Role of the Li$^+$ node in the Li-BH$_4$ substructure of double-cation tetrahydroborates

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Abstract

The phase diagram LiBH$_4$-ABH$_4$ (A = Rb, Cs) has been screened and revealed ten new compounds Li$_i$Aj[(BH$_4$)$_{i+j}$] (A = Rb, Cs), with $i$, $j$ ranging between 1 and 3, representing eight new structure types amongst homoleptic borohydrides. An approach based on synchrotron X-ray powder diffraction to solve crystal structures and solid-state first principles calculations to refine atomic positions allows characterizing multi-phase ball-milled samples. The Li-BH$_4$ substructure adopts various topologies as a function of the compound's Li content, ranging from one-dimensional isolated chains to three-dimensional networks. It is revealed that the Li$^+$ ion has potential as a surprisingly versatile cation participating in framework building with the tetrahydroborate anion BH$_4$ as a linker, if the framework is stabilized by large electropositive counter-cations. This utility can be of interest when designing novel hydridic frameworks based on alkaline metals and will be of use when exploring the structural and coordination chemistry of light-metal systems otherwise subject to eutectic melting.

Reference


DOI : 10.1107/S2052520614017351
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The phase diagram LiBH$_4$–ABH$_4$ ($A =$ Rb,Cs) has been screened and revealed ten new compounds Li$_i$A$_j$(BH$_4$)$_i$/$j$ ($A =$ Rb, Cs), with $i$, $j$ ranging between 1 and 3, representing eight new structure types amongst homoleptic borohydrides. An approach based on synchrotron X-ray powder diffraction to solve crystal structures and solid-state first principles calculations to refine atomic positions allows characterizing multiphase ball-milled samples. The Li-BH$_4$ substructure adopts various topologies as a function of the compound’s Li content, ranging from one-dimensional isolated chains to three-dimensional networks. It is revealed that the Li$^+$ ion has potential as a surprisingly versatile cation participating in framework building with the tetrahydroborate anion BH$_4$ as a linker, if the framework is stabilized by large electropositive counter-cations. This utility can be of interest when designing novel hydridic frameworks based on alkaline metals and will be of use when exploring the structural and coordination chemistry of light-metal systems otherwise subject to eutectic melting.

1. Introduction

Future sustainable energy systems call for abundant, cheap and high-energy density carriers. Hydrogen meets these requirements and its storage has been suggested to be most viable in chemical hydrides, in the solid state. Lightweight complex hydrides are the most competitive contenders due to their high gravimetric and volumetric capacities. However, their direct application is hampered by slow kinetics, poor thermodynamics and high hydrogen-release temperatures (Ley et al., 2014). Borohydrides store hydrogen in covalent bonds and hydrogen is released by thermolysis or hydrolysis of the tetrahydroborate anion BH$_4$ and chemical reactions involving it. Crystal structures amongst borohydrides range from packed predominantly ionic compounds (Filinchuk et al., 2008) to three-dimensional frameworks (Černý et al., 2007, 2009), as well as open nanoporous frameworks (Filinchuk et al., 2011). There exists a multitude of topologically intermediate structures, based mostly on the building principle of complex anions of the type $[M_n^{m+}(BH_4)_p]^{(p-m)n-}$, that are counterbalanced by alkali cations. Aside solid-state hydrogen storage, two energy-related fields are being ventured into by the complex hydrides’ community. These concern solid-state electrolytes (Unemoto et al., 2014), where the electrochemical stability as well as structural dynamics of the BH$_4$ anion are assumed to be favourable properties. On the other hand, the hydridic nature of hydrogen in the tetrahydroborate anion has been suggested as a means of enhanced and selective physical gas storage (Filinchuk et al., 2011). These arising applications call for a more precise and extensive characterization of...
cations that may act as mobile species in supraionic or framework builders in porous networks in different coordination polyhedra defined by the BH$_4$ ligand.

At the same time, many potentially useful ‘real life’ energy materials present major challenges concerning their structural characterization. Such material systems are often nano-crystalline, multiphase and poorly crystallized. The above problems are considered major issues when it comes to the structural characterization of new compounds, which forms the basis of any crystal design. As systems become more complex, poor data are in many cases the best kind available. Herein, we adopt an approach based on a structural solution in direct space and structural refinement by optimizations in the framework of periodic density functional theory to characterize the versatile coordination environment of the Li$^+$ cation in a homoleptic borohydride environment, based on ball-milled multi-phase powder samples. The use of large electropositive counter-cations provides diverse Li-BH$_4$ sub-lattices. We use topological arguments and crystal chemistry relationships to verify our results.

Recently we reported on the first trinmetallic homoleptic borohydride (Černý et al., 2013), which forms a three-dimensional framework with an underlying net of mco-c type, derived from the basic tfa tile (O’Keeffe et al., 2008). This (4,3)-connected framework had not been observed previously. In another recent work (Schouwink et al., 2014) we presented a series of compounds, AlLiM(BH$_4$)$_4$ ($A = K$ or Rb; $M = Mg$ or Mn) and K$_2$Li$_2$Mg$_2$(BH$_4$)$_9$, which represent the first two-dimensional topologies amongst homoleptic borohydrides. The layered Li–Mg–BH$_4$ substructure in these compounds forms negatively charged 4-connected networks, counter-balanced by the larger alkaline metal cations. It was shown that this connectivity cannot generate the long sought-after bimetallic Li–Mg borohydrides without counter-cations, when preferred coordination polyhedra are assumed as found in Mg(BH$_4$)$_2$ and LiBH$_4$.

Iono-covalent metal borohydrides tend to crystallize in structures related to the isoelectronic oxides or simple close-packed aristotypes. While directional bonding has been suggested to be at the origin of open frameworks as in the different modifications of Mg(BH$_4$)$_2$ (Filinchuk et al., 2011), it should be of less importance in packed compounds containing more electropositive cations. The question as to whether the strongly ionic packed compounds LiBH$_4$ and ABH$_4$ form solid solutions has hardly been addressed. The hitherto sole reported double alkaline-metal borohydride, LiK(BH$_4$)$_2$ (Nickels et al., 2008), was shown by first principles calculations to be unstable with respect to the decomposition to LiBH$_4$ and KBH$_4$ (Kim & Sholl, 2010).

The paper is organized in the following way: First we analyse the phase compositions for different compositional mixtures in the systems Rb–LiBH$_4$ and Cs–LiBH$_4$, formally presenting the different discovered compounds and their thermal stabilities. We then continue with the discussion of solved crystal structures and the optimization of structural details by first principles calculations. In the third part the role of the Li$^+$ cation as a framework-builder is discussed for different threefold and fourfold coordination environments in one-, two- and three-dimensional Li-BH$_4$ substructures.

2. Experimental

All samples presented herein were prepared by ball-milling appropriate molar ratios of starting materials LiBH$_4$ and ABH$_4$ ($A = Rb$, Cs) in a Fritsch planetary ball mill at 600 r.p.m. The total milling time amounted to 120 min, at 60 repetitions of 2 min each, interrupted by 5 min cooling breaks. A complete list of samples is provided in Table S1 of the supporting information.

2.1. Synchrotron radiation X-ray powder diffraction (SRXPD)

The data used for crystal structure solution and refinements in this study were collected between room temperature and 500 K at two different sources. At the Swiss–Norwegian Beamlines of ESRF (European Synchrotron Radiation Facility, Grenoble, France) diffraction data was measured on a Dectris Pilatus M2 detector at a wavelength of 0.8226 and 0.8210 Å. The temperature was controlled with the Oxford Cryostream 700+ or hot air blower and the two-dimensional images were integrated and treated with FIT2D (Hammersley et al., 1996). At the Materials Science Beamline of the Swiss Light Source of PSI (Villigen) high-resolution data were obtained on a curved MYTHEN-II silicon strip detector at a wavelength of 0.8271 Å and the temperature was controlled with the Stoe high-temperature attachment. For all measurements the samples were loaded into borosilicate capillaries of diameter 0.5 mm, which were spun during data acquisition. The wavelength was calibrated using the external NIST SRM660b standard.

The data from the SLS have a higher resolution in reciprocal space and a narrower profile of the diffraction peaks, and were therefore preferred for indexing. On the other hand, two-dimensional images from the area detector at the SNBL benefit from better powder averaging and lesser sensitivity to the grainy state of powder samples. This is especially the case after the phase transition of m-LiRb(BH$_4$)$_2$ to o-LiRb(BH$_4$)$_2$, or when stable borohydrides crystallize from the melt, and intensities from one-dimensional detectors become unreliable as the samples turn grainy.

2.2. In-situ ball milling

Synchrotron powder diffraction was also performed using an in-situ ball milling setup at ID15A of ESRF, at a wavelength of 0.1467 Å. The data were collected at room temperature on a medical Perkin–Elmer detector allowing for a time resolution of 5 s per frame. The ball mill used for this experiment is a shaker-type mill, Retsch MM200, using plastic vials and stainless steel balls, which can be run between 5 and 30 Hz. The results presented here were measured at 20 Hz.

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1 Supporting information for this paper is available from the IUCr electronic archives (Reference: DK5027).
The symmetry of the optimized models was analysed using the program PLATON (Spek, 2006). The orientation of the lattice vectors corresponds to the optimized symmetry. The calculated energy is shown in the last column. To facilitate the comparison between different structures the calculated energies were normalized by dividing by the total number of electrons in a respective cell.

Table 1
Lattice parameters from Rietveld refinements, space groups and energies (scaled to the number of electrons in the unit cell) from the DFT optimization of novel phases observed in ball-milled samples with the molar ratios LiBH₄: ABH₄ of 1:1 and 2:1 (A = Rb, Cs), and 3:1 and 4:1 (A = Cs).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Starting symmetry</th>
<th>Optimized symmetry</th>
<th>V (Å³)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>T (K)</th>
<th>Energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-LiRb(BH₄)₂</td>
<td>P2₁/c</td>
<td>C2₁m</td>
<td>1855.52 (3)</td>
<td>23.5931 (4)</td>
<td>4.6178 (7)</td>
<td>17.1893 (3)</td>
<td>97.7761 (1)</td>
<td>296</td>
<td>-966.63</td>
</tr>
<tr>
<td>o-LiRb(BH₄)₂</td>
<td>Cmc₂₁</td>
<td>Cmc₂₁</td>
<td>561.7 (1)</td>
<td>4.571 (1)</td>
<td>15.485 (1)</td>
<td>7.9355 (6)</td>
<td>-</td>
<td>411</td>
<td>-966.38</td>
</tr>
<tr>
<td>h-Li₂Rb(BH₄)₃</td>
<td>C2cm</td>
<td>C2cm</td>
<td>561.7 (1)</td>
<td>4.571 (1)</td>
<td>15.485 (1)</td>
<td>7.9355 (6)</td>
<td>-</td>
<td>411</td>
<td>-964.66</td>
</tr>
<tr>
<td>o-LiCs(BH₄)₃</td>
<td>P₆₃</td>
<td>P₆₃</td>
<td>560.4 (3)</td>
<td>7.474 (2)</td>
<td>-</td>
<td>11.585 (3)</td>
<td>300</td>
<td>-</td>
<td>901.43</td>
</tr>
<tr>
<td>h-Li₂Cs(BH₄)₃</td>
<td>P₆₃</td>
<td>P₆₃</td>
<td>593.2 (2)</td>
<td>4.6817 (7)</td>
<td>15.950 (3)</td>
<td>7.944 (1)</td>
<td>368</td>
<td>-</td>
<td>757.83</td>
</tr>
<tr>
<td>m-Li₂Cs(BH₄)₃</td>
<td>Cc</td>
<td>Cc</td>
<td>775.4 (3)</td>
<td>7.574 (2)</td>
<td>7.948 (2)</td>
<td>12.880 (3)</td>
<td>293</td>
<td>-</td>
<td>747.67</td>
</tr>
<tr>
<td>m-Li₂Cs(BH₄)₃</td>
<td>C2/c</td>
<td>C2/c</td>
<td>1985.0 (5)</td>
<td>7.602 (1)</td>
<td>15.160 (2)</td>
<td>7.935 (1)</td>
<td>293</td>
<td>-</td>
<td>598.39</td>
</tr>
<tr>
<td>o-Li₂Cs(BH₄)₃</td>
<td>Fddd</td>
<td>Fddd</td>
<td>5620.1 (6)</td>
<td>13.5838 (8)</td>
<td>17.300 (1)</td>
<td>23.915 (1)</td>
<td>293</td>
<td>-</td>
<td>855.18</td>
</tr>
<tr>
<td>m-Li₂Cs(BH₄)₃</td>
<td>P₂₁/c</td>
<td>P₂₁/c</td>
<td>1535.3 (2)</td>
<td>14.444 (1)</td>
<td>7.4218 (6)</td>
<td>14.791 (1)</td>
<td>293</td>
<td>-</td>
<td>648.15</td>
</tr>
<tr>
<td>m-Li₂Cs(BH₄)₃</td>
<td>P₂₁/c</td>
<td>P₂₁/c</td>
<td>988.09 (7)</td>
<td>8.1992 (3)</td>
<td>12.3044 (5)</td>
<td>11.9009 (5)</td>
<td>293</td>
<td>-</td>
<td>-1129.0</td>
</tr>
</tbody>
</table>

2.3. Computational details
All the solid-state calculations were performed using the VASP code (Kresse & Hafner, 1993; Kresse & Furthmüller, 1996a,b). To optimize the structures a hybrid PBE0 functional (Perdew et al., 1996) was used. Plane waves formed a basis set and the calculations were performed using the projector-augmented wave method (Blöchl, 1994; Kresse & Joubert, 1999) and atomic pseudo-potentials (Kresse & Hafner, 1994). The energy cutoff controlling the accuracy of calculations was set to 700 eV and the Brillouin zones were sampled in four k-points (Teter et al., 1989; Bylander et al., 1990). The positions of all atoms in the computational cells were fully relaxed while the lattice parameters were either relaxed or fixed to the values from Rietveld refinement.

3. Results and discussion
3.1. Initial phase analysis from SRXPD
The lattice parameters, space groups and relevant structural features of all compounds presented in this section are summarized in Tables 1 and Tables S2 and S3. We do not discuss the quantitative phase analysis, as we do not consider these results to be accurate enough due to impurities that were not identified and the impossible quantification of amorphous components. Note that neither the phase composition nor the true phase diagram are the main topics of this article. The different compositions of ball-milled mixtures discussed in the following are abbreviated as e.g. LiRb₂₁, where we refer to a ratio of starting materials LiBH₄:RbBH₄ as 2:1.

3.1.1. Li–Rb borohydrides. The formation of m-LiRb(BH₄)₂ is observed in the ball-milled mixture LiRb₁₁, together with unreacted RbBH₄. The Li-rich ball-milled mixture LiRb₂₁ contains h-Li₂Rb(BH₄)₃ and m-LiRb(BH₄)₂ as major phases. Unreacted LiBH₄ was not observed in either mixture as a crystalline phase, and is assumed to have suffered from mechano-chemical amorphization. Residual NaBH₄ stemming from the synthesis of RbBH₄ was identified by phase analysis. It does not take part in the reaction.

The monoclinic polymorph m-LiRb(BH₄)₂ transforms to o-LiRb(BH₄)₂ at 403 K, which then melts at 414 K (Fig. S1). Recrystallization takes place upon cooling at 409 K, and the high-temperature phase transforms back to m-LiRb(BH₄)₂ at 375 K, and is stable down to room temperature (Fig. S2). The hysteresis of 28 K of the m–o transformation is compliant with a first-order character of the transformation in LiRb(BH₄)₂. This phase transition is interesting because it represents an uncommon case of a reversible reconstructive transformation, as manifested by different topologies in the Li–BH₄ substructure (Fig. 1) and the local environment of A.

The hexagonal phase h-Li₂Rb(BH₄)₃ is stable up to 392 K where it melts. No T-ramp (temperature ramp) was measured on cooling for the mixture LiRb₂₁, nevertheless, the identical case in the LiCs₂₁ mixture (see below) suggests that h-Li₂Rb(BH₄)₃ is the stable polymorph of Li₂Rb(BH₄)₃ at room temperature. No mixtures with ratios 3:1 or 4:1 were studied for the system Li–Rb-BH₄.

3.1.2. Li–Cs borohydrides. The nature of the system Li–Cs–BH₄ is much more complex and presumably subject to various metastable phase equilibria. The thermal phase stabilities as determined from in-situ powder diffraction are schematized for three different samples LiCs₁₁, LiCs₂₁ and LiCs₃₁ (Fig. 1). A fourth mixture, LiCs₄₁, was prepared and produced a single phase sample of the most Li-rich phase Li₃Cs(BH₄)₂. This phase is already a major phase in the mixture LiCs₃₁. We hence assume that the maximum Li content in the phase diagram LiBH₄–CsBH₄ is reached with this phase, at least under the present synthetic conditions. The mixture LiCs₄₁ is thus not reported in Fig. 1.

Complementary to in-situ T-ramping we recently performed in-situ ball-milling experiments on the system Li–Cs–BH₄; selected results can be found in the supplementary information (Fig. S15). We would like to point out that this method is, although still in its infancy, quite adapted to study reactions taking place during mechano-chemical synthesis (Halasz et al., 2014). Our preliminary findings show that the sheet-structured m-Li₂Cs(BH₄)₃ is formed as the first phase in every mixture, together with the unidentified phase.
3.2. Crystal structures from SRXPD data

The crystallography on samples such as those reported herein presents demanding powder diffraction and requires that more than one phase be indexed and solved at a time. In particular, the characterization of the system Li-Cs-BH$_4$ implies the treatment of as many as 3–4 unknown phases in the very same sample. To achieve this we apply what is known as 'decomposition-aided indexing' by means of temperature ramps (Černý & Filinchuk, 2011), separating the peaks of individual phases by correlating them to their temperature-dependent disappearance from the diffraction pattern. After the assignment of peaks with this method each novel phase was indexed on the basis of 10–15 peaks with the dichotomy routine implemented in FOX (Favr-Nicolin & Černý, 2002). The resulting cells are given in Table 1 (cell parameters from Rietveld refinement). The extinction symbol was obtained by a careful visual inspection of powder patterns and identification of unobserved, i.e. extinct, Bragg reflections. Structure solution was always attempted in the highest symmetry space group compatible with the extinction symbol. The structures were modelled with Li and Rb (Cs) as free atoms and BH$_4$ groups compatible with the extinction symbol. The resulting cells are given in Table 1 (cell parameters from Rietveld refinement). The extinction symbol was obtained by considering that BH$_4$ is treated as rigid body, by defining appropriate Li—B and Li—H anti-bump distances and controlling the charge balance until a satisfactory structural model with acceptable cation coordination and interatomic distances was obtained.

All structural models were refined with TOPAS (Coelho, 2007), treating the BH$_4$ tetrahedra as semi-rigid bodies with a fixed ideal tetrahedral angle and refining one common B—H distance, constrained to adopt a value within 1.13 and 1.20 Å. The orientation of BH$_4$ was generated by introducing anti-bump constraints, which were defined in order to keep H—H intermolecular distances above 2.1 Å, and Li—H distances above 1.8 Å. Rietveld plots (Figs. S4–S6, S9–S12 and S14) are provided in the supporting information. The structural models obtained this way were used as starting models for density functional theory (DFT) optimizations.

3.3. DFT optimized crystal structures.

The computational optimization of structural models obtained from SRXPD by means of solid-state calculations allows us to examine structural details with higher accuracy. The space-group symmetries of experimentally determined structural models were either confirmed or modified (see Table 1). Two different sets of DFT calculations were performed, with (i) fixed and (ii) optimized lattice parameters. Optimizing lattice parameters serves as an evaluation of the stability with respect to balanced interatomic forces of the structural model proposed by powder diffraction. The calculations on a fixed lattice are relevant to determine the final atomic positions. In the case of borohydrides, the correct space group depends largely on the orientation of the BH$_4$ ligand itself. As opposed to XPD, solid-state optimization is sensitive to the position of H atoms. The symmetry analysis of the optimized models (and the respective starting symmetry pre-optimization), reported in Table 1, thus also includes H atoms.

The most significant change of the crystal structure post-optimization was registered for $m$-LiRb(BH$_4$)$_2$ where the starting symmetry $P2_1/c$ was modified by the optimization to $A2/m$ (standard setting is $C2/m$ with swapped $a$ and $c$ axes). The coordination numbers for all atoms as well as the topology of underlying nets are unchanged for both models. Since $P2_1/c$ is a maximal subgroup of $A2/m$, and the centring in this special case reveals itself only at higher Bragg angles (short $b$ axis), it is of no surprise that it was missed.

The crystal structure of $o$-LiRb(BH$_4$)$_2$ and $o$-LiCs(BH$_4$)$_2$ was identified to be derived from an analogous halide compound, LiRbCl$_2$ (Gaebell et al., 1983), with the space-group symmetry Cmcm. However, and assuming that the BH$_4$ groups are ordered, the true symmetry of $o$-LiRb(BH$_4$)$_2$ can only be lower than Cmcm and can then not be determined from XPD due to the insensitivity of the method to BH$_4$ orientation. Two maximal subgroups of Cmcm with the same extinction symbol are C2cm and Cmc2$_1$, both allowing for full orientational order of BH$_4$ groups. Rietveld refinements on

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**Figure 1**

Phase stability for the system LiBH$_4$–CsBH$_4$, as determined from in-situ powder diffraction. The phase composition on the left of the temperature scale concerns the as-milled samples. The Li most rich mixture Li-Cs 4:1 produced a single phase sample of Li$_4$Cs(BH$_4$)$_4$, hence the mixture 3:1 is considered the limit of Li solubility, which is why 4:1 is not reported in this figure.
structural models corresponding to these space-group symmetries, \( C2cm \) and \( Cmc2 \), respectively, result in a comparable goodness of fit. Both models retain their starting symmetry after the optimization. The calculated normalized energy, however, is slightly lower for the structural model \( Cmc2 \) than for \( C2cm \) (Table 1), which is why the former was accepted as the true symmetry of \( o-LiRb(BH_4)_2 \) and used as a starting symmetry for the optimization of \( o-LiCs(BH_4)_2 \). The calculated energies of both the low- and high-temperature polymorphs of \( LiRb(BH_4)_2 \) differ by just 0.25 meV (0.024 kJ mol\(^{-1}\)), this matches the reversible character of the reconstructive transition very well.

The starting symmetry \( P6_2 \) of \( h-Li_2Rb(BH_4)_3 \) was modified to \( P6_222 \) by the optimization and this symmetry was likewise used as the starting model for the optimization of \( h-Li_2Cs(BH_4)_3 \), and was confirmed. The missed symmetry is due exclusively to the orientation of \( BH_4 \) groups, i.e. the details largely hidden to X-ray powder diffraction. A similar case has been reported, where twofold rotational axes were overlooked during the experimental structure solution and structural analysis of \( \alpha\)-Mg(BH\(_4\))\(_2\) (\( \check{C} \)erny et al., 2007; Dai et al., 2008). The \( m-h \) transformation in \( Li_2Cs(BH_4)_3 \) is also of reconstructive character; we may find a reason for the non-reversibility of this case in the considerable energy differences between ground states of the high- and low-temperature polymorphs, which is 0.25 meV (0.024 kJ mol\(^{-1}\)) for \( LiRb(BH_4)_2 \) and 238.6 meV (23 kJ mol\(^{-1}\)) for \( Li_2Cs(BH_4)_3 \). From this point of view the energy difference to overcome by heating during the transition is roughly a factor of \( \times1000 \) higher than for the \( m-o \) transition in \( LiRb(BH_4)_2 \). The structural reasoning for the large difference in \( \Delta E \) (ground state) between low- and high-temperature polymorphs of \( LiRb(BH_4)_2 \) and \( Li_2Cs(BH_4)_3 \) may be found in the change of coordination number of \( Li \) for the latter case, which increases from 3 to 4, while it stays fourfold for the former (Fig. 2). Hence, this coordination change could pose a considerable energetic barrier between the two ground states of \( Li_2Cs(BH_4)_3 \), in turn explaining the quenching of the high-temperature polymorph \( h-Li_2Cs(BH_4)_3 \) upon cooling, which however has the higher energy (Table 1).

All the resulting structural models were checked with the ADDSYM routine implemented in the PLATON software (Spek, 2006). The CIF files reported in the supporting information were generated based on the results of DFT optimizations with fixed lattice parameters, and space-group symmetries analysed with ADDSYM.

### 3.4. Topology of the Li-BH\(_4\) substructure

The herein adopted stepwise approach between experimental powder diffraction and theoretical first principles calculations has revealed an unexpected variety of lithium coordinations, and substantially different topologies of the Li-BH\(_4\) substructure (Table 1, and Figs. 1 and 2) in the Li–Rb and Li–Cs borohydrides. By coordination environment we refer to the coordination polyhedron defined by the Li atom as the metal centre and the BH\(_4\) ligands as the coordination sphere. The refinement of atomic positions by DFT optimizations has further allowed us to access structural details such as the hydrogen coordination mode in all compounds. However, we do not wish to make any statements regarding the chemical bonding between the metal centre and H atoms, as it would have required application of more sophisticated calculation methods not yet available for the solid state. Therefore, in the following we limit ourselves to the description of \( Li(BH_4)_x \)
polyhedra only. The different types of Li coordination (by BH4) observed in the novel compounds are summarized in Fig. 2. The coordination of Li varies from the usual tetrahedral to the hitherto unobserved square coplanar for the coordination number 4, and to triangular for the coordination number 3. The triangular coordination appears only in Li-rich compounds. With respect to the coordination number for Rb and Cs, it increases from 7 and 8 to 10 and even to 12 with increasing Li content.

The topologies of different dimensionalities of the Li-BH4 substructure range from isolated chains, and chains of double rings to sheet structures and three-dimensional frameworks as the Li content increases in the structure: Isolated chains [Li(BH4)2]3− of tetrahedra sharing two vertices are found in lithium poor m-LiCs2(BH4)4, see Fig. 2. Increasing the Li content leads to the phase m-Li2Cs3(BH4)5 containing isolated chains [Li2(BH4)5]3− of tetrahedra sharing one edge and one vertex. Further increasing the Li content brings us to the composition o-Li3(BH4)4 where two different topologies are observed: (i) isolated chains [Li3(BH4)4]5− of double 4-rings made from six tetrahedra and one square coplanar coordination by sharing all vertices in m-LiRb(BH4)2; (ii) puckered [Li(BH4)2]3− sheets built from vertex-sharing tetrahedra in the high-temperature phases of both Rb+ and Cs+ counter-cations. Yet another increase of the Li content leads to the phase o-Li2Cs2(BH4)6, which is built from sheets of [Li2(BH4)3]3− containing tetrahedra and triangles in the ratio 1:1, and sharing all vertices. No phase with this composition and topology was observed for Rb. Increasing the Li content even more takes us to m-Li2Cs4(BH4)10, which is made of puckered pseudo-hexagonal [Li2(BH4)3]3− sheets built from triangles sharing all vertices, and finally to the frameworks of the stable room-temperature phases h-Li2A(BH4)3 and m-Li3Cs(BH4)6. With the latter phase we have reached a limited amount of Li in this compound series, a further increase must result in the generation of a pure o-LiBH4 framework (Fig. 2) without counter-cations.

3.4.1. 4-connected substructure: tetrahedral Li. In the following we will compare the topologies of the Li-BH4 substructure based on different Li coordination modes with halides and oxides, such as silicates. This comparison is based on solid homoeotopic borohydrides and other ioni-covalent compounds alludes to what we recently suggested as the borohydride–oxide analogy (Schouwink et al., 2014).

The vertex-sharing tetrahedral chain [Li(BH4)2]3− in m-LiCs2(BH4)4 is an analogue of the 2-periodic (zweier) chain underlying the architecture of inosilicates. The most architecturally similar structure may be found with the anion [SiO3]2− in the pyroxene enstatite, MgSiO3 (Morimoto & Koto, 1969). In o-LiA(BH4)2, these chains condense into the vertex-sharing tetrahedral sheet [Li(BH4)2]3−. The sheet [Li(BH4)2]3− finds no analogue amongst the silicates, and is known only from SrZnO2 as a [ZnO2]3− sheet (Schnering & Hoppe, 1961). This sheet is also observed in LiK(BH4)2 (Nickels et al., 2008) and is likewise found as a [LiX3]− sheet in LiRbX3 (X = Cl, Br; Gaebell et al., 1983; Gaebell & Meyer, 1984). The relation between o-LiA(BH4)2 and LiK(BH4)2 becomes obvious when regarding the similarity of orthorhombic lattice parameters, and the relationship between the two space groups: A2/m (in the setting cab) and Pnma, respectively. Both space groups have the common maximal sub-group (Pmc21). In orthorhombic o-LiBH4 (Soulie et al., 2002) the sheets [Li(BH4)]3− condense into an sra-type framework of edge-sharing tetrahedra, which presents quite a rare tetrahedral connectivity. The framework [Li3(BH4)]3− observed in the most Li-rich compound m-Li3Cs(BH4)6 can be derived from the o-LiBH4 framework by replacing a quarter of the Li atoms by Cs, thus breaking the infinite stripes of edge-sharing tetrahedra into fragments of three tetrahedra each, which are shown in two different projections in Fig. 2, bottom left.

The edge- and vertex-sharing tetrahedral chain [Li3(BH4)4]3− in m-Li2Cs3(BH4)5 does not find a match amongst inorganic compounds. It can be compared to the chain [Fe3(SO4)]3− in Ba3Fe3S4, with 2/3 of the tetrahedral sharing edges and 1/3 sharing vertices (Grey et al., 1971). The chain [Li3(BH4)4]3− condenses into the edge- and vertex-sharing tetrahedral sheet [Li(BH4)]2− as a basic sheet of h-Li2A(BH4)3, which is also found as an [LiMg(BH4)4]− sheet in LiKMg(BH4)4 (Schouwink et al., 2014). The [Li2F]− sheet in LiRbF2 presents an analogue of the same topology (Burns & Busing, 1965). However, the sheet [Li(BH4)]2− creates a [Li3(BH4)]1− framework in h-Li2A(BH4)3 by sharing the off-plane borohydrides. Similar edge- and vertex-sharing sheets and frameworks can be found amongst the high-pressure phases of borates (Knýrim et al., 2007).

The observation of two different kinds of tetrahedral architecture in [Li(BH4)]1− sheets shows that for the very same Li node, the linker BH4− may play a part as a small anion leading to a connectivity based on common edges but also as a larger anion with a vertex-sharing scheme. The sharing of tetrahedral edges, very rare among the silicates and found only for few borates, has already been observed in four different Li-BH4 topologies. This surely is due to the smaller formal charge of the metal centre and hence lesser repulsion between cations. As the borohydride anion is nearly twice the size of the oxide anion (Abrahams & Kalnajs, 1954; Pistorius, 1974) the distance between the central cations from edge-sharing tetrahedra increases from ~2.5 Å, which is the Si–Si distance in a fibrous SiO2 modification (Weiss, 1954) to ~3.3 Å (Li–Li distance in our borohydrides), while the charge on the cation decreases from +4 to +1. No significant changes in Li–B distances are registered for these two different tetrahedral connectivities of Li(BH4)4 tetrahedra (Fig. S3). Compared to the tetrahedral Li coordination the distances Li–B are shorter in the triangular and longer in the square coplanar coordination.

3.4.2. 3-connected substructure: triangular Li. The 3-connected triangular [Li3(BH4)3]3− sheet in m-Li2Cs(BH4)6 has the topology of a graphene-like Li sheet expanded by borohydride linkers. Topologically this is called a honeycomb layer. It may be compared to the basic tetrahedral sheet [Si2O6]2− in phyllosilicates. In silicates these tetrahedra sheets alternate with octahedral layers. In m-Li2Cs(BH4)6 the triangular sheets are not linked by layers of larger coordination polyhedra.
Here the connectivity between sheets is ensured by Cs* cations occupying sites within the plane defined by the [Li$_2$(BH$_4$)$_3$]$^{2-}$ sheet.

The symmetry of the honeycomb layer [Li$_2$(BH$_4$)$_3$]$^{2-}$ is lowered over an orthorhombic C-centred cell down to the monoclinic Cc, monoclinic angle $\beta = 90^\circ$, by the rotation and translation of BH$_4$ groups. Strong pseudosymmetry of the sheet in m-Li$_2$Cs(BH$_4$)$_3$ can be seen in Fig. 2 as a vertical mirror plane passing through Li atoms and leading to the orthorhombic supergroup Cmc2$_1$. The pseudosymmetry is broken by the H atoms (omitted in Fig. 2) as follows from the DFT optimization. A nearly perfect triangular complex [Zn(BH$_4$)$_3$]$^-$ is found in KZn(BH$_4$)$_3$ (Černý et al., 2012), but contrary to m-Li$_2$Cs(BH$_4$)$_3$, all its borohydrides are terminal ligands. The Zn-coordinating H–H edges of all three BH$_4$ tetrahedra are not perpendicular to the plane of the three B atoms but instead are co-rotated by 16.1$^\circ$ (Fig. 2 in Černý et al., 2012) to minimize repulsive H–H interactions. In m-Li$_2$Cs(BH$_4$)$_3$ all BH$_4$ groups are linear linkers, bridging two Li atoms. This situation does not allow for a general Li–H coordination scheme where all H–H distances are maximized. Therefore, the monoclinic distortion has its origin in different rotations of the three H–H edges from the vertical direction, and two symmetrically independent Li(BH$_4$)$_3$ triangles. The [Li$_2$(BH$_4$)$_3$]$^{2-}$ net may be rationalized as a frustrated net with respect to the ideal conrotation of the three vertical H–H edges. Such a situation may promote specific dynamics of the BH$_4$ groups, such as 180$^\circ$ jump motions around the twofold operation of the 4 axes.

3.4.3. (4,3)-connected substructure: tetrahedral and triangular Li. The (4,3)-connected tetrahedral–triangular sheet in $\alpha$-Li$_2$Cs$_2$(BH$_4$)$_3$ may be compared to the tetrahedral–triangular framework in LiZn$_2$(BH$_4$)$_3$ (Ravnsback et al., 2009) and Li$_2$MZn$_5$(BH$_4$)$_3$ ($M = Mg$, Mn; Černý et al., 2013); the first compound contains tetrahedral Li and triangular Zn, the second contains tetrahedral Li, Mg and triangular Li, Zn. Mixed triangular and tetrahedral coordination may be found among the borates. Unlike silicon and carbon, boron has the ability to bind to either three or four O atoms to form a BO$_3$ triangle or a BO$_4$ tetrahedron. The same ability is observed in our compounds for Li with the borohydride ligand. Amongst silicates a combination of triangular and tetrahedral coordination exists in the sodalites, which belong to the zeolite family, however, here the 3-connected node is the larger monovalent cation (Na$^+$, Ag$^+$, TI$^+$; Latturner et al., 1999).

3.4.4. (4,4)-connected substructure: tetrahedral and square-planar Li. (4,4)-connected chains [Li(BH$_4$)$_4$]$^{2-}$ observed in m-LiRb(BH$_4$)$_2$ are made from two 4-rings which share one Li in a square coplanar coordination, the other Li atoms are in a tetrahedral BH$_4$ environment. Such chains do not occur in silicates but may be found in several other oxides. In particular, the rare square planar coordination occurs for intercalated lithium in battery electrode materials (Pérez-Flores et al., 2012). The same situation is found in the perovskite-type ionic conductor La$_{0.5}$Li$_{0.5}$TiO$_3$ (Alonso et al., 2000). Substituting for the small Li$^+$ here creates A-site vacancies which account for the high mobility, while Li itself occupies a square planar position face-centred on the cubic unit cell.

3.5. Other structural relations

The cation arrangement in the hexagonal phase $h$-Li$_2$A(BH$_4$)$_3$ can be related to the CrSi$_2$ type (Tanaka et al., 2001) by placing Li atoms on the Si site and A atoms on the Cr site (Fig. S16). As a packed compound $h$-Li$_2$A(BH$_4$)$_3$ stands alone in the herein presented series. This is obvious regarding its volume/formula unit (V/f.u.), which is roughly 35% smaller (V/f.u. = 23.25 Å$^3$ for Rb,Cs) with respect to the much higher and quite uniform value throughout the rest of the borohydride series (35–40 Å$^3$).

We would like to draw attention to an extensive theoretical study that was carried out on compositionally related halide systems, Li–Rb/Cs–X ($X = F, Cl, Br, I$), over a broad range of stoichiometries (Pentin et al., 2007, 2008). The prediction at an ab initio level (both Hartree–Fock and density functional theory) was done by a global exploration of the enthalpy landscapes (simulated annealing algorithm) for many different compositions in these systems, and without any recourse to experimental information. In agreement with our observation on Li–Rb-BH$_4$ and Li–Cs-BH$_4$ systems, only ordered crystalline phases were predicted, i.e. solid solutions between Li and A cations do not correspond to minima in the energy surface.

However, contrary to these results on borohydrides, only the LiRb$X_2$ phase can be directly related to our o-LiA(BH$_4$)$_3$, which is derived from the halide prototype by lowering the symmetry to Cmc2$_1$. This phase is observed not only for smaller Rb$^+$ cations, but also for larger Cs$^+$, again contrasting the predicted halides.

4. Conclusions

Ten new dual-cation tetrahydroborates combining Li with Rb or Cs were prepared by mechano-chemical grinding and characterized by theory and experiment. Their crystal structures comprise different various topologies of the Li-BH$_4$ substructure, revealing an entirely unexpected diversity regarding the behaviour of the Li$^+$ cation in a homoedpidetic BH$_4$ environment. The chosen approach where the XPD experiment is used for structure determination, and the final structural refinement proceeds via first principles solid-state calculations, has allowed us to identify minute structural details, such as the hydrogen coordination mode in all compounds.

Alongside the common tetrahedral coordination of Li by four BH$_4$ groups, and a rare triangular coordination, a third, square coplanar, coordination type was observed. The topology of the Li-BH$_4$ substructure varies from isolated chains, and chains of double rings over sheet structures towards a framework as the Li content increases in the compound. The Li(BH$_4$)$_4$ tetrahedra in sheets and frameworks share common vertices but also edges, a somewhat rare kind of tetrahedral connectivity. The edge-sharing tetrahedral scheme has hitherto been found four times...
amongst tetrahydroborates. We have thus identified the Li$^+$ cation to have the potential of a coordination centre in borohydride, and complex hydride frameworks, in general. Its ability to act both as a 3- and 4- connected node in the same compound is proven in this study; this feature is not observed for carbon or silicon, for instance. It should be noted, however, that for the stabilization of porous structures the use of Li$^+$ alone is likely not sufficient due to its highly ionic character. The design of open hydridic frameworks is challenging and will require the use of linkers that adopt more specific roles on a chemical bonding level, other than BH$_4^-$. Crystal engineering by means of linkers may be the most promising approach to porous complex hydride structures, the highly coordinating substructures should be of use when engineering functional transition metal nodes usually being subject to reduction by the tetrahydroborate anion.

Improved knowledge on different Li-BH$_4$ coordination modes, and the high number of topologically different Li-BH$_4$ substructures should be of use when engineering functional borohydrides in the future, be it for ionic conductors or hydric frameworks. We would like to note that molten borohydrides not suffering from decomposition, i.e. stable in the melt, can be of interest as ionic liquids.

This work was supported by the Swiss National Science Foundation. Calculations were performed in the Computing Centre of the Slovak Academy of Sciences using the supercomputing infrastructure acquired in project ITMS 26230120002 and 26210120002 (Slovak Infrastructure for High-Performance Computing) supported by the Research & Development Operational Programme funded by the ERDF. Partial financial support from the Slovak Grant Agency VEGA under the contract 2/0131/12 is acknowledged. We acknowledge SLS and SNBL for the allocation of beamtime and help with the data collection. We thank Hans Hagemann and Vincenza D’Anna for the synthesis of RbBH$_4$.

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