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LiBSe₃: A NOVEL PERSELENOBORATE WITH POLYMERIC ANION NETWORK

Steffen Pütz^a; Matthias Döch^a; Arno Lindemann^a; Adrienne Hammerschmidt^a; Bernt Krebs^a Universität Münster, Münster, Germany

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LibSe₃: A NOVEL PERSELENOBORATE WITH POLYMERIC ANION NETWORK

Steffen Pütz, Matthias Döch, Arno Lindemann, Adrienne Hammerschmidt, and Bernt Krebs Universität Münster, Münster, Germany

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We now report the synthesis and crystal structure of LiBSe₃, a new perselenoborate with anionic layers. LiBSe₃ crystallizes in the orthorhombic space group $Pca2_1$ (No. 29), a=12.770(3) Å, b=5.777(2) Å, c=10.726(2) Å.

Keywords: Boron; crystal structure; ternary selenoborate

Over the past two decades improved solid state preparation techniques, particularly the preparation of high quality single crystals, has allowed a rapid progress in the understanding of chalcogenoborate chemistry. A wide variety of ternary and quaternary seleno- and perselenoborates has been synthesized and structurally characterized over the last 35 years. ¹⁻⁶

EXPERIMENTAL

LiBSe₃ was synthesized by reaction of stoichiometric amounts of lithium selenide, amorphous boron, and selenium. The reaction mixture was filled into a carbon coated silica tube, evacuated, sealed, and inserted into a metal cylinder, which fit into a horizontal one-zone furnace. During the reaction and the subsequent annealing, respectively, a specific temperature profile was applied to the reaction mixture. From the crystalline product single crystals for x-ray crystallography were

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Address correspondence to Bernt Krebs, Westfälische Wilhelms, Universität Münster and Collaborative Research Center 458, Wilhelm, Klemm, Straße 8, D-48149 Münster, Germany. E-mail: krebs@uni-muenster.de

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selected and manipulated into Mark capillaries. As some of the starting compounds as well as the product are moisture and air sensitive. All steps were carried out under dry inert gas atmosphere.

CRYSTAL STRUCTURE

For LiBSe₃ the following orthorhombic lattice parameters were determined on a STOE IPDS: $a=12.770(3)\,\mathring{A},\,b=5.777(2)\,\mathring{A},\,c=10.726(2)\,\mathring{A}.$ The structure solution in space group Pca2₁ (No. 29) yielded residuals of R1 = 0.036 and wR2 = 0.078. The structure of LiBSe₃ contains infinite layered [(BSe₃)⁻]_n anions (Figure 1), which are not isotypic to the hitherto known MBSe₃ perselenoborates (M = Na, Rb, Cs, Tl).^{7–9} The boron-selenium tetrahedra in LiBSe₃ are linked via corners to two neighboring tetrahedral units forming "Zweiereinfachketten" along.¹⁰ However, the linkage between two chains is performed by diselenide bridges resulting in a 2D polymeric network containing B₆Se₈-macrocycles.

Furthermore, no five-membered B_2Se_3 -rings occur in the structure. Thus, $LiBSe_3$ reveals the only perselenoborate besides $Li_2B_2Se_5$ with lack of this characteristic structural feature.

The boron-selenium tetrahedra are fairly distorted with a mean deviation from the ideal tetrahedral angle of 8.2°. B—Se bond lengths vary from 2.029 to 2.098 Å (mean 2.060 Å), which is in good agreement with perselenoborates such as RbBSe₃ (2.060 Å), CsBSe₃ (2.064 Å), TlBSe₃ (2.058 Å) Li₂B₂Se₅ (2.061 Å), and Li₂B₂Se₇ (2.048 Å). Compared to other perselenoborates of MBSe₃ type the average Se—Se bond (calculated to 2.375 Å) is slightly elongated. In the center of a B₆Se₈ macrocycle Li(1)

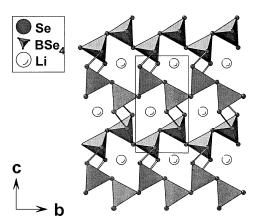


FIGURE 1 One layer of LiBSe₃ (along the a-axis).

can be described as five-fold coordinated while Li(2) possess a severe distorted octahedral coordination sphere with respect to Li···Se distances up to 3.03 Å. Li···Se bond lengths are in a range of 2.56 to 2.76 Å (mean 2.68 Å) for Li(1), 2.64 to 3.03 Å (mean 2.80 Å) for Li(2). The shortest intermetallic distance is found for Li(1)···Li(2) with 3.51 Å, all other are longer than 4.0 Å thus cation mobility is not expected.

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