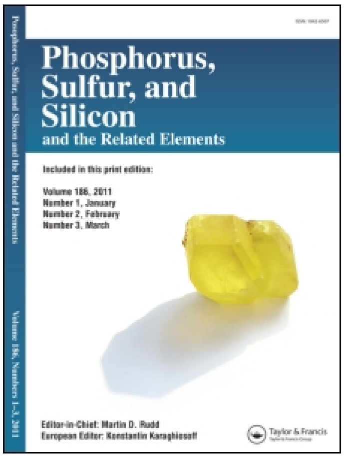

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The First Perselenoborate with a Novel Three-Dimensional Anion Network

Arno Lindemann; Joachim Kuchinke; Christian Köster; Adrienne Hammerschmidt; Matthias Döch; Timo Pruss; Bernt Krebs

To cite this Article Lindemann, Arno , Kuchinke, Joachim , Köster, Christian , Hammerschmidt, Adrienne , Döch, Matthias , Pruss, Timo and Krebs, Bernt(2001) 'The First Perselenoborate with a Novel Three-Dimensional Anion Network', Phosphorus, Sulfur, and Silicon and the Related Elements, 169: 1, 169 — 172

To link to this Article: DOI: 10.1080/10426500108546617

URL: http://dx.doi.org/10.1080/10426500108546617

Phosphorus, Sulfur and Silicon, 2001, Vol. 169, pp. 169-172
Reprints available directly from the publisher
Photocopying permitted by license only

The First Perselenoborate with a Novel Three-Dimensional Anion Network

ARNO LINDEMANN, JOACHIM KUCHINKE, CHRISTIAN KÖSTER, ADRIENNE HAMMERSCHMIDT, MATTHIAS DÖCH, TIMO PRUSS and BERNT KREBS*

Anorganisch-Chemisches Institut der Universität Münster Wilhelm-Klemm-Straße 8, D-48149 Münster, Germany

(Received August 24, 2000)

The lithium perselenoborate $Li_2B_2Se_5$ was prepared from stoichiometric amounts of lithium selenide Li_2Se, amorphous boron and selenium in an evacuated carbon-coated silica tube by solid state reaction at 800 °C. The crystal structure was refined from single crystal X-ray diffraction data. The new compound contains a novel three-dimensional boron-selenium network in which lithium cations are situated between. The boron atoms are in a tetrahedral BSe_4 coordination. Lithium cations are surrounded by five selenium atoms in a range of 2.543 Å to 2.824 Å.

Keywords: selenoborates; perselenoborates; network structures; boron

INTRODUCTION

The chemistry of selenoborates represents a relatively new and still unexplored research field. Only a dozen boron selenium compounds of alkali metal and of monovalent thallium are structurally characterized by single crystal X-ray structure analysis [1]. This fact is surprising considering the multitude of oxo- and thioborates which contain a very

---

* Corresponding author. Tel.: +49 251 833 3131. Fax: +49 251 833 8366. E-mail: krebs@uni-muenster.de

large number of structural features showing boron in three different chalcogen coordinations. Binary boron selenide $[BSe_2]_n$ [2] and the thallium selenoborate Tl_3BSe_3 [3] contain boron in only trigonal-planar coordination by selenium. Boron tetrahedrally surrounded by selenium can be found in polymeric chain [4] or layered structures [5]. Novel isolated $[B_{12}(BSe_3)_6]^{8-}$-anions exist in the ternary and quaternary compounds $M_8[B_{12}(BSe_3)_6]$ and $M_4Hg_2[B_{12}(BSe_3)_6]$ (M = Rb, Cs) [6]. These anions consist of B_{12} *closo*-clusters completely saturated with selenium by six BSe_3 entities.

In this work we report the synthesis and crystal structure of the new lithium perselenoborate $Li_2B_2Se_5$. This is the first example of a boron-selenium compound containing a 3D-anion network structure.

EXPERIMENTAL

The lithium perselenoborate was prepared in a silica tube coated with an inner surface of glassy carbon, which can be manufactured by slowly turning the ampoule filled with acetone vapour helically through the flame of an oxygen-hydrogen operated welding torch at about 1300 K. For the synthesis of $Li_2B_2Se_5$ stoichiometric amounts of Li_2Se, amorphous boron and elementary selenium were mixed and filled into the silica tube which was thereafter sealed off at a pressure of approximately 6 Pa. The sample was heated in a horizontal one-zone furnace following the specified temperature program:

$$\mathrm{RT} \xrightarrow{15\,\mathrm{h}} 800^\circ\mathrm{C}\ (8\mathrm{h}) \xrightarrow{48\,\mathrm{h}} 650^\circ\mathrm{C} \xrightarrow{240\,\mathrm{h}} 300^\circ\mathrm{C} \xrightarrow{4\,\mathrm{h}} \mathrm{RT}.$$

$Li_2B_2Se_5$ is air and moisture sensitive and has to be handled under a dry argon atmosphere.

RESULTS and DISCUSSION

The lithium selenoborate contains a novel three-dimensional anionic boron-selenium network of general composition $[(B_2Se_5)^{2-}]_n$ and coordinating lithium cations. The boron atoms are tetrahedrally surrounded by selenium. Each BSe_4 tetrahedron is connected via three corners to neighboring entities forming polymeric boron-selenium layers running parallel to the a-b plane. Figure 1 represents a part of one layer in projection along the c-axis. These two-dimensional layers exhibiting macrocyclic twelve-membered B_6Se_6 rings, are bridged via diselenide contacts to form a polymeric framework (Figure 2).

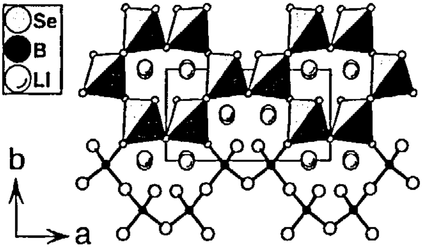

FIGURE 1: Projection on a boron-selenium layer in $Li_2B_2Se_5$ along [001]

The average B-Se-bond length in the crystal structure of $Li_2B_2Se_5$ [7] amounts to 2.061 Å which is significantly longer than those observed in other alkali metal perselenoborates with tetrahedrally coordinated boron ($Li_2B_2Se_7$: 2.048 Å [1], $Na_2B_2Se_7$: 2.044 Å [4], $K_2B_2Se_7$: 2.050 Å [4], $Rb_2B_2Se_7$: 2.049 Å [1]). A comparison to bond length in selenoborates with trigonal-planar coordinated boron indicates clear differences. The latter range from 1.90 Å (i.e. in $[BSe_2]_n$ [2]) to 2.02 Å (i.e. in $M_4Hg_2[B_{12}(BSe_3)_6]$ (M = Rb, Cs) [6]). The Se-Se distance is calculated to be 2.378 Å. Lithium cations are five-fold coordinated by selenium in the range of 2.543 Å to 2.824 Å. They form a slightly distorted square pyramid (Figure 3).

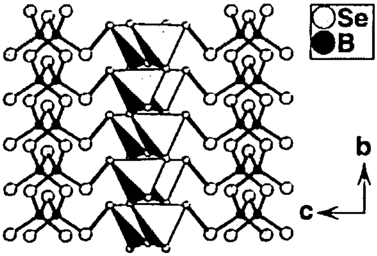

FIGURE 2: View of the anionic framework in the crystal structure of $Li_2B_2Se_5$ along [100]

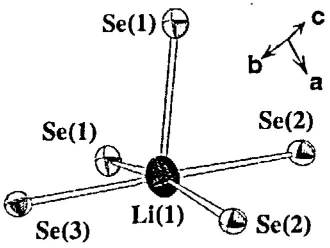

FIGURE 3: Elliposid-plot of the lithium coordination in $Li_2B_2Se_5$ (50% probability)

ACKNOWLEDGEMENTS

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for substantial support of this work.

References

[1] a) O. Conrad, C. Jansen, B. Krebs, *Angew. Chem.* **110** 3396 (1998); *Angew. Chem. Int. Ed.* **37** 3208 (1998); b) O. Conrad, B. Krebs, *Phosphorus, Sulfur, and Silicon* **124/125** 37 (1997).

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

[3] B. Krebs, W. Hamann, *J. Less-Common Met.* **137** 143 (1988).

[4] a) A. Hammerschmidt, J. Küper, L. Stork, B. Krebs, *Z. Anorg. Allg. Chem.* **620** 1898 (1994); b) A. Lindemann, J. Kuchinke, C. Köster, B. Krebs, *Z. Anorg. Allg. Chem.* (in preparation).

[5] A. Lindemann, J. Kuchinke, C. Köster, B. Krebs, *Z. Anorg. Allg. Chem.* (in preparation).

[6] a) J. Küper, O. Conrad, B. Krebs, *Angew. Chem.* **109** 1995 (1997); *Angew. Chem. Int. Ed. Engl.* **36** 1903 (1997); b) A. Lindemann J. Kuchinke, B. Krebs, *Z. Anorg. Allg. Chem.* **625** 1165 (1999).

[7] $Li_2B_2Se_5$: monoclinic; space group: C2/c; a = 10.616(2) Å, b = 5.318(1) Å, c = 12.382 Å, $\beta = 109.97(3)°$; $V = 657.0(2)$ $Å^3$; $\mu = 27.4$ mm^{-1}; Z = 4; R1 = 0.0207 for 710 reflections with $I \geq 2\sigma(I)$; wR2 = 0.0572 for all 775 unique reflections; MoKα-radiation; graphite monochromator; structure solution with SHELXS-97; refinement with SHELXL-97 (G. M. Sheldrick, University of Göttingen). Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, (Fax: (+49)7247–808–666, e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-411410.