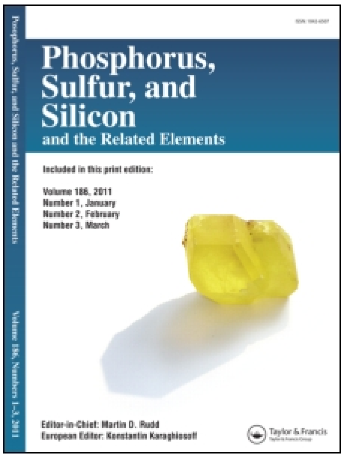

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$LiBSe_3$: A NOVEL PERSELENOBORATE WITH POLYMERIC ANION NETWORK

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$LiBSe_3$: A NOVEL PERSELENOBORATE WITH POLYMERIC ANION NETWORK

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We now report the synthesis and crystal structure of $LiBSe_3$, a new perselenoborate with anionic layers. $LiBSe_3$ 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

$LiBSe_3$ 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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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 $LiBSe_3$ the following orthorhombic lattice parameters were determined on a STOE IPDS: a = 12.770(3) Å, b = 5.777(2) Å, c = 10.726(2) Å. The structure solution in space group $Pca2_1$ (No. 29) yielded residuals of R1 = 0.036 and wR2 = 0.078. The structure of $LiBSe_3$ contains infinite layered $[(BSe_3)^-]_n$ anions (Figure 1), which are not isotypic to the hitherto known $MBSe_3$ perselenoborates (M = Na, Rb, Cs, Tl).[7–9] The boron-selenium tetrahedra in $LiBSe_3$ 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 B_6Se_8-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 $RbBSe_3$ (2.060 Å), $CsBSe_3$ (2.064 Å), $TlBSe_3$ (2.058 Å) $Li_2B_2Se_5$ (2.061 Å), and $Li_2B_2Se_7$ (2.048 Å). Compared to other perselenoborates of $MBSe_3$ type the average Se—Se bond (calculated to 2.375 Å) is slightly elongated. In the center of a B_6Se_8 macrocycle Li(1)

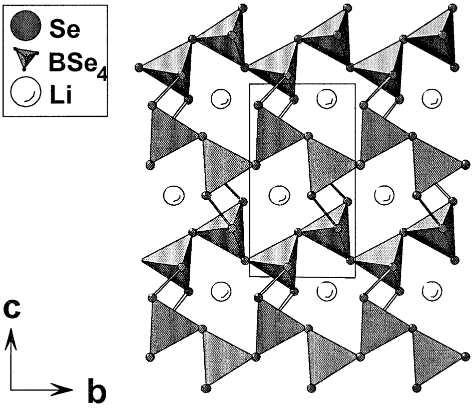

FIGURE 1 One layer of $LiBSe_3$ (along the a-axis).

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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