

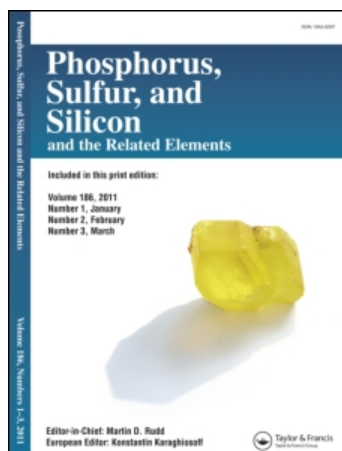
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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### $\text{Li}_{6-x}\text{Cs}_x\text{B}_{10}\text{Q}_{18}$ (Q = S, Se; x~1): New Polymeric Layered Anion Networks in Chalcogenoborates

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## $\text{Li}_{6-x}\text{Cs}_x\text{B}_{10}\text{Q}_{18}$ ( $\text{Q} = \text{S}, \text{Se}; x \sim 1$ ): New Polymeric Layered Anion Networks in Chalcogenoborates

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The chalcogenoborates  $\text{Li}_{6-x}\text{Cs}_x\text{B}_{10}\text{S}_{18}$  and  $\text{Li}_{6-x}\text{Cs}_x\text{B}_{10}\text{Se}_{18}$  ( $x \sim 1$ ) were prepared from stoichiometric amounts of lithium sulfide (selenide), cesium sulfide (selenide), boron and sulfur (selenium) in solid state reactions at higher temperatures. Single crystal X-ray diffraction was used to determine and refine the structures. Crystal data for  $\text{Li}_{6-x}\text{Cs}_x\text{B}_{10}\text{S}_{18}$  are: space group  $\text{I4}_1/\text{amd}$  (No. 141),  $a = 9.458(1) \text{ \AA}$ ,  $c = 26.507(5) \text{ \AA}$  with  $Z = 4$ , and  $a = 10.028(2) \text{ \AA}$ ,  $c = 27.743(6) \text{ \AA}$  for the isotypic  $\text{Li}_{6-x}\text{Cs}_x\text{B}_{10}\text{Se}_{18}$ . Both compounds are composed of corner-sharing super-adamantane analogous  $\text{B}_{10}\text{S(e)}_{20}$ -units, forming anionic layers, connected by lithium and cesium cations. The resulting structure represents a new structure type in thio- and selenoborate chemistry.

**Keywords:** thioborates; selenoborates; boron; network structures

### INTRODUCTION

Many thio- and selenoborates have been synthesized and described in the last decades [1,2]. For several years now practical applications of lithium containing solids, e.g. in batteries, fuel cells and related devices, have drawn interest on the mechanisms of cationic conductivity and the relations to structural features. Lithium thioborates have shown ionic conductivity in the glassy state [3]. The lithium thioborates  $\text{Li}_9\text{B}_{19}\text{S}_{33}$ ,  $\text{Li}_{4-2x}\text{Sr}_{2+x}\text{B}_{10}\text{S}_{19}$  ( $x \sim 0.27$ ),  $\text{Li}_3\text{B}_7\text{S}_{13}$  and  $\text{Li}_{6+2x}[\text{B}_{10}\text{S}_{18}]\text{S}_x$  ( $x \sim 2$ ) have been synthesized by our group and Li-NMR data were reported [4-9]. These compounds show signs of mobile cations in the crystal structures

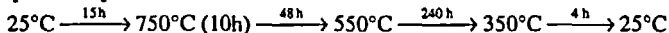
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as well as in the Li-NMR experiments. Especially the occupational disorder of lithium, as derived from single crystal analysis induced us to synthesize new compounds with the structural feature of anionic frameworks.

To modify the structural properties of  $\text{Li}_{6+2x}[\text{B}_{10}\text{S}_{18}]\text{S}_x$  ( $x \sim 2$ ) we started to substitute some of the lithium cations by cesium. The same experiments with the analogous selenium compounds were performed. Using  $\text{Li}_2\text{Q}$ ,  $\text{Cs}_2\text{Q}$ , B and Q ( $\text{Q} = \text{S}, \text{Se}$ ) in the ratio 2.5 : 0.5 : 10 : 15 an ordered structure is formed built-up by layers of corner-sharing  $\text{B}_{10}\text{Q}_{20}$  macrotetrahedra. These compounds represent a new structure type in the chemistry of chalcogenoborates.

## EXPERIMENTAL

The new compounds were prepared by reaction of lithium chalcogenide, cesium chalcogenide (synthesized by following the instructions of Klemm *et al.* [9]), amorphous boron and the chalcogen at 750° C in sealed and evacuated silica tubes using one-zone furnaces following this temperature profile:



The quartz glass reaction vessels to be used were protected against the attack of boron with a tight layer of glassy carbon formed by thermal decomposition of pure acetone. The crystalline products are colourless and sensitive to moisture and air.

## DESCRIPTION OF THE STRUCTURE

The crystal structures of the new compounds were determined from single crystal X-ray diffraction data.  $\text{Li}_{6-x}\text{Cs}_x\text{B}_{10}\text{S}_{18}$  and  $\text{Li}_{6-x}\text{Cs}_x\text{B}_{10}\text{Se}_{18}$  are isotypic and crystallize in space group  $\text{I4}_1/\text{amd}$ . The most important crystal parameters are given in table 1.

TABLE 1: Crystal parameters and measurement details [10]

	$\text{Li}_{6-x}\text{Cs}_x\text{B}_{10}\text{S}_{18}$	$\text{Li}_{6-x}\text{Cs}_x\text{B}_{10}\text{Se}_{18}$
Formula weight	852.79	1696.99
Crystal system	tetragonal	tetragonal
Space group	$\text{I4}_1/\text{amd}$ (No. 141)	$\text{I4}_1/\text{amd}$ (No. 141)
Unit cell dimensions	$a = 9.458(1) \text{ \AA}$ $c = 26.507(5) \text{ \AA}$	$a = 10.028(1) \text{ \AA}$ $c = 27.743(6) \text{ \AA}$
Volume	$2371.2(6) \text{ \AA}^3$	$2790.1(8) \text{ \AA}^3$
Z	4	4
R	$[I > 2\sigma(I)]$ 0.0404	0.0520
wR2	[all data] 0.1059	0.1175

Each of them is a further example of a polymeric anionic framework containing superadamantane-analogous  $B_{10}Q_{20}$ -macrotetrahedra as shown in figure 1. These  $B_{10}Q_{20}$ -macrotetrahedra are connected via all corners forming corrugated layers perpendicular to the c-axis as represented in figure 2.

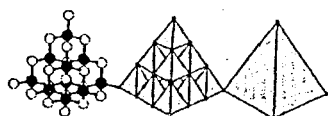


FIGURE 1:  $B_{10}Q_{20}$ -units shown as 10  $BQ_4$  groups and one macrotetrahedron for simplification

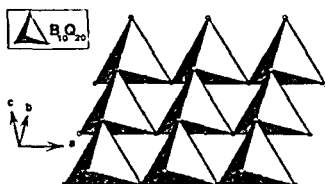


FIGURE 2: One layer of  $Li_{6-x}Cs_xB_{10}Q_{18}$  shown as macrotetrahedral plot

The layers are stacked on each other by rotation of 90 degrees. They are only connected via the cations and have no covalent interlayer contacts. Three cation positions are distinguishable, but only one of the cation positions is large enough for the cesium (occupation numbers are  $98 \pm 1\%$  for the thioborate and  $95 \pm 1\%$  for the selenoborate). The cesium cation is tenfold coordinated by the chalcogen in the range of  $3.435 \text{ \AA}$  to  $3.663 \text{ \AA}$  for the thioborate and  $3.511 \text{ \AA}$  to  $3.860 \text{ \AA}$  for the selenoborate. Two further sites are occupied by lithium in fourfold

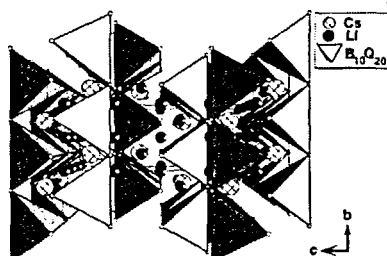


FIGURE 3: Unit cell in isometric view along the a-axis with drawn macrotetrahedra of six layers

chalcogen coordination. The lithium-chalcogen distances vary from  $2.502 \text{ \AA}$  to  $2.834 \text{ \AA}$  in the thioborate and  $2.607 \text{ \AA}$  to  $2.777 \text{ \AA}$  in the selenoborate. The free refinement of the cation positions results in a formula of  $Li_{6-x}Cs_xB_{10}Q_{18}$  with  $x \sim 1$  for the compounds. Figure 3 shows a unit cell in a perspective view with drawn macrotetrahedra of six layers.

## CONCLUSION

The new compounds represent a new class of thio- and selenoborates with polymeric anions. The occupational disorder of lithium as derived from the X-ray diffraction analysis makes these compounds interesting for further investigations e.g. ionic conductivity.

## ACKNOWLEDGEMENTS

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