confirmed [5].
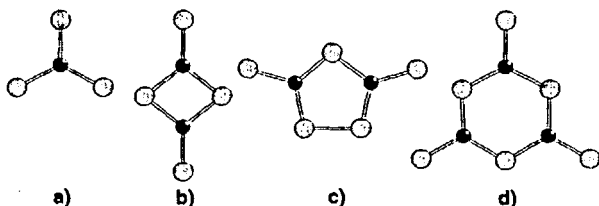
Fig. 2:   Anions containing boron in trigonal-planar coordination:
a) $BS(Se)_3^{3-}$ b) $B_2S_4^{2-}$ c) $B_2S_5^{2-}$ d) $B_3S_6^{3-}$

It is only in these discrete anions that boron shows only trigonal-planar
coordination. However, chalcogenoborates containing polymeric chain
anions or three-dimensional network structures exhibit boron in
tetrahedral coordination. These tetrahedra are the elementary building
unit for a large variety of 1D, 2D, and 3D anionic frameworks including
spirocyclically four-, five-, or six-membered rings.

Boron in trigonal-planar coordination

Binary boron sulfides contain boron-sulfur rings connected via bridging
sulfur atoms forming layers in the case of B_2S_3, chains in $(BQ_2)_n$ ($Q = S$,
Se) and macrocycles in B_8S_{16}. Without exception these rings, chains,
layers, and macrocycles are perfectly planar. The transannular sulfur-
sulfur distances in the porphin-like B_8S_{16} of more than 4.6 Å could be
suitable for the formation of d^8 and d^9 transition metal complexes. MO
calculations on a hypothetical $[CuB_8S_{16}]^{2+}$ complex indicated a stability
comparable to the corresponding thioether complexes [6].

A large number of derivatives of molecular B_3Q_3 and B_2Q_3 ring
compounds have been reported in solution [7-9], some of them have
been characterized by single crystal X-ray structure determination.
Again, planarity of the boron-chalcogen system is observed in these
compounds as well but substitution of exocyclic chalcogen atoms by
organic ligands or halogens leads to deviations from the planar
geometry in these ring systems.

Besides a large number of orthothioborates only one orthoseleno-borate with isolated BSe_3^{3-} anions was synthesized and fully characterized as Tl_3BSe_3 (Fig. 3) [10].
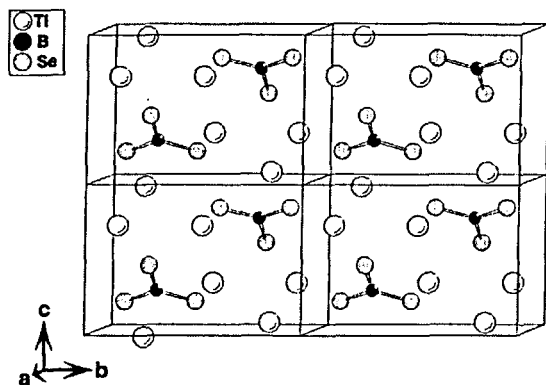
Fig. 3:   Crystal structure of Tl_3BSe_3 [10]

The thallium selenoborate structure is isotypic to Tl_3BS_3 [10] but not to any other M_3BQ_3 structure. The mean B-S (B-Se) bond length is 1.83 Å (1.95 Å), in the unit cell two crystallographically independent thallium sites with irregular 6+1 or 6+2 sulfur (selenium) coordinations are found. The lone electron pair at the thallium cation shows strong stereochemical activity.

Condensation of three BS_3^{3-} units leads to $B_3S_6^{3-}$ anions containing a six-membered B_3S_3 ring as they are present in the crystal structures of the metathioborates with M = Na, K, Rb [3, 11].

A different structural feature, a five-membered B_2S_3 ring, is observable in $Li_2B_2S_5$ and $Na_2B_2S_5$ [12] (Fig. 4), while in the structure of $Cs_2B_2S_4$ [13] a strained four-membered B_2S_2 ring is found as it is already known from the binary B_2S_3 compound.

Up to now no isolated cyclic selenoborate with boron in trigonal-planar coordination has been reported. For steric reasons a lack of sufficient (p-p)π interactions does not give any significiant energy

stabilization. Therefore, tetrahedral coordination of boron is observed in most boron selenium compounds (Fig. 5).
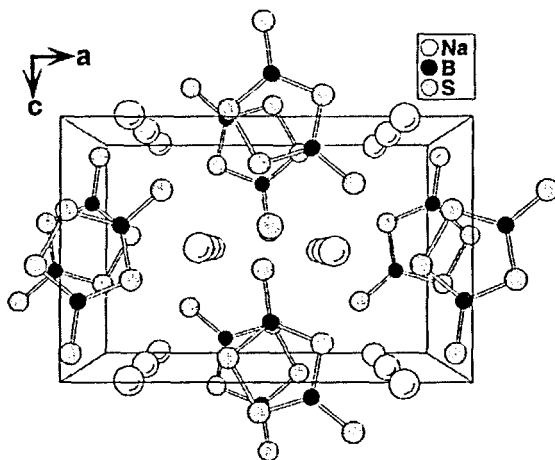
Fig. 4: Crystal structure of $Na_2B_2S_5$ [12]

Nevertheless, stabilization of trigonal-planar coordination in B_3Se_3 and B_2Se_3 rings can be achieved with exocyclic –I substituents as observed in $(XBSe)_3$ and $X_2B_2Se_3$ (X = Br, I) as well as in $((C_6H_5)BSe)_3$ and $(C_6H_5)_2B_2Se_3$ [9,14].
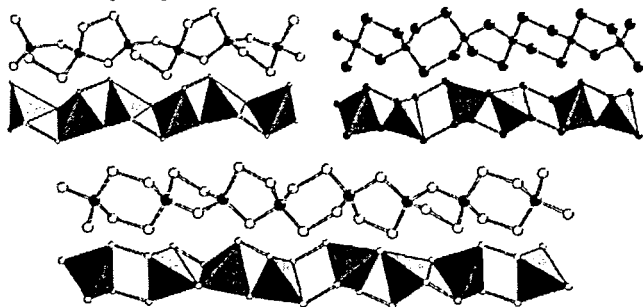
Fig. 5: Chain structures of MBQ_3 (top left), $M_2B_2Q_7$ (top right), and $M_3B_3Q_{10}$ (bottom) compounds

Boron in tetrahedral coordination

If a molecule contains trigonal-planar coordinated boron besides sulfide or disulfide the formation of intermolecular donor-acceptor complexes is possible. This leads to dimeric, trimeric or even polymeric molecules. Two cases of intermolecular interaction may be present:

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

For example, the formation of the polymeric $[BS_2^-]_n$ anion in TlBS$_2$ [15] can be interpreted as a donor-acceptor complex formation of exocyclic sulfur atoms and endocyclic boron atoms of $B_3S_6^{3-}$ units. Therefrom four-membered B_2S_2 rings containing tetrahedrally coordinated boron atoms arise. The formerly planar six-membered B_3S_3 ring changes into chair conformation leading to a connection of three more B_3S_3 rings via B_2S_2 rings. Besides the small B_2S_2 and B_3S_3 rings $(BS)_{12}$ macrocycles are present in the structure.
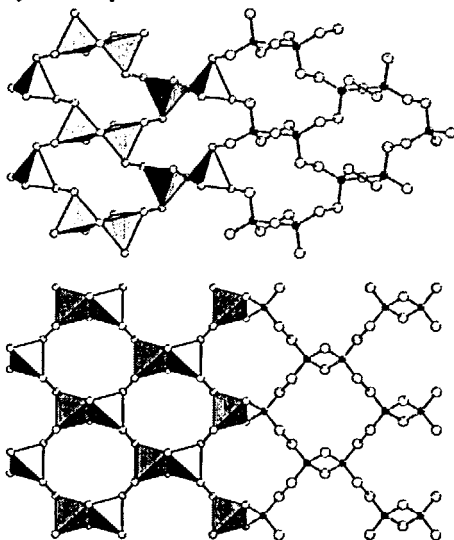

Fig. 6:   Anionic network in the layered structures of Li$_2$B$_2$Se$_7$ (top) and Ba$_2$B$_2$Se$_6$ (bottom)

Similar structures are obtained in the Li/B/Se and Ba/B/Se phase systems (Fig. 6). The layered structure of $Li_2B_2Se_7$ contains B_2Se_3 rings connected via diselenide units. All boron atoms show tetrahedral coordination by selenium atoms. Besides B_2Se_3 rings the structure contains $B_6(Se_2)_6$ and $B_6(Se_2)_4Se_2$ macrocycles. The lithium counterions are situated between the layers. Strikingly, $Li_2B_2Se_7$ is not isotypic to the known $M_2B_2Q_7$ compounds with M = Na, K, Rb and Q = S, Se [16] that consist of B_2Q_3 rings connected via Q_2 units forming chains. The small lithium cations in $Li_2B_2Se_7$ and resulting small coordination numbers force a more compact anion structure than the chain structure found for the other alkaline chalcogenoborates of the $M_2B_2Q_7$ type. In the case of BaB_2Se_6 four-membered B_2Se_4 rings are connected via diselenide units giving B_6Se_{10} macrocycles forming large voids in which the barium cations are located. Further connection of layers via chalcogen atoms leads to three-dimensional network structures as observed in the structure of $Li_2B_2Se_5$ (Fig. 7), which is not isotypic to the corresponding sulfur compound $Li_2B_2S_5$ [12].

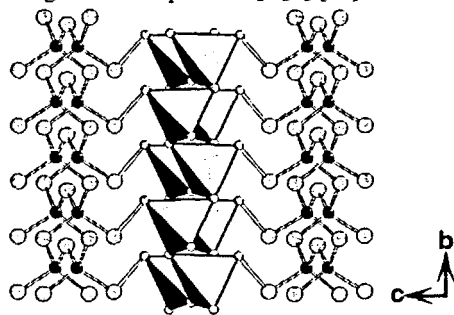Fig. 7: Anionic network in the structure of $Li_2B_2Se_5$

Another type of three-dimensional network can be found in a variety of chalcogenoborates. The structural features of B_4Q_{10} and $B_{10}Q_{20}$ units can be interpreted as a fragment of the ZnS structure type. The adamantane-like B_4S_{10} unit is presumeably formed by reaction of a B_3S_6 ring with a BS_3 unit and one additional sulfur atom. The only

thioborate with this isolated structural pattern hitherto known is $Pb_4B_4S_{10}$ [3,17]. Further condensation leads to „superadamantane" $B_{10}S_{20}$ units, a common feature in a large number of compounds, while different types of polymerization lead to structures containing $B_{10}S_{18}S_{2/2}$ chains e.g. as in $Li_{4-2x}Sr_{2+x}B_{10}S_{19}$ (x=2) [18] or $B_{10}S_{16}S_{4/2}$ frameworks in which all four corners of the macrotetrahedra are connected to neighbouring units. Two independent interpenetrating infinite three-dimensional networks are resulting in the structures of $Ag_6B_{10}S_{18}$ and $Na_6B_{10}S_{18}$ [18]. $Li_{6-x}Cs_xB_{10}Q_{18}$ (x≈1) and $Li_{3+x}Na_{5-x}B_{10}Q_{19}$ with Q = S, Se (Fig. 8) show similar structures. $Li_{6-x}Cs_xB_{10}Q_{18}$ (x≈1) represents a new structure type where $B_{10}Q_{18}$ macrotetrahedra are connected via corners to infinite layers.

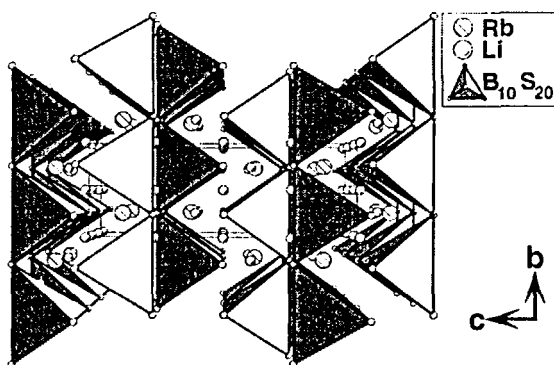Fig. 8:   Infinite layered structure of $Li_{6-x}Cs_xB_{10}Q_{18}$ (x≈1) (Q = S, Se)

The boron chalcogen framework of $Li_{3+x}Na_{5-x}B_{10}Q_{19}$ is isotypic to the anion network found in $Li_{4-2x}Sr_{2+x}B_{10}S_{19}$ where $B_{10}S_{18}S_{2/2}$ units are connected to chains.

The smallest possible tetrahedral unit, an isolated BQ_4^{5-} anion with Q = S, Se has not been observed so far due to its high charge, but a BQ_4 unit serves as a linkage between $B_{10}Q_{16}Q_{4/2}$ units in the structures of $Li_9B_{19}Q_{33}$ with Q = S, Se [18] (Fig. 9). Therein, the $B_{10}S_{20}$ entities

have one common BQ_4 tetrahedron forming infinite polymeric anions of overall formula $B_{19}Q_{30}Q_{6/2}$. Two independent interpenetrating anion networks build up the crystal structure in which the lithium cations are located in channels.
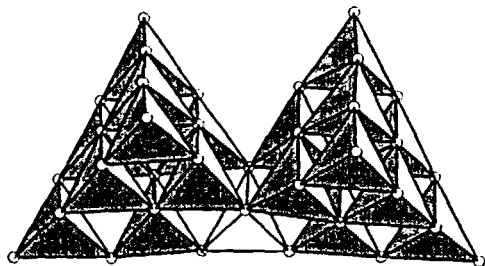

Fig. 9: $B_{19}Q_{30}Q_{6/2}$ unit in $Li_9B_{19}Q_{33}$ with Q = S, Se [18]

Icosahedral boron clusters

Recently, novel chalcogenoborates containing a B_{12} icosahedron completely saturated with chalcogen ligands were synthesized and characterized. $M_8[B_{12}(BSe_3)_6]$ with M = Rb, Cs (Fig. 10) [19] contains chelate-bonded trigonal-planar selenoborate units completing the B_{12} icosahedron to form a persubstituted *closo*-dodecaborate anion, which is the first representative of a new type of boron cluster compounds.

Wade's rules for cluster compounds apply: with 2n+2 binding electrons per B_{12} unit and six negative charges located on the terminal selenium atoms two negative charges remain on the central cluster. Eight negative charges result for the whole *closo*-borate anion which is proved by the cations found by single crystal X-ray structure determination. Complete substitution by non-hydrogen atoms of a *closo*-borate opens new ways to the understanding of the reaction paths toward a novel class of boron-chalcogen compounds in solid sate chemistry.
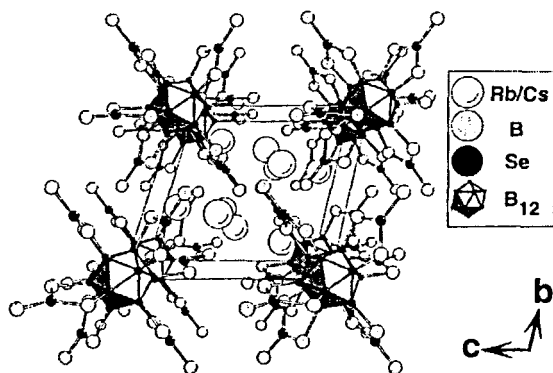
Fig. 10 : Crystal structure of $M_8[B_{12}(BSe_3)_6]$ with M = Rb, Cs [19]

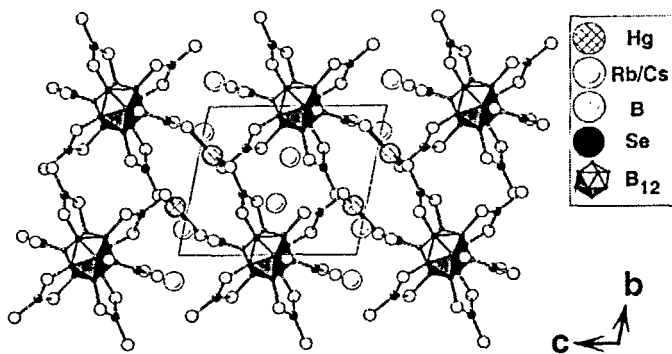Fig. 11: Infinite layers of $M_4Hg_2B_{18}Se_{18}$ clusters with M = Rb, Cs [20]

$M_4Hg_2B_{18}Se_{18}$ with M = Rb, Cs (Fig. 11) [20] contains $B_{12}(BSe_3)_6$
entities linked via mercury atoms. Three terminal selenium atoms of the
BSe_3 ligands are connected to one mercury atom, resulting in infinite
layers. The chain structure of $Na_6B_{18}Se_{17}$ (Fig. 12) is built up by
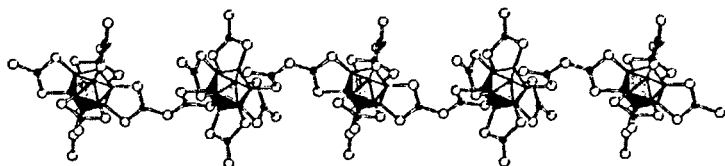polymerized $B_{18}Se_{16}Se_{2/2}$ units.

Fig. 12: Infinite chains of $[B_{12}(BSe_3)_6Se_{2/2}^{6-}]_n$ anions in $Na_6B_{18}Se_{17}$

Future work will include the synthetic route to a new class of compounds likely accessible by selenium-sulfur exchange.

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