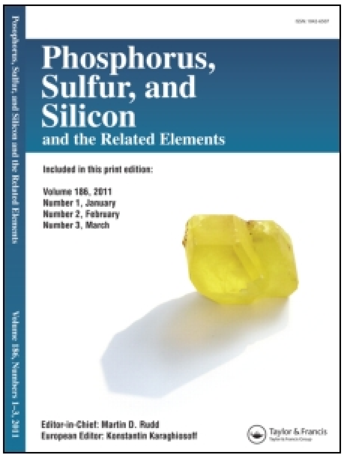
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Inorganic Rings in Thio-and Selenoborates

Olaf Conrad; Bernt Krebs

To cite this Article Conrad, Olaf and Krebs, Bernt(1997) 'Inorganic Rings in Thio-and Selenoborates', Phosphorus, Sulfur, and Silicon and the Related Elements, 124: 1, 37 — 49

To link to this Article: DOI: 10.1080/10426509708545609

URL: http://dx.doi.org/10.1080/10426509708545609

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1997, Vol. 124 & 125, pp. 37–49
Reprints available directly from the publisher
Photocopying permitted by license only

INORGANIC RINGS IN THIO- AND SELENOBORATES

OLAF CONRAD and BERNT KREBS
Anorganisch-Chemisches Institut der Universität Münster, Wilhelm-Klemm-Str. 8, 48149 Münster, Germany

Dedicated to Professor Hartmut Bärnighausen

A comprehensive overview on the structural diversity of thio- and selenoborates is given with special focus to the molecular features of boron-sulfur and boron-selenium chemical systems in binary and ternary compounds.

Keywords: thioborates; selenoborates

INTRODUCTION

As early as 1901 Stock and coworkers reported the existence of the "adducts" $B_2S_3 \cdot BCl_3$ and $B_2S_3 \cdot BBr_3$,[1] which by Wiberg and Sturm in 1953 were shown to be derivatives of a cyclic trimeric metathioboric acid $B_3S_3X_3$ (X = Cl, Br).[2] In the 1960's Muetterties, Schmidt, Siebert, Hagenmuller, Chopin and others spent much effort in both solution chemistry and solid state chemistry of boron-sulfur and boron-selenium compounds and succeeded in the preparation and characterization of compounds like $(Et_2N\text{-}BS)_2$,[3] $(ClBS)_2S$[4] and $(NaBS)_3$.[5]

Over the past two decades an improved solid state preparation technique, particularly the synthesis of high quality single crystals, has made possible a rapid progress in the understanding of chalcogenoborate chemistry. The tool of single crystal X-ray structure analysis gives undisputable data on bond lengths, bond angles, coordination spheres, and alike.

STRUCTURAL PRINCIPLES IN THIO- AND SELENOBORATES

Starting from the binary boron sulfides B_2S_3, $(BS_2)_n$ and B_8S_{16} and boron selenide $(BSe_2)_n$[6-8] (Fig. 1) four building blocks may be extracted, that serve as characteristic structural features for each group

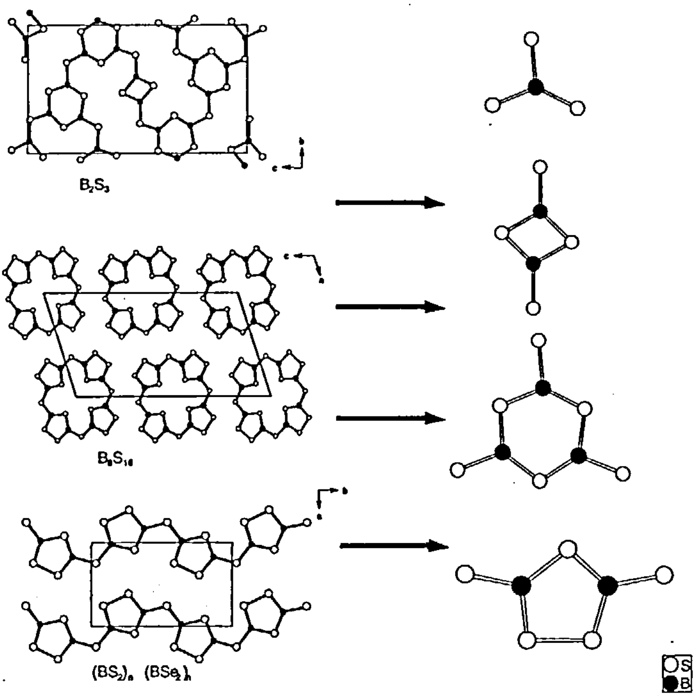
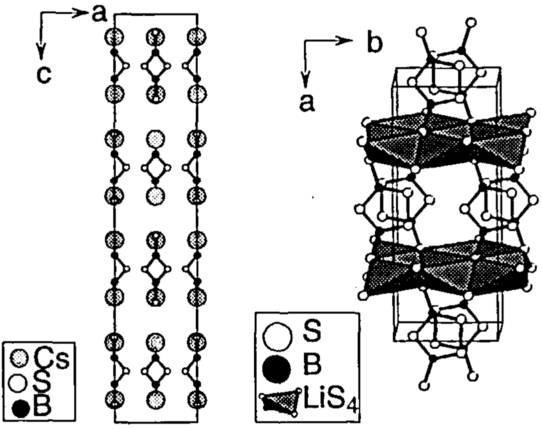


FIGURE 1: Crystal structures of binary boron sulfides and building blocks extracted

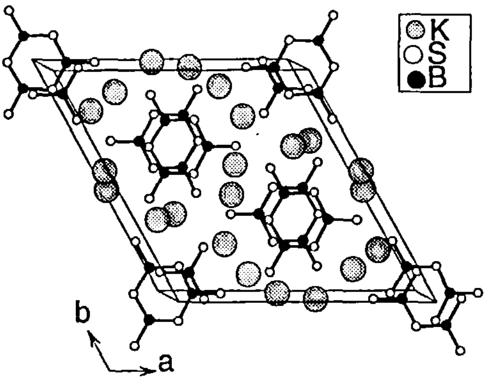
of chalcogenoborates: a trigonal-planar BS_3 entity, a strained four-membered B_2S_2-ring containing B_2S_4 unit, a B_3S_6 entity with a planar six-membered B_3S_3 ring and the B_2Q_5 (Q = S, Se) unit presenting a planar five-membered $B_2(Q_2)Q$ ring with a direct Q-Q contact. The corresponding anions of these building blocks are observed in a large number of thioborates and in Tl_3BSe_3. They are considered as salts of the - in part hypothetical - thioboric and selenoboric acids, respectively. In these discrete anions boron in solely trigonal-planar coordination is present. However, most of the selenoborates and still a considerable number of thioborates contain polymeric anions with boron in tetrahedral coordination, i. e. boron has been rehybridized from sp^2 to sp^3. This corresponds to an elevation of the two-dimensional building units into the third dimension by adding another chalcogen atom on top of each BQ_3 triangle. In this way a large variety of polymeric 0D, 1D, 2D and 3D anionic frameworks is built. These include four-, five- or six-membered rings that are spirocyclically fused or edge-sharing.

Boron in trigonal-planar coordination

The binary boron sulfides contain boron-sulfur rings that are connected via sulfur atoms to form layers in B_2S_3, chains in $(BS_2)_n$ and macrocycles in B_8S_{16}.[6-8] All rings, chains, layers and macrocycles are perfectly planar. In B_2S_3 the predominant structural elements, a B_3S_3 ring and a strained 1.3.2.4-dithiadiboretane ring, are present in a 2:1 ratio. The connection pattern forms a planar, layered structure that contains a 34-membered $(BS)_{17}$ macrocycle. $(BS_2)_n$ and $(BSe_2)_n$ include 1.2.4.3.5-trithia-(selena)diborolane rings. In the case $n = \infty$ infinite planar chains of $B_2Q_3Q_{2/2}$ are formed. In one special case (n = 4) four B_2S_3 rings are connected via sulfur atoms to form a porphin-analogous macrocyle. The transannular sulfur-sulfur distances of more than 4.6 Å in this compound 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 stabilization comparable to corresponding thioether complexes.[9]



$Cs_2B_2S_4$ $Li_2B_2S_5$



$K_3B_3S_6$

FIGURE 2: Boron in trigonal-planar coordination: $Cs_2B_2S_4$, $Li_2B_2S_5$ and $K_3B_3S_6$

In solvent chemistry a large number of derivatives of B_3Q_3 and B_2Q_3 ring compounds have been reported,[4,10,11] many of which have been characterized by means of single crystal X-ray structure determination. The main structural feature of the high-temperature synthesized compounds, the planarity of the boron-chalcogen system, is observed in many of these products as well. Obviously the substitution of the exocyclic chalcogen atoms by organics or halogens has some influence on the geometry of the ring system.

Besides a large number of orthothioborates several metathioborates with an anionic inorganic ring have been synthesized by high temperature techniques. Among these $Na_3B_3S_6$, $K_3B_3S_6$ and $Rb_3B_3S_6$[7,12] contain a six-membered B_3S_3 ring (figure 2). They are alkaline salts of $(HSBS)_3$.[13] $Li_2B_2S_5$ and $Na_2B_2S_5$[14] include a five-membered B_2S_3 ring and $Cs_2B_2S_4$[15] holds a strained four-membered B_2S_2 ring. These compounds can be considered as salts of the hypothetical dimeric metathioboric acid "$H_2B_2S_4$", and the hypothetical cyclic perthioboric acid "$H_2B_2S_5$", respectively. In correspondence to the charge location on the exocyclic sulfur atoms of the anions the mean B-S distance in the rings (1.82 Å) is somewhat larger than the exocyclic ones (1.77 Å). Up to now no cyclic selenoborate with boron in trigonal-planar coordination has been reported. It is likely that due to steric inadequacies $(p\text{-}p)\pi$ interactions don't give any stabilizing energy gains. Consequently a tetrahedral coordination of boron is observed in most boron selenium compounds. Nevertheless, stabilization of trigonal-planar coordination in B_3Se_3 and B_2Se_3 rings can be achieved with exocyclic -I-substituents as is observed in $(XBSe)_3$ and $X_2B_2Se_3$ (X = Br, I) as well as in $((C_6H_5)BSe)_3$ and $(C_6H_5)_2B_2Se_3$.[11, 16]

Boron in tetrahedral coordination

If in a molecule trigonal-planar coordinated boron coexists with sulfide or disulfide, the formation of intermolecular donor-acceptor complexes is possible. This gives dimeric, trimeric or even polymeric molecules. An early example of this kind is $X_2B\text{-}SCH_3$ (X = Cl, Br) that in solid state is trimeric.[17] Boron is tetrahedrally coordinated with a mean B-S distance of 1.95 Å. In boron-chalcogen ring compounds 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 of different rings

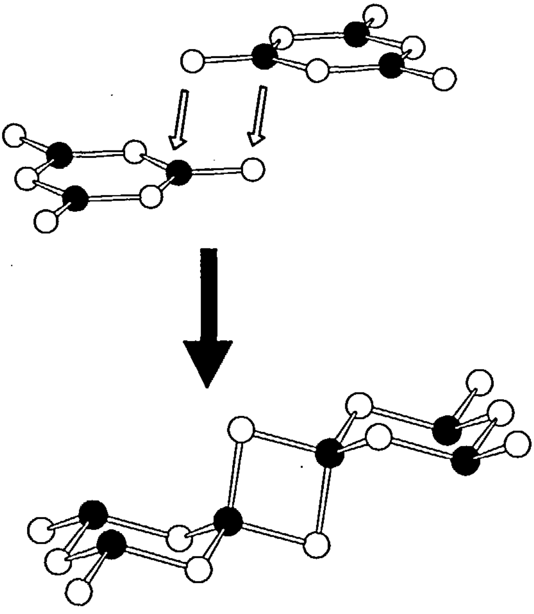


FIGURE 3: Formation of a donor-acceptor complex in $TlBS_2$

In figure 3 the formation of the polymeric $(BS_2^-)_n$ anion in $TlBS_2$[18] is shown as interpreted as donor-acceptor complex formation of 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 other than in B_2S_3 contain tetrahedrally coordinated boron. Consequently the formerly planar six-membered B_3S_3-ring now is in the chair conformation and is connected to three more B_3S_3-rings via B_2S_2-rings. A layered structure of polymerized B_3S_6 units is formed. A rehybridization of boron from sp^2 to sp^3 has taken place.

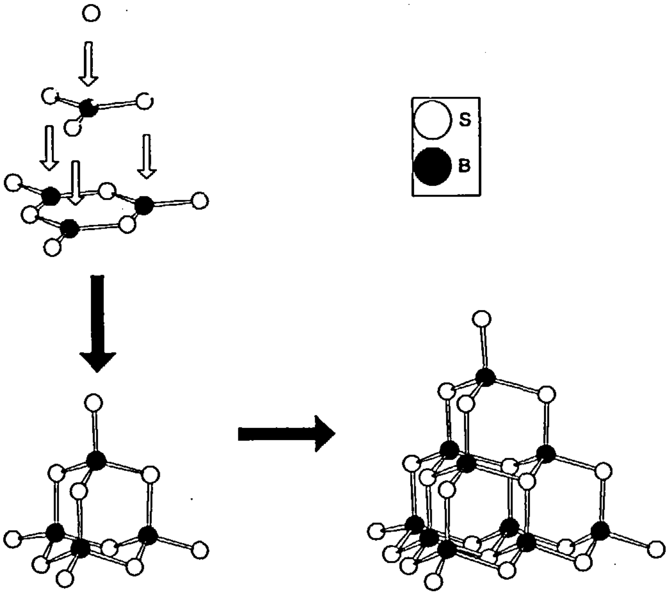
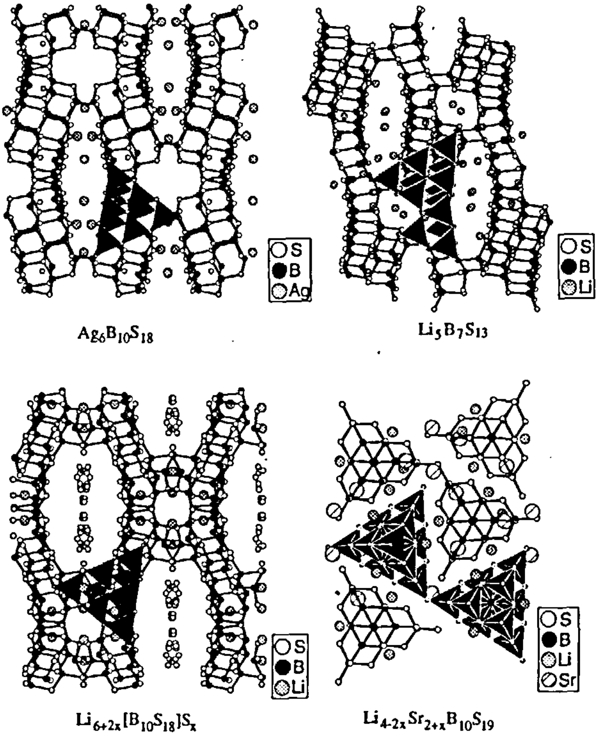


FIGURE 4: Formation of B_4S_{10} and $B_{10}S_{20}$ macrotetrahedra

In figure 4 a possible interpretation of the formation of the adamantane-like $B_4S_{10}^{4-}$ anion is proposed. With just one additional sulfide this macrotetrahedron can be built starting from planar boron-sulfur units. Each sulfur atom of a planar BS_3^{3-} entity coordinates to one of the boron atoms in a B_3S_3-ring, that needs to be rehybridized to sp^3. A sulfur atom on top of the remaining boron atom completes the $B_4S_{10}^{4-}$ -unit. This relatively highly charged fragment is found in $Pb_4B_4S_{10}$.[7,19] Covalent interactions between lead and terminal sulfur atoms are discussed to partially compensate the charges. The „superadamantane" $B_{10}S_{20}$ unit is built in a similar way. These fragments are found in a variety of compounds with different types of polymerization. In $Li_{4-2x}Sr_{2+x}B_{10}S_{19}$ ($x \approx 2$) chains of $B_{10}S_{18}S_{2/2}$ are present,[20] in

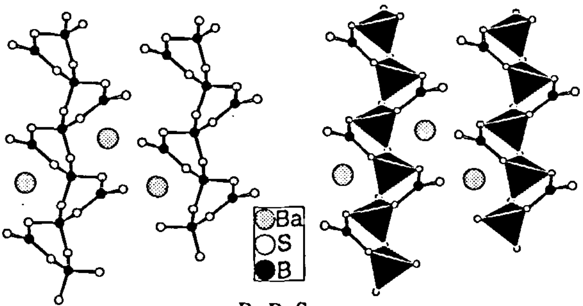


$Ag_6B_{10}S_{18}$ $Li_5B_7S_{13}$

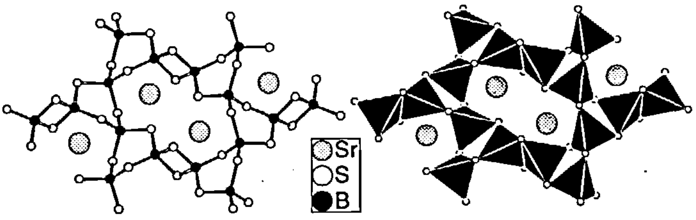
$Li_{6+2x}[B_{10}S_{18}]S_x$ $Li_{4-2x}Sr_{2+x}B_{10}S_{19}$

FIGURE 5: Macrotetrahedral polymeric thioborate networks

$Ag_6B_{10}S_{18}$ and $Na_6B_{10}S_{18}$[20] all corners of a $B_{10}S_{16}S_{4/2}$ are connected to neighbouring units and two independent, interpenetrating infinite three-dimensional networks are formed in this way. The smallest possible unit of this kind, a BS_4^{5-}-anion, has never been observed due to its high charge, but it is a very strong Lewis base. In $Li_9B_{19}S_{33}$[20] it serves as a linkage between $B_{10}S_{16}S_{4/2}$ entities to again form two independent, interpenetrating infinite three-dimensional networks. Another example of this kind is found in $Li_5B_7S_{13}$,[20] where an alternation of $B_4S_6S_{4/2}$-tetrahedra and $B_{10}S_{16}S_{4/2}$-supertetrahedra forms the networks. Compounds with infinite networks of macrotetrahedra form a very rigid three-dimensional anionic framework with fairly large voids and channels. These spaces are of a similar energetic environment; consequently the movement of cations is not much hindered. Solid state NMR spectroscopy on ^{7}Li-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.[21]



BaB_2S_4



SrB_2S_4

FIGURE 6: The crystal structures of BaB_2S_4 and SrB_2S_4

Not only Lewis basicity is important for the formation of donor-acceptor complexes but also sterical demands of the cations. The anion in BaB_2S_4[22] forms an infinite chain of spirocyclically fused six-membered B_3S_3 rings. Figure 6 shows this situation. The bridging boron atoms inside a six-membered ring are tetrahedrally coordinated, whereas those with a terminal sulfur atom are trigonal-planar coordinated. The nearest distance between a terminal sulfur atom of one chain to a trigonal-planar boron atom in a neighbouring chain is 3.62 Å.

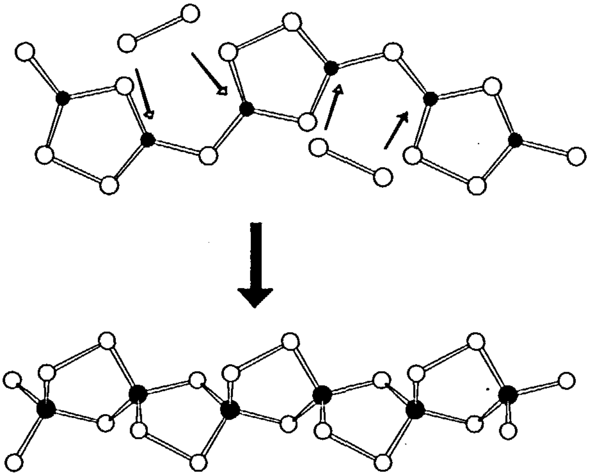


FIGURE 7: Formation of $(BSe_3^-)_n$ by nucleophilic attack of diselenide

In SrB_2S_4[18] the situation is comparable, but here the donor-acceptor complex has been formed. All boron atoms are in sp^3-hybridization and a four-membered B_2S_2 ring has been formed. Obviously the larger Ba^{2+} ion prevented the formation of the infinite two-dimensional cation. An alternative way to look at the cation structure is given in figure 6: In BaB_2S_4 infinite chains of corner-sharing BS_4 tetrahedra with an additional B-S bridge are present, in SrB_2S_4

these chains of corner-sharing BS_4 tetrahedra are connected to neighbouring chains via a B_2S_6 unit of two edge-sharing tetrahedra.

Most of the thioborates with boron in tetrahedral coordination do not contain a disulfide fragment, whereas all known selenoborates with tetrahedrally coordinated boron contain diselenide units. The nucleophilic attack of diselenide to $(BSe_2)_n$ is shown in figure 7. This process results in an infinite chain of spirocyclically fused five-membered B_2Se_3 rings with boron in tetrahedral coordination.

Selenoborates and icosahedral boron-clusters

Just recently the novel chalcogenoborate $Cs_8[B_{12}(BSe_3)_6]$ was synthesized starting from caesium selenide, boron and selenium.[23] This compound contains a B_{12} icosahedron completely saturated with chalcogen ligands (figure 8). Thus, during the synthesis the B_{12} icosahedron is preserved rather than being fragmented by nucleophilic attack, as is known from all earlier chalcogenoborate syntheses. The new $Cs_8[B_{12}(BSe_3)_6]$ contains chelate-bonded trigonal planar selenoborate entities that complete the B_{12} icosahedron to form a persubstituted *closo*-dodecaborate anion. Thus, the caesiumhexaselenoborato-*closo*-dodecaborate is the first representative of a new type of boron cluster compounds.

The electronic counts of the selenium-substituted dodecaborate unit obey Wade's rules for cluster compounds. The *closo*-cluster contains 2n+2 binding electrons in a B_{12} unit, six negative charges are located mainly on the terminal selenium atoms leaving two negative charges on the central cluster. The $[B_{12}(BSe_3)_6]^{8-}$ species is of additional general interest because of the *complete* substitution of a *closo*-borate by non-hydrogen atoms. These results open new ways to the understanding of the reaction paths toward a novel class of boron-chalcogen compounds. On the other hand they give access to a new field of interesting materials, first of all by replacement of selenium by the homologous sulfur. The size of the selenoboratoborate anion is particularly interesting for the use of small cations like Li^+, Ag^+, or Cu^+ to synthesize new ionic conductors. As another strategy to synthesize polyhedric chalcogenoborates one can probably start from metal borides with pre-formed B_{12}, B_6, or other clusters rather than from elemental boron.

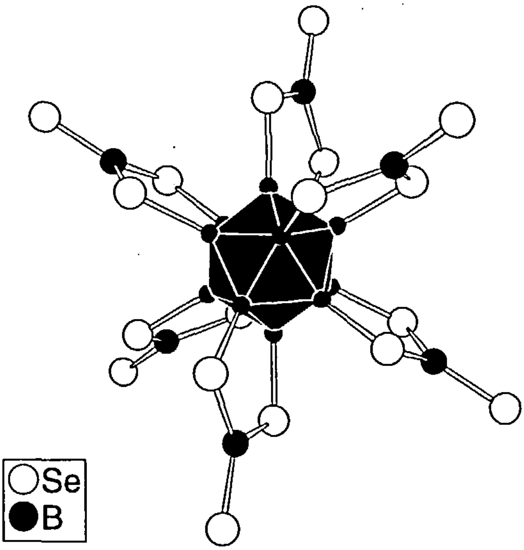


FIGURE 8: $[B_{12}(BSe_3)_6]^{8-}$-anion in $Cs_8[B_{12}(BSe_3)_6]$

REFERENCES

[1] A. Stock, F. Blix, Ber. Deut. Chem. Ges. 34, 3039, (1901).
[2] E. Wiberg, W. Sturm, Angew. Chem. 67 483 (1955).

[3] a) J. A. Forstner, E. L. Muetterties, Inorg. Chem. **5** 164 (1966); b) G. W. Bushell, G. A. Rivett, Can. J. Chem. **55** 3294 (1975).

[4] a) H. M. Seip, R. Seip, W. Siebert, Acta Chem. Scand. **27** 15 (1973); b) A. Almenningen, H. M. Seip, P. Vassbotn, Acta Chem. Scand. **27** 21 (1973).

[5] a) F. Chopin, A. Hardy, C. R. Acad. Sci. **261** 142 (1965); b) F. Chopin, G. Turrell, J. Mol. Struct. **3** 57 (1969).

[6] H. Diercks, B. Krebs, Angew. Chem. **89** 327 (1977); Angew. Chem. Int. Ed. Engl. **16** 313 (1977).

[7] B. Krebs, Angew. Chem. **95** 113 (1983); Angew. Chem. Int. Ed. Engl. **22** 113 (1983).

[8] B. Krebs, H. U. Hürter, Angew. Chem. **92** 479 (1980); Angew. Chem. Int. Ed. Engl. **19** 481 (1980).

[9] B. M. Gimarc, J.-K. Zhu, Inorg. Chem. **22** 479 (1983).

[10] a) M. Schmidt, W. Siebert, Angew. Chem. **76** 687 (1964); Angew. Chem. Int. Ed. Engl. **3** 637 (1964); b) M. Schmidt, W. Siebert, Z. Anorg. Allg. Chem. **87** 345 (1966); c) M. Schmidt, W. Siebert, Angew. Chem. **78** 607 (1966); Angew. Chem. Int. Ed. Engl. **5** 597 (1966); d) M. Schmidt, W. Siebert, F. Rittig, Chem. Ber. **191** 281 (1968); e) M. Schmidt, W. Siebert, E. Gast, Z. Naturforsch. **22b** 557 (1967).

[11] R. Conrady-Pigorsch, W. Müller-Warmuth, G. Schwetlik, M. Wienkenhöver, B. Krebs, Ber. Bunsenges. Phys. Chem. **95** 453 (1991)

[12] C. Püttmann, H. Diercks, B. Krebs, Phosphorus, Sulfur, Silicon **65** 1 (1992).

[13] W. Schwarz, H. D. Hausen, H. Hess, J. Mandt, W. Schmelzer, B. Krebs, Acta Crystallogr. **B29** 2029 (1973)

[14] C. Jansen, J. Küper, B. Krebs, Z. Anorg. Allg. Chem. **621** 1322 (1995).

[15] A. Hammerschmidt, C. Jansen, J. Küper, C. Püttmann, B. Krebs, Z. Anorg. Allg. Chem. **621** 1330 (1995).

[16] W. Siebert,Chemiker-Ztg. **98** 479 (1974).

[17] S. Pollitz, F. Zettler, D. Forst, H. Hess, Z. Naturforsch. **31b** 897 (1976).

[18] C. Püttmann, W. Hamann, B. Krebs, Eur. J. Solid State Inorg. Chem. **29** 856 (1992).

[19] A. Hardy, Bull. Soc. Fr. Mineral. Cristallogr. **91** 111 (1968).

[20] a) C. Püttmann, P. zum Hebel, A. Hammerschmidt, B. Krebs, Acta Crystallogr. **A46** C279 (1990); b) F. Hiltmann, P. zum Hebel, A. Hammerschmidt, B. Krebs, Z. Anorg. Allg. Chem. **619** 293 (1993); c) A. Hammerschmidt, P. zum Hebel, F. Hiltmann, B. Krebs, Z. Anorg. Allg. Chem. **622** 76 (1996); d) B. Krebs, H. Diercks, Z. Anorg. Allg. Chem. **518** 101 (1984).

[21] a) P. zum Hebel, B. Krebs, M. Grüne, W. Müller-Warmuth, Solid State Ionics **43** 133 (1990); b) M. Grüne, H. Meierkord, W. Müller-Warmuth, P. zum Hebel, B. Krebs, M. Wulff, Ber. Bunsenges. Phys. Chem. **93** 1313 (1989).

[22] M. Wulff, B. Krebs, unpublished results.

[23] J. Küper, O. Conrad, B. Krebs, Angew. Chem. (1997), in press