

## PAPER

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## Solubility of metal–boron–hydrogen compounds†

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Boron–hydrogen compounds are of increasing importance as electrolytes in solid state batteries, for hydrogen storage and possibly as high temperature super conductors. Solvent based methods are of increasing importance to obtain pure products, for purification of materials and also for the synthesis of novel compounds. In this context, the solubility information of several classes of metal–boron–hydrogen compounds such as borohydrides, *closo*-decahydridodecaborates, *closo*-dodecahydridododecaborates, *arachno*- and *nido*-hydridoborates in typical solvents is vital. This information is currently dispersed in the literature, hence the need to present a cohesive summary and comparison of these properties. This review collects, analyses and discusses the available data to provide inspiration for the future design of new synthesis routes and the discovery of novel materials.

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## Introduction

Metal borohydrides, based on the tetrahydridoborate complex,  $\text{BH}_4^-$ , and metal-polyhydridoborates, based on boron–hydrogen anions,  $\text{B}_x\text{H}_y^{n-}$ , have found application in multiple fields as reducing agents, reagents in synthetic reactions, hydrogen-rich fuels, or novel optical, magnetic, medical, ion conductivity purposes, and as hydrogen storage materials.<sup>1–3</sup> Metal–boron–hydrogen materials are a diverse class of compounds, but perhaps the archetypical example is metal borohydride (e.g.  $\text{NaBH}_4$ ). Aluminium borohydride,  $\text{Al}(\text{BH}_4)_3$ , was first discovered by Schlesinger *et al.* in 1939 in an attempt to prepare aluminium hydride ( $\text{AlH}_3$ ) using diborane and trimethyl aluminium.<sup>4</sup> Today, the most well-known and large-scale industrially produced member of this class of compounds is sodium borohydride,  $\text{NaBH}_4$ , which is typically used as a reducing agent in organic synthesis,<sup>5</sup> and is now also considered as a hydrogen export vector.<sup>6</sup> The current commercially practiced process to produce  $\text{NaBH}_4$  is the Brown–Schlesinger process, which is based on the reaction between sodium hydride ( $\text{NaH}$ ) and trimethylborate ( $\text{B}(\text{OMe})_3$ ),<sup>7</sup> but there are also other alternatives such as metallothermic reduction, mechano-

chemical synthesis, and electrochemical methods.<sup>8</sup> The second most used metal borohydride is lithium borohydride ( $\text{LiBH}_4$ ). This compound was first synthesised by Schlesinger and Brown in 1940 using ethyl lithium and diborane<sup>9</sup> however, because of difficulties and dangers in handling diborane gas as a synthetic agent, solvent-based and mechanochemical approaches have been developed.<sup>1</sup>

Mechano-chemical synthesis is one of the most common synthetic routes for metal–boron–hydrogen compounds.<sup>10</sup> This approach usually utilises solid–solid metathesis reactions, which produce the desired metal borohydride along with a relatively stable and inert metal halide by-product.<sup>11–13</sup> Thus, normally a pure material cannot be obtained. Pure products can be obtained *via* mechano-chemical solid–gas reactions, for example where diborane is reacted with a metal hydride but it is challenging to scale-up owing to the use of toxic diborane gas.<sup>14</sup> On the other hand, within the last decades, solvent-based synthesis has revealed numerous advantages in the production of selected materials with high purity, even in preferred structural polymorphs.<sup>15</sup> This approach offers feasible isolation and purification of desired reaction products from by-products based on differences in solubility.<sup>16–22</sup> A good choice of solvents can optimise synthetic reactions and produce pure metal borohydrides that are fundamental in their own right, or as building-blocks for derivatives. The success of solvent-based synthesis is closely related to the choice of solvent and the solubilities of reactants, products and unwanted by-products. This can lead to discovery of novel materials with unobserved properties, which may find technological applications in the future.

One aspect that inhibits large scale solvent-based synthesis and the application of metal–boron–hydrogen compounds, and many other materials, is the lack of knowledge about solu-

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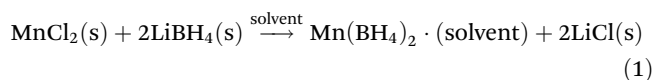
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bilities in solvents. A material's solubility relates closely to the dielectric constant ( $\epsilon$ ) of the solvent. Understanding of the correspondence between solubility and dielectric constant of the solvent may be useful in choosing reaction and extracting solvents to optimise the yield and purification of desired reaction products. Because metal borohydrides and metal-boron-hydrogen materials are known to be highly reactive, the chemical reactivity of the solvent is also of importance, where the most significant adverse reactivities are highlighted in the presented solubility figures. For example, metal borohydrides typically undergo hydrolysis in water, but water can still be used as a solvent, especially when a stabiliser, such as NaOH, is used to raise the pH.<sup>23</sup> Therefore, in this study, we provide a coherent summary of available data on the solubility of these materials in various solvents charted as a function of dielectric constant of the solvent and cation charge density of the cations. We also highlight some reactions that have been reported in liquid media, including reactions with borane donor solvents (e.g. tetrahydrofuran borane, THF-BH<sub>3</sub>), functionalisation of *closo*-hydridoborates, solvothermal synthesis, mechano-chemistry using a solvent as grinding media, reactions in supercritical fluids, ionic liquids (IL) and low boiling point solvents, and solution-based electrochemistry. Solvent effects in each synthetic approach are analysed and discussed.

### Solvent-based synthesis of metal borohydrides

Historically, solvent based metathesis reactions employed organometallic compounds, such as ethyl lithium, diethyl magnesium or trimethyl aluminium as precursors. However, a solvent based metathesis reaction can also be conducted using a metal halide MX<sub>n</sub>, X = Cl, Br or I, in conjunction with an industrially produced metal borohydride, such as NaBH<sub>4</sub> or LiBH<sub>4</sub>, as a precursor.<sup>13,24</sup> These reactions are then partially driven by the formation of a stable alkali metal halide and occur despite low solubility of the reactants. This is illustrated by the synthesis of manganese borohydride, Mn(BH<sub>4</sub>)<sub>2</sub>,<sup>25</sup> although metathesis reactions have been used to form a variety of other borohydrides.<sup>13,26,27</sup>



The obvious advantage of the above-mentioned strategy is that the product is dissolved in the selected solvent, which in the case of eqn (1) is a mixture of toluene and dimethylsulphide, (CH<sub>3</sub>)<sub>2</sub>S. The latter is denoted a co-solvent or extraction solvent, which coordinates to the metal and increases the solubility of the metal borohydride. This allows for the redundant metal halide by-product to be filtered away. In fact, the ionic metal halide is not necessarily an inert by-product. In some cases, secondary reactions can take place where the metal borohydride reacts with the metal halide and forms new (bi-)metal borohydride halide with ordered structures or as solid solutions.<sup>28–30</sup>

The removal of the solvent post-reaction often produces a solid solvated product, *i.e.* manganese borohydride hemidimethylsulphide, Mn(BH<sub>4</sub>)<sub>2</sub>·0.5((CH<sub>3</sub>)<sub>2</sub>S). The utilisation of rela-

tively weakly coordinating co-solvents and/or extraction solvents allows for the removal of the solvent molecule at moderate conditions and production of a pure metal borohydride. Interestingly, optimisation of the exact physical conditions (time, temperature, pressure *etc.*) may allow formation of polymorphically pure crystalline products. This is illustrated by the treatment of Mn(BH<sub>4</sub>)<sub>2</sub>·0.5((CH<sub>3</sub>)<sub>2</sub>S) at room temperature (RT) in vacuum, which produces an open-structured polymorph,  $\gamma$ -Mn(BH<sub>4</sub>)<sub>2</sub> (isostructural to  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub>), whereas solvent removal at elevated temperatures (RT < *T* < 100 °C) in vacuum provides a polymorph with a more dense crystal structure,  $\alpha$ -Mn(BH<sub>4</sub>)<sub>2</sub>.

Diethylether (Et<sub>2</sub>O) has also been used as a solvent for the synthesis of  $\alpha$ -Mn(BH<sub>4</sub>)<sub>2</sub> *via* a metathesis reaction between MnCl<sub>2</sub> and LiBH<sub>4</sub>.<sup>31</sup> After the reaction, diethylether was removed and replaced by an extraction solvent, (CH<sub>3</sub>)<sub>2</sub>S, but a phase-pure product was not obtained. In all cases the synthetic product was  $\alpha$ -Mn(BH<sub>4</sub>)<sub>2</sub> with varying amounts of Li<sub>2</sub>Mn(BH<sub>4</sub>)<sub>4</sub>. This was assumed to be due to a minor solubility of remaining LiBH<sub>4</sub> in (CH<sub>3</sub>)<sub>2</sub>S or *via* formation of the coordination framework compound [(Li(Et<sub>2</sub>O)<sub>2</sub>(Mn<sub>2</sub>(BH<sub>4</sub>)<sub>5</sub>)]<sup>32</sup>. This example demonstrates some of the complexity in solvent-choice and problems that can be associated with solubility. The use of a more strongly coordinating co-solvent such as tetrahydrofuran (THF) does not allow for the synthesis of pure Mn(BH<sub>4</sub>)<sub>2</sub>. The product from the synthesis is the solvate, Mn(BH<sub>4</sub>)<sub>2</sub>·3THF, and the solvent molecule (THF) is only released at *T* > 140 °C. Unfortunately, this temperature is above the thermal stability range and leads to instant decomposition of Mn(BH<sub>4</sub>)<sub>2</sub> leaving an amorphous product.<sup>33</sup>

The examples provided above for Mn(BH<sub>4</sub>)<sub>2</sub> are also largely true for many other borohydride systems. The selection of solvents is important for the synthesis of many metal borohydride materials due to the formation of strongly bonded complexes and the difficulty to break these bonds without decomposing the borohydride materials. Mg(BH<sub>4</sub>)<sub>2</sub> has been shown to be soluble in a range of solvents such as diethyl ether, THF, dimethylsulphide and a range of amines, but some solvents such as tetramethylethylenediamine (TMEDA) coordinate too strongly to be removed.<sup>26,27,34,35</sup> This illustrates the importance of careful evaluation of solubilities of by-products and the co-solvents ability to coordinate the metal and dissolve the wanted product. The solubilities of metal borohydrides are illustrated in Fig. 1.

A fruitful approach is to utilise solid-liquid synthesis using metal hydrides and borane donating solvents as reactants. The metal hydride often needs to be mechanochemically activated to reduce the particle size and increase the surface area. This procedure significantly increases the kinetics of the reactions as compared to using hand-ground material. Then the metal hydride is suspended in an anhydrous non-coordinating solvent, *e.g.* toluene, or a coordinating solvent such as THF or diethyl ether. A borane donating complex such as dimethylsulphide borane complex (DMSB, (CH<sub>3</sub>)<sub>2</sub>SBH<sub>3</sub>) or triethylamine borane complex, (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>NBH<sub>3</sub>, typically with an excess of 50%, a concentration of 1–5 M and reaction time of 24–48 h under stirring. Thus, the reaction takes place between the

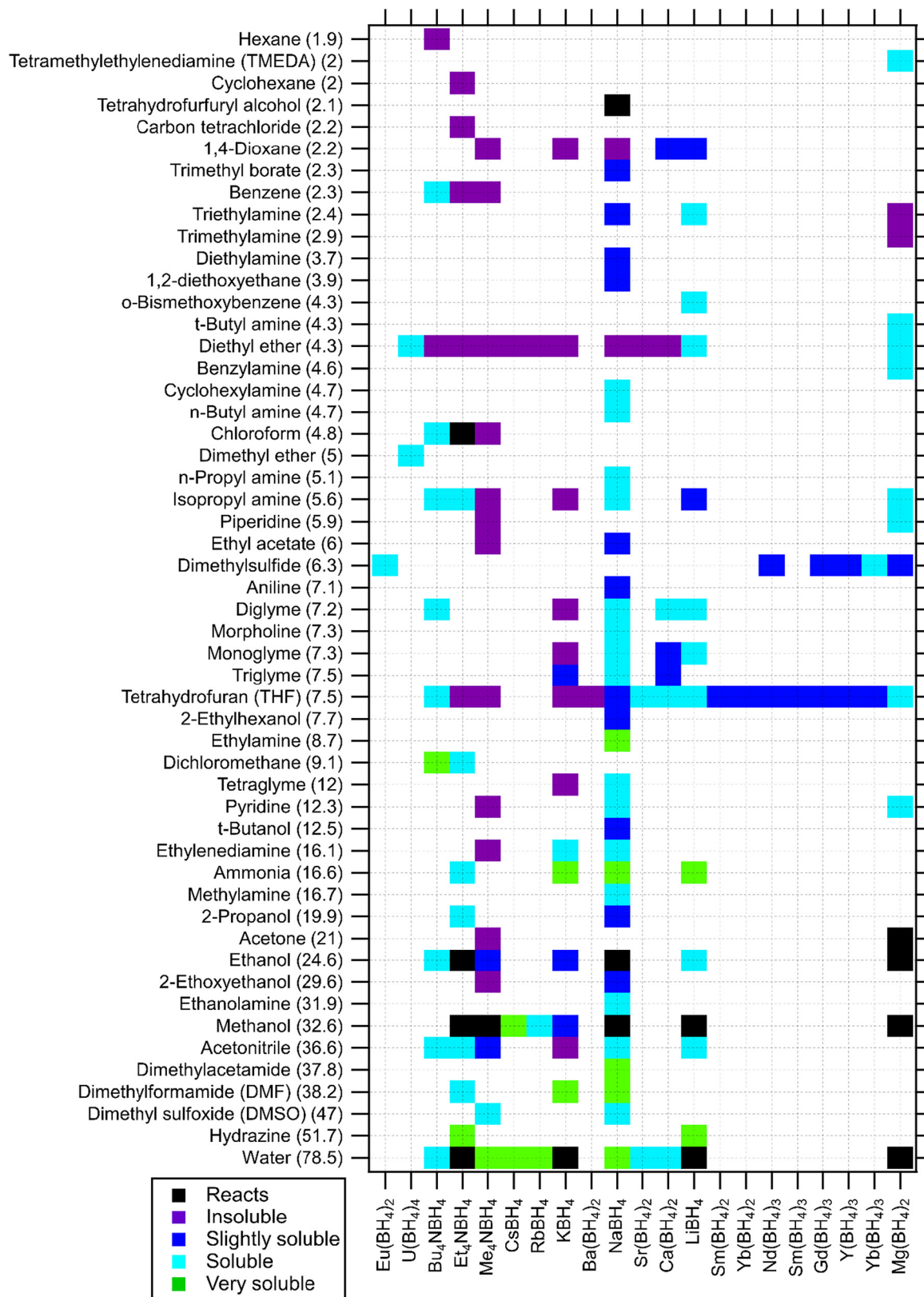


Fig. 1 Solubility of borohydrides in solvents (listed by dielectric constant in brackets). Borohydride species are listed by cationic charge density (low to high).<sup>7,10,15,24,36–49</sup>

borane donor complex in solution and a solid metal hydride surface. The reaction mechanism can be described as a nucleophilic addition mechanism where a hydride ion,  $\text{H}^-$ , is transferred forming the borohydride complex,  $\text{BH}_4^-$ , and a cation, which can be solvated and removed from the surface and allows the reaction to proceed. Thus, the reaction involves the solvent mediated dissolution of  $\text{M}(\text{BH}_4)_x$  that is transported away from the reactive hydride interface.<sup>10</sup> The selected solvent or combination of solvents will determine whether the metal borohydride formed stays in solution or precipitates in its pure form or as a solvate. A solution of dissolved metal borohydride will allow further purification by filtration to remove possible impurities of metal, metal hydrides or oxides. In a similar manner, borohydride synthesis can also be undertaken by solvent aided mechano-chemical methods, e.g.  $\text{Na}_3(\text{NH}_2)_2\text{BH}_4$ . This was achieved by ball milling  $\text{NaNH}_2$  and  $\text{NaBH}_4$  in a 2 : 1 ratio, doped with a Co–Ni–B catalyst in cyclohexane.<sup>50</sup> The solvent aids to absorb heat generated during the reaction and prevent oxidation.

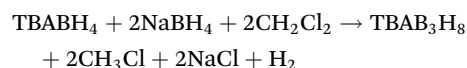
As mentioned, the reaction mechanism for metal borohydride synthesis from a metal hydride and a borane complex is a nucleophilic addition mechanism, which is only possible for ionic or polar covalent M–H bonds, such as those formed by alkali- and earth alkali metals and rare earth metals. This is illustrated by the rare earth metal neodymium, which forms a metallic  $\text{NdH}_2$  hydride upon hydrogenation at moderate conditions and an ionic hydride at more harsh conditions,  $\text{NdH}_3$ . By using the above mentioned synthetic strategy it was shown that the metallic  $\text{NdH}_2$  hydride cannot react with DMSB complex, but the ionic  $\text{NdH}_3$  readily formed the solvate,  $\text{Nd}(\text{BH}_4)_3 \cdot (\text{CH}_3)_2\text{S}$ .<sup>10</sup> In this case, desolvation provides a trivalent neodymium(III) borohydride,  $\alpha\text{-Nd}(\text{BH}_4)_3$ . In some cases, solvate formation stabilises trivalent metal borohydrides where a reductive desolvation leads to the formation of divalent  $\text{M}(\text{BH}_4)_2$  and release of diborane gas. This is observed for the ytterbium(III) borohydride solvent complex  $\text{Yb}(\text{BH}_4)_3 \cdot x(\text{CH}_3)_2\text{S}$ , where desolvation leads to the formation of  $\gamma\text{-Yb}(\text{BH}_4)_2$ . However, reacting samarium(III) hydride in a solution of weak/non-coordination solvents, e.g. DMSB in toluene, leads directly to  $\text{Sm}(\text{BH}_4)_2$ , whereas with stronger coordination solvents, e.g. THF in toluene, forms  $\text{Sm}(\text{BH}_4)_3 \cdot 1.5\text{THF}$ . A similar ‘solvent metal protection’ strategy was developed using ammonia in dimethylsulfide to produce  $[\text{Fe}(\text{NH}_3)_6](\text{BH}_4)_2$  and  $[\text{Co}(\text{NH}_3)_6](\text{BH}_4)_2$ , where  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  otherwise would be reduced by  $\text{BH}_4^-$ .<sup>51</sup>

Transition metal borohydrides, which are stable at room temperature can only be prepared with metals in a low transition state and with the d electron configurations,  $d^0$ ,  $d^5$  or  $d^{10}$ .<sup>52</sup> The transition metal borohydrides,  $\text{M}(\text{BH}_4)_2$ ,  $\text{M} = \text{Cr}^{2+}$  ( $d^4$ ),  $\text{Fe}^{2+}$  ( $d^6$ ) and  $\text{Co}^{2+}$  ( $d^7$ ) are stable in solution only at  $T < -30^\circ\text{C}$  but not yet in the solid state at RT.<sup>51</sup> The molecular titanium borohydride,  $\text{Ti}(\text{BH}_4)_3$  with the  $d^1$  electron configuration has an in-between stability and decompose at  $T < 0^\circ\text{C}$ .

### Solvent-based synthesis of polyhydridoborates

High temperature solvothermal synthesis of metal hydridoborates were typically performed in high boiling point solvents

(e.g., glymes, dimethoxyethane) to synthesise so-called “polyhydridoborates” such as *arachno*-, *nido*- and *closo*-hydridoborates.<sup>2,53</sup> The choice of solvent and reaction temperature may lead to different final products. For example, when triethylamine is used as the solvent for the reaction between  $\text{B}_2\text{H}_6$  and  $\text{NaBH}_4$ ,  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  is formed at  $100\text{--}180^\circ\text{C}$ .<sup>54</sup> When dimethoxyethane is used,  $\text{NaB}_3\text{H}_8$  is formed at a reaction temperature of  $25^\circ\text{C}$  and further heating the reaction to above  $50^\circ\text{C}$  produces  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  in a mixture with  $\text{NaB}_{11}\text{H}_{14}$ . However, one drawback of this approach is that the high boiling point solvents are experimentally difficult to remove from the final product. For this reason, solvothermal synthesis routes have also been explored and successfully applied to prepare compounds of  $\text{B}_3\text{H}_8^-$ ,  $\text{B}_{10}\text{H}_{10}^{2-}$  and  $\text{B}_{12}\text{H}_{12}^{2-}$ .<sup>43,55</sup> Performing the reaction in a closed vessel, i.e. an autoclave, allows for the temperature to be raised above the solvent boiling point at autogenous pressures created by the vapour pressure of the solvent(s). The solubility of the reactants is often higher at elevated temperatures above the usual boiling point, which contributes to a higher yield of product. The solvothermal reactions typically involve one or more intermediates, e.g.  $\text{B}_3\text{H}_8$ , and then proceeds to form the thermodynamically more stable *closo*-hydridoborates,  $\text{B}_{10}\text{H}_{10}^{2-}$  and  $\text{B}_{12}\text{H}_{12}^{2-}$ . Here, a tetraalkylammonium borohydride (either tetrabutylammonium (TBA) or tetraethylammonium (TEA)) borohydride were used. These starting materials can be obtained commercially, but also by a metathesis reaction of  $\text{NaBH}_4$  with the either  $\text{TBABr}$  or  $\text{TEACl}$  by ball milling. Alternatively, the exchange reaction can also be performed using different solutions (e.g. acetonitrile ( $\text{CH}_3\text{CN}$ ) for  $\text{TEACl}$  and isopropylamine for  $\text{NaBH}_4$ ), which are then mixed to precipitate  $\text{NaCl}$ , while  $\text{TEABH}_4$  remains in the solution. The first reaction step is, for example:



is performed at  $80^\circ\text{C}$  for 1 h with TBA. It is interesting to note that in this reaction, the solvent dichloromethane is reduced to chloroform, i.e. it actively takes part in the reaction. The tetraalkyl salt can then either be used as obtained, purified or transformed into  $\text{NaB}_3\text{H}_8$  using  $\text{NaB}(\text{Ph})_4$  (sodium tetraphenylborate) to precipitate  $\text{TEAB}(\text{Ph})_4$  or  $\text{TBAB}(\text{Ph})_4$ .

In the second step,  $\text{TEAB}_3\text{H}_8$  was suspended in toluene and reacted at  $185^\circ\text{C}$  in a closed container to produce an approximately equimolar mixture of  $(\text{TEA})_2\text{B}_{10}\text{H}_{10}$  and  $(\text{TEA})_2\text{B}_{12}\text{H}_{12}$ . Converting this mixture into the corresponding sodium salts using  $\text{NaB}(\text{Ph})_4$  in hot water produces, upon solvent evaporation, a mixture of  $\text{Na}_2\text{B}_{10}\text{H}_{10}$  and  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ . The recrystallization of this mixture in isopropanol yields the solid ionic conductor  $\text{Na}_4(\text{B}_{10}\text{H}_{10})(\text{B}_{12}\text{H}_{12})$ .<sup>43</sup> The mixture of  $(\text{TEA})_2\text{B}_{10}\text{H}_{10}$  and  $(\text{TEA})_2\text{B}_{12}\text{H}_{12}$  can also be separated by fractional crystallisation in methanol, as  $(\text{TEA})_2\text{B}_{10}\text{H}_{10}$  is more soluble in methanol than  $(\text{TEA})_2\text{B}_{12}\text{H}_{12}$ .

One further example is the thermolysis of  $\text{KB}_3\text{H}_8$ , which typically yields a mixture of products containing  $\text{BH}_4^-$ ,

$B_{10}H_{10}^{2-}$ ,  $B_{12}H_{12}^{2-}$  and  $B_{11}H_{14}$ . From this mixture,  $B_{10}H_{10}^{2-}$  is isolated and purified by first precipitating  $TEAB_{12}H_{12}$  in MeOH, then  $TEAB_{11}H_{14}$  is precipitated in water before recovering the water soluble  $TEAB_{10}H_{10}$ .<sup>56</sup> Sequential extraction based on difference in solubility towards different extracting solvents can allow isolation of each boron–hydrogen product with high purity. The solubility of a wide range of metal *closo*-hydridoborates based on the complex anions,  $B_nH_n^{2-}$ , provided in Fig. 2 can help designing effective purification sequences.

Reactions of metal borohydrides with Lewis base borane-solvent adducts has been long used to synthesis polyhedral hydridoborate compounds. A good example is the synthesis of  $NaB_{12}H_{12}$  and  $KB_{12}H_{12}$  from reactions of  $NaBH_4$  or  $KBH_4$  with borane-trimethylamine and -triethylamine at 200–250 °C in high-boiling point alkane solvents.<sup>57,58</sup> The formation mechanism of polyhydridoborate compounds is an aggregation or polycondensation of small borane complexes based on the nucleophilicity of B–H bonds.

Recently, a high-yield selective synthesis based on this approach has been developed and gained success in synthesising high purity alkali salts of some polyhydridoborate anions such as  $B_{12}H_{12}^{2-}$ ,  $B_3H_8^-$  and  $B_{11}H_{14}^-$ . Solvothermal reactions of  $NaBH_4$  and  $KBH_4$  with DMSB in diglyme form  $Na_2B_{12}H_{12}$  and  $K_2B_{12}H_{12}$  at a yield greater than 80%.<sup>59</sup>  $K_2B_{12}H_{12}$  can be directly isolated from the reaction solution due to its poor solubility in diglyme while solvent-free  $Na_2B_{12}H_{12}$  is obtained after removal of the solvent by heating under vacuum.

$MB_3H_8$  with M = Na, K, Rb, Cs can be synthesised by reactions of their respective metal borohydrides with DMSB in 1,4-dioxane at 90 °C for 48 h.<sup>60</sup> The final product is a precipitate mixture of the metal octahydrotriborate and unreacted metal borohydride. Unsolvated  $MB_3H_8$  salts of K, Rb and Cs can be purified by dissolution in THF followed by recrystallisation using dichloromethane (DCM) but  $NaB_3H_8$  is obtained in a solvated form due to strong coordination of the solvent with  $Na^+$ . Unsolvated  $NaB_3H_8$  can be obtained by reaction with  $THF \cdot BH_3$  in THF under reflux conditions.<sup>61</sup> This method can also be used to synthesise  $LiB_3H_8$  but the final product is solvated  $LiB_3H_8 \cdot 1.5THF$  as a clear oil.  $LiB_3H_8$  can be formed in the reaction of  $LiBH_4$  with DMSB in 1,4-dioxane but the formed  $LiB_3H_8$  reacts with  $LiBH_4$ , which is slightly soluble in 1,4-dioxane resulting in formation of  $B_9H_{14}^-$  and  $B_{11}H_{14}^-$ .<sup>60</sup>

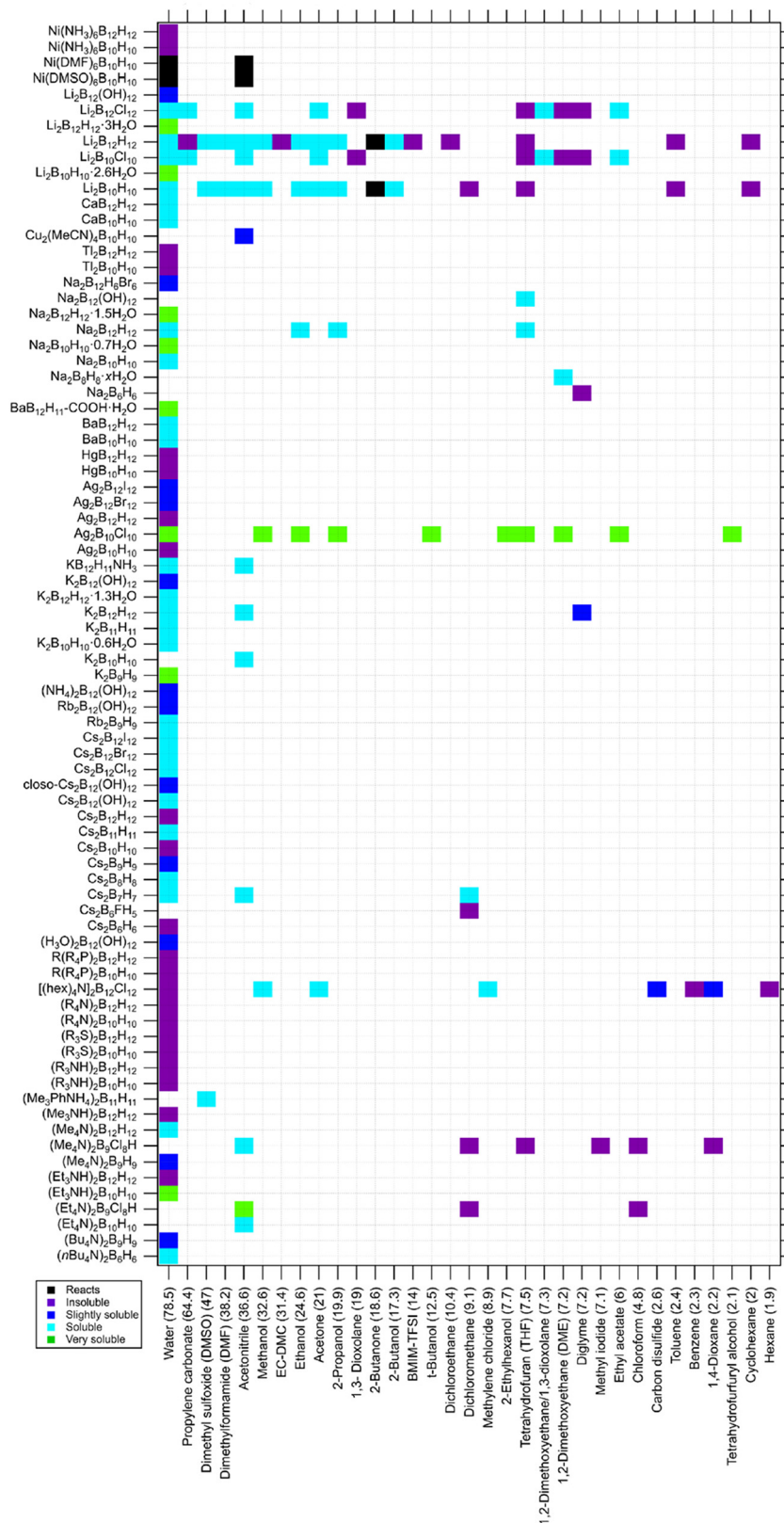
Adjustment of parameters such as temperature, molar ratio of the reactants and reaction time of above reactions leads to the synthesis of *nido*-hydridoborates. Reaction of  $KBH_4$  and DMSB at a molar ratio of 1 : 10 in 1,4-dioxane at 90 °C for 5 d produces  $KB_{11}H_{14}$  as the major product, which can be purified at 86% yield.<sup>16</sup> Replacing  $KBH_4$  with  $LiBH_4$  or  $NaBH_4$  results in 1,4-dioxane solvated  $LiB_{11}H_{14}$  and solvent-free  $NaB_{11}H_{14}$ , respectively. The alkali *nido*-hydridoborates can also be formed when using 1,2-dimethoxyethane as the solvent, but solvent-free products cannot be obtained because of strong coordination of the cations with 1,2-dimethoxyethane. Increasing reaction temperature to break cation-solvent bonds causes formation of more unwanted-products.

## Solvent-based synthesis of *closo*-hydridoborate derivatives

Solvent based methods have successfully been developed and used during decades for the synthesis of novel metal–boron–hydrogen compounds and their derivatives.<sup>21,62</sup> These methods have been previously reviewed.<sup>1,2,15,17,18,20,21,63</sup> The functionalisation of *closo*-hydridoborates is an important field of boron chemistry to develop new chemicals and to modify the properties of this class of materials. In 1962 Knoth synthesised the first organic *closo*-hydridoborate derivative followed by a raft of *closo*-hydridoborate derivatives based on decahydrido-*closo*-decaborate(2-) ( $B_{10}H_{10}^{2-}$ ) and dodecahydrido-*closo*-dodecaborate(2-) ( $B_{12}H_{12}^{2-}$ ) anions, including the substitution of H groups for acyl, hydroxy, alkoxy, alkyl, mercapto, and alkylthio groups.<sup>64,65</sup> The synthesis of these functionalised *closo*-hydridoborates was typically undertaken with solvent-based chemical approaches in a range of solvents and solvent mixtures. It is clear that the solubility and reactivity of the *closo*-hydridoborates and their products is integral to achieving high yield and purity.<sup>2</sup>

The functionalisation of *closo*-hydridoborates can be achieved to varying degrees, whereby one, multiple, or the complete exchange of all terminal hydrogen atoms can occur for particular functional groups, *e.g.* formation of  $B_{12}H_{11}(OH)^{2-}$  or  $B_{12}(OH)_{12}^{2-}$ .<sup>21,65,66</sup> These functional groups can also be further modified to expand the class of *closo*-hydridoborates to an indefinite degree akin to organic chemistry, for instance, the conversion of  $B_{12}(OH)_{12}^{2-}$  to  $B_{12}(OR)_{12}^{2-}$ .<sup>66</sup> Thus, a rich chemistry is possible based on the foundation of *closo*-hydridoborates, allowing fine tuning of chemical and physical properties. These compounds also form fascinating solvated complexes with a range of solvents.<sup>19</sup>

It is also possible to substitute a B–H group in the boron cages for another group, such as C–H, *i.e.* in the production of carbaborates such as  $CB_{11}H_{12}^-$ .<sup>67,68</sup> This class of derivatives has received enormous attention in recent years as promising solid-state electrolyte materials for battery applications. Solid solutions of *closo*-carbaborates, *e.g.*  $Na_3(CB_9H_{10})(B_{12}H_{12})$ ,  $Na_3(CB_{11}H_{12})(B_{12}H_{12})$ ,  $Na_2(CB_9H_{10})(CB_{11}H_{12})$  and  $Na_{2-y}(CB_{11}H_{12})_y(B_{12}H_{12})_{1-y}$ , have been shown to deliver high ionic conductivity at moderate temperatures and some have been utilised for fabrication of all-solid-state batteries.<sup>69–73</sup> Typically, the synthesis of *closo*-carbaborates is undertaken from *nido*- or *arachno*-boranes or hydridoborates, which are not yet *closo*-hydridoborates and have accessible sites for deprotonation and subsequent insertion into the cage. They can be conveniently synthesised from decaborane ( $B_{10}H_{14}$ ) reacted with formaldehyde (HCHO) in basic (KOH) solution, which initially form *arachno*-6- $CH_2B_9H_{12}^-$ .<sup>74,75</sup> Thermolysis at temperatures in the range 160 to 220 °C (in vacuum) provide mixed anion compounds  $NH(CH_3)_3(CB_8H_9)_x(CB_9H_{10})_y(CB_{11}H_{12})_z$ , where the sample heated at 200 °C has the composition  $NH(CH_3)_3(CB_8H_9)_{0.26}(CB_9H_{10})_{0.66}(CB_{11}H_{12})_{0.08}$ .<sup>76</sup> Initially *closo*-2- $CB_9H_{10}^-$  is formed, which converts to the thermodynamically more stable configuration *closo*-1- $CB_9H_{10}^-$  after heating to 150 °C. At lower thermolysis temperatures (160 to 180 °C) the reaction resulted in minor amounts of unreacted NH



**Fig. 2** Solubility of *closo*-hydridoborates and derivatives in solvents (listed by dielectric constant in brackets). The compounds are listed by cationic charge density (low to high).<sup>43,47,59,77–104</sup> Abbreviation: EC-DMC: ethylene carbonate : dimethyl carbonate (1 : 1 vol%), BMIM-TFSI: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

(CH<sub>3</sub>)<sub>3</sub>(*arachno*-6-CH<sub>2</sub>B<sub>9</sub>H<sub>12</sub>), whereas higher temperatures facilitated the formation of *closo*-CB<sub>11</sub>H<sub>12</sub><sup>−</sup> rather than *closo*-CB<sub>8</sub>H<sub>9</sub><sup>−</sup>.<sup>76</sup>

A new and low-cost solvent-based synthesis of CB<sub>11</sub>H<sub>12</sub><sup>−</sup> using common laboratory reagents<sup>68</sup> has been recently proposed. This method avoids the use of the toxic, flammable and expensive decaborane, B<sub>10</sub>H<sub>14</sub>, precursor. (CH<sub>3</sub>)<sub>3</sub>NH[B<sub>11</sub>H<sub>14</sub>], which can be feasibly synthesised by thermal treatment of NaBH<sub>4</sub> with bromopentane in diglyme, is used as the starting material. The *nido*-hydridoborate precursor is converted to Na<sub>2</sub>B<sub>11</sub>H<sub>13</sub> in excess aqueous NaOH at 80 °C and then, to CB<sub>11</sub>H<sub>12</sub><sup>−</sup> by the insertion of CCl<sub>2</sub> from chloroform in dimethoxyethane with the presence of basic NaOH and K<sub>2</sub>CO<sub>3</sub>. Dimethoxyethane is chosen as the reaction solvent instead of THF because it is more polar, which improves the solubility of NaOH. Conducting the reaction in diethyl ether and dioxane produces no CB<sub>12</sub>H<sub>11</sub><sup>−</sup> since Na<sub>2</sub>B<sub>11</sub>H<sub>13</sub> does not dissolve in these solvents (Fig. 3).

Again, solvent-based synthesis is key to achieving high yields and purities of the *closo*-carbaborate products. With the rich chemistry of B–H bond, it is also possible to insert other groups or atoms into the boron-cage, such as the case of heavy metals like Pb or Sn, which cause modifications to the thermal, structural, and ionic conductivity properties of the solid-state compounds, *e.g.* B<sub>11</sub>H<sub>11</sub>Pb<sup>2−</sup> and B<sub>11</sub>H<sub>11</sub>Sn<sup>2−</sup>.<sup>105,106</sup> In this case, the use of aqueous or non-aqueous synthesis is key to controlling the reaction pathways and formed products from a B<sub>11</sub>H<sub>14</sub><sup>−</sup> precursor.

Ionic liquids (IL) have been demonstrated to provide new synthetic pathways for functionalised decaborane (B<sub>10</sub>H<sub>14</sub>) and *ortho*-carbaborane clusters.<sup>107</sup> For instance, B<sub>10</sub>H<sub>14</sub> reacts with

an excess of RCH=CH<sub>2</sub> in a biphasic mixture of 1-butyl-3-methyl-imidazolium (Bmim) or 1-butyl-4-methyl-pyridium (Bmpy)BF<sub>4</sub> salts forming 6-R-B<sub>10</sub>H<sub>13</sub>.<sup>107</sup> Hydrocarbons are insoluble in these IL's and so the decaborane is added to the IL and stirred vigorously with the olefin and toluene to form an emulsion. Separation is then relatively easy with high yields. Similar reactions can take place with a range of olefins. Decaborane reactions with alkynes in ILs do not yield hydroboration products, but instead result in alkyne insertion, thereby providing an important new route to *ortho*-carbaboranes.<sup>107</sup> For example B<sub>10</sub>H<sub>14</sub> reacts with 2 equivalents of a ligand (L) to form B<sub>10</sub>H<sub>12</sub>L<sub>2</sub>, where L is SET<sub>2</sub> or CH<sub>3</sub>CN. Alkyne insertion then can then be undertaken where B<sub>10</sub>H<sub>12</sub>L<sub>2</sub> reacts with RC≡CH to form 1,2-RC<sub>2</sub>B<sub>10</sub>H<sub>11</sub> + 2L. This is undertaken in a biphasic toluene/1-butyl-3-methylimidazolium chloride (Bmim)Cl system. These reactions have been demonstrated for a wide range of functional alkynes.

Dehydrocondensation reactions are key steps in many polyborane transformations leading to the formation of higher-order boron–hydrogen systems. For example, the thermally induced dissociation of DMS from 4-Me<sub>2</sub>S–B<sub>9</sub>H<sub>13</sub> forms a Lewis acidic B<sub>9</sub>H<sub>13</sub> fragment in xylene or *in vacuo*, which can then undergo fusion, accompanied by dehydrogenation, with another such fragment to produce *n*-B<sub>18</sub>H<sub>22</sub>.<sup>107</sup> When carried out in an IL (in 1-butyl-3-methylimidazolium chloride (Bmim)Cl) under biphasic conditions, only *n*-B<sub>18</sub>H<sub>22</sub> is formed with a B<sub>10</sub>H<sub>14</sub> side product.

Borohydride based ionic liquids have also been developed including 1-butyl-2,3-dimethylimidazolium (BMMIM), 1-ethyl-3-methylimidazolium (EMMIM), 1-propyl-1-methylpiperidinium

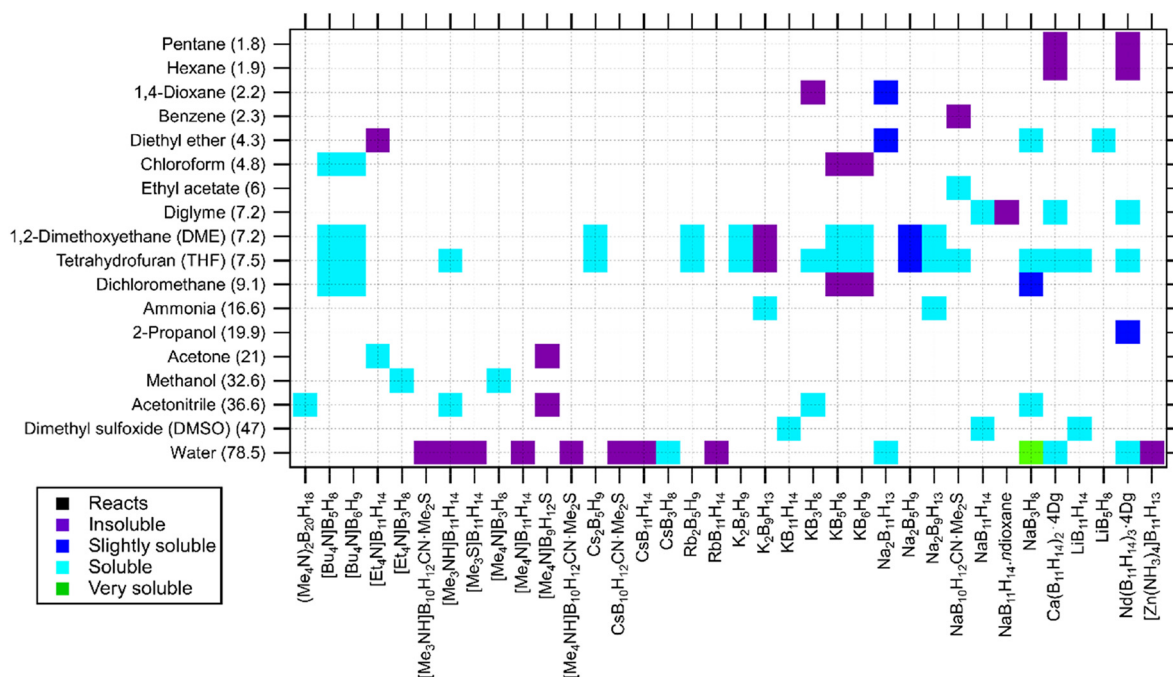


Fig. 3 Solubility of *arachno*- and *nido*-hydridoborates in solvents (listed by dielectric constant in brackets). The compounds are listed by cationic charge density (low to high).<sup>53,56,60,68,78,92,103,118–132</sup>

(PropMPip), and 1-butyl-1-methylpyrrolidinium (BMP) borohydride. AmimBH<sub>4</sub> and BmimBH<sub>4</sub> were prepared and have a melting point below  $-60\text{ }^{\circ}\text{C}$ .<sup>108</sup> These have been successfully used for the selective reduction of carbon-carbon double bonds in conjugated alkenes as well as the  $\alpha,\beta$ -carbon-carbon double bonds in highly activated  $\alpha,\beta,\gamma,\delta$ -unsaturated alkenes. In addition, ionic liquids of B<sub>3</sub>H<sub>8</sub><sup>−</sup> have been developed including [EMMIM][B<sub>3</sub>H<sub>8</sub>], [PropMPip][B<sub>3</sub>H<sub>8</sub>], [N(Bu)<sub>4</sub>][B<sub>3</sub>H<sub>8</sub>] and [BMMIM][B<sub>3</sub>H<sub>8</sub>].<sup>109</sup>

A raft of organic cation salts of B<sub>12</sub>Cl<sub>12</sub><sup>2−</sup> show low melting points and interesting physicochemical properties and potential as ionic liquids for electrochemical applications. These salts also show favourable solubilities at room temperature with miscibility in MeCN, DMSO and Me<sub>2</sub>CO, whilst being non-miscible in H<sub>2</sub>O, EtOH and Et<sub>2</sub>O.<sup>110</sup> Interestingly, the class of B<sub>12</sub>X<sub>12</sub><sup>2−</sup> (X = F, Cl, Br, I) also show quasi-reversible electrochemical oxidation to B<sub>12</sub>X<sub>12</sub><sup>−</sup> and further non-reversible oxidation to B<sub>12</sub>X<sub>12</sub> in liquid SO<sub>2</sub>, MeCN, or organic

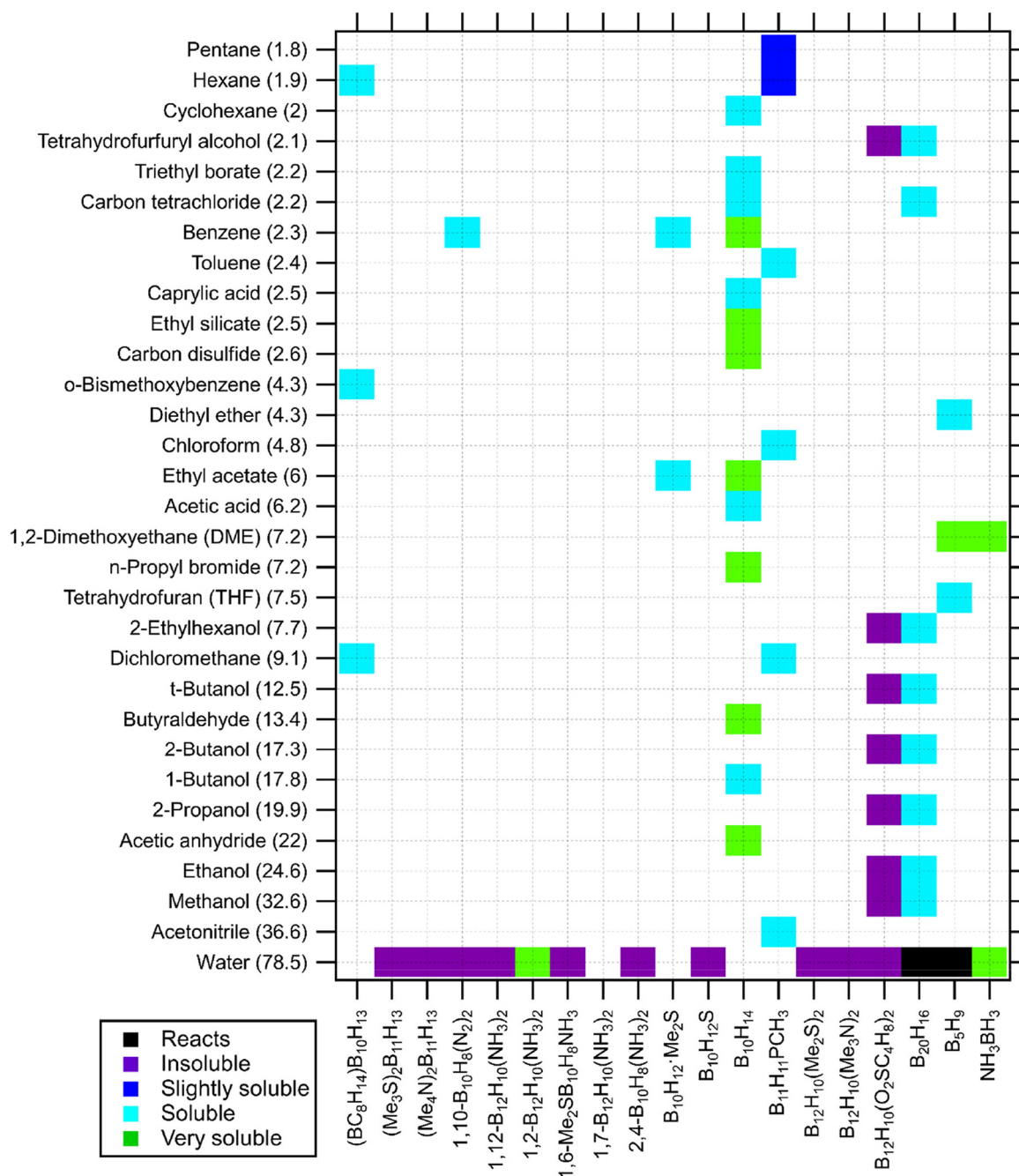


Fig. 4 Solubility of neutral boranes in solvents (listed by dielectric constant in brackets). Borane species are listed alphabetically.<sup>39,78,90,119,121,123,127–129,138–143</sup>

carbonates.<sup>111–113</sup> Halogenated derivatives of sodium-dodecahydrido-*closo*-dodecaborate,  $\text{Na}_2\text{B}_{12}\text{Cl}_{12}$ ,  $\text{Na}_2\text{B}_{12}\text{Br}_{12}$ , and  $\text{Na}_2\text{B}_{12}\text{I}_{12}$ , have high thermal stability and high sodium ion conductivity at elevated temperatures.<sup>114,115</sup> As such, the electrochemical properties of a wide array of boron compounds have been published and reviewed.<sup>116</sup>

## Results and discussion

The solubility of inorganic salts in non-aqueous and organic solvents is of great interest across the fields of synthetic chemistry to industrial production. Of particular importance is the dielectric constant of these solvents, which dramatically range from very low (e.g. pentane at 1.8) to remarkably high (e.g. *n*-methylacetamide at 165) with water at 78.5.<sup>117</sup> Despite solubility trends being shown across dielectric constant, the resulting solubility is not solely based on this one parameter and there is much complexity surrounding the prediction of the solubility in solvent classes that are often divided into protic, aprotic, and inert groups. One further consideration may be the solvent liquidus temperature range, its viscosity, coordinating nature, purity, and/or other physical and chemical (Lewis acidity) properties.

Herein, we have provided graphical representations of the solubilities of well-known metal–boron–hydrogen compounds (and derivatives) in typical solvent systems, sourced from the available literature (Fig. 1–4). The data is classified and graphically presented in separate charts for borohydrides, *closo*-hydridoborates, *arachno*- and *nido*-hydridoborates and some of their derivatives, and neutral boranes. Although incomplete, these solubility charts do show certain trends and indications to predict unknown solubilities. To aid in discovering trends the solvents are listed by dielectric constant, the boron compounds are sorted by cationic charge density where appropriate. The solubility of each compound in a particular solvent is categorised qualitatively as insoluble, slightly soluble (<1 wt%), soluble (1–10 wt%), very soluble (>10 wt%), and reactive (denoting chemical incompatibility). A table of solubility information is also available in the ESI† that provides a mixture of qualitative and quantitative solubility information where available (including more detailed references).

Fig. 1 shows the solubility of borohydrides in water and a variety of non-aqueous organic solvents. In certain publications, metal borohydrides are stated to be soluble in water. This is true, but  $\text{BH}_4^-$  experiences hydrolysis when water is used as a solvent, forming  $\text{B}(\text{OH})_4^-$  and releasing  $\text{H}_2$ .<sup>49</sup> This characteristic can be used to destroy borohydride impurities into forms that are removable from a product mixture.<sup>61</sup> The hydrolysis of  $\text{BH}_4^-$  anion can be dramatically slowed down in alkaline solutions, e.g. NaOH. This is addressed as notation in the ESI.†  $\text{NaBH}_4$  has extensive solubility data in the literature as the most well-known metal borohydride. It is soluble in various organic solvents but insoluble in diethyl ether and 1,4-dioxane. This compound is reported to be only slightly soluble

in alcohol solvents such as *tert*-butanol, 2-propanol and reacting with methanol and ethanol.

Fig. 2 provides solubility of *closo*-hydridoborates and their derivatives. Most of the data is reported for solubility in water. Alkaline and earth alkaline metal decahydrido-*closo*-decaborates and dodecahydrido-*closo*-dodecaborates and their halogenated relatives are soluble in water, except for Cs. Meanwhile, compounds of heavy metals such as Ag, Hg and Tl are not soluble in this solvent. *closo*-Hydridoborates of organic cations are also insoluble in water, except for a very few cases such as  $(\text{Me}_4\text{N})_2\text{B}_{12}\text{H}_{12}$  and  $(\text{nBu}_4\text{N})_2\text{B}_{12}\text{H}_{12}$ . This may be related to the hydrophobic property of these cations.

Fig. 3 and 4 show solubility of *archano*- and *nido*-hydridoborates and some neutral boron–hydrogen compounds, respectively. Their solubility data is mostly hidden in synthesis procedures reported in the literature. Such little available data is not enough to establish specific trends for these branches of boron–hydrogen compounds but still, significant information can be drawn out from the charts. For instance, solubility data of alkaline octahydridotriborates ( $\text{KB}_3\text{H}_8$  and  $\text{NaB}_3\text{H}_8$  in Fig. 3) can aid in designing synthesis routes for borates with higher boron numbers, namely *closo*- and *nido*-hydridoborates.

## Conclusions and outlook

The chemistry of boron hydrogen compounds is very rich as outlined by the examples cited above, while the necessity for knowledge about solubilities and solvent metal borohydride interactions (such as ability to coordinate the metals) is undeniable. Solvent-based purification of specific salts such as *closo*- and *nido*-hydridoborates formed from the thermolysis of  $\text{BH}_4^-$  or  $\text{B}_3\text{H}_8^-$  salts may be the cheapest approach for the synthesis on a large scale due to the use of the least expensive starting materials. The present information of solubilities can also lead to other new synthesis strategies to prepare pure compounds in high yields. These compounds can be utilised directly or used as precursors for synthesis of derivatives. Currently there is much focus on development of novel types of batteries based on multivalent metals, such as magnesium and calcium. They can form the basis for more sustainable, safe and cheap solid-state batteries with higher energy contents to replace the well-known lithium ion battery. Most of the recently developed liquid state electrolytes for magnesium batteries are based on boron hydrides or fluorides.<sup>133</sup> Recently, significant progress within solid state magnesium ionic conductors have been made by the discovery of derivatives of magnesium borohydride,  $\text{Mg}(\text{BH}_4)_2 \cdot x\text{NH}_3$  and  $\text{Mg}(\text{BH}_4)_2 \cdot x\text{NH}_2\text{CH}_3$ .<sup>134–136</sup> They have very high  $\text{Mg}^{2+}$  conductivity at room temperature and show stability towards a metallic Mg anode. This has been demonstrated by development of a solid-state inorganic magnesium battery, which was charged and discharged several times.<sup>137</sup> This illustrates that synthesis of boron-based compounds may have significant future societal impact, e.g. within efficient storage of renewable energy. Here

we provide new inspiration for development of novel synthesis strategies, which may lead to novel compounds with unseen properties. Further synthetic innovations may be feasible by the exploration of sequential addition of solvents rather than utilising single or mixed solvent systems. This may improve the solubility of this class of compounds and further the range of reactions that may be possible.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 M. Paskevicius, L. H. Jepsen, P. Schouwink, R. Černý, D. B. Ravnsbæk, Y. Filinchuk, M. Dornheim, F. Besenbacher and T. R. Jensen, *Chem. Soc. Rev.*, 2017, **46**, 1565–1634.
- 2 B. R. S. Hansen, M. Paskevicius, H.-W. Li, E. Akiba and T. R. Jensen, *Coord. Chem. Rev.*, 2016, **323**, 60–70.
- 3 E. M. Dematteis, M. B. Amdisen, T. Autrey, J. Barale, M. E. Bowden, C. E. Buckley, Y. W. Cho, S. Deledda, M. Dornheim and P. De Jongh, *Prog. Energy*, 2022, **4**, 032009–032049.
- 4 H. Schlesinger, R. T. Sanderson and A. Burg, *J. Am. Chem. Soc.*, 1939, **61**, 536.
- 5 P. Rittmeyer and U. Wietelmann, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
- 6 A. Ibrahim, M. Paskevicius and C. E. Buckley, *Sustainable Energy Fuels*, 2023, **7**, 1196–1203.
- 7 H. Schlesinger, H. C. Brown and A. Finholt, *J. Am. Chem. Soc.*, 1953, **75**, 205–209.
- 8 Y. Wu, M. T. Kelly, J. V. Ortega, *Review of chemical processes for the synthesis of sodium borohydride*, Millennium Cell Inc, 2004.
- 9 H. Schlesinger and H. C. Brown, *J. Am. Chem. Soc.*, 1940, **62**, 3429–3435.
- 10 B. Richter, J. B. Grinderslev, K. T. Møller, M. Paskevicius and T. R. Jensen, *Inorg. Chem.*, 2018, **57**, 10768–10780.
- 11 J. Huot, F. Cuevas, S. Deledda, K. Edalati, Y. Filinchuk, T. Grosdidier, B. C. Hauback, M. Heere, T. R. Jensen, M. Latroche and S. Sartori, *Materials*, 2019, **12**, 2778–2821.
- 12 J. Huot, D. B. Ravnsbæk, J. Zhang, F. Cuevas, M. Latroche and T. R. Jensen, *Prog. Mater. Sci.*, 2013, **58**, 30–75.
- 13 C. Frommen, M. Sørby, M. Heere, T. Humphries, J. Olsen and B. Hauback, *Energies*, 2017, **10**, 2115–2138.
- 14 O. Friedrichs, A. Remhof, A. Borgschulte, F. Buchter, S. I. Orimo and A. Züttel, *Phys. Chem. Chem. Phys.*, 2010, **12**, 10919–10922.
- 15 H. Hagemann and R. Černý, *Dalton Trans.*, 2010, **39**, 6006–6012.
- 16 Y. Jing, X. Wang, H. Han, X.-R. Liu, X.-C. Yu, X.-M. Chen, D. Wei, L.-S. Wang and X. Chen, *Sci. China: Chem.*, 2024, **67**, 876–881.
- 17 S. Körbe, P. J. Schreiber and J. Michl, *Chem. Rev.*, 2006, **106**, 5208–5249.
- 18 X. Zhao, Z. Yang, H. Chen, Z. Wang, X. Zhou and H. Zhang, *Coord. Chem. Rev.*, 2021, **444**, 214042–214968.
- 19 V. V. Avdeeva, S. E. Korolenko, E. A. Malinina and N. T. Kuznetsov, *Russ. J. Gen. Chem.*, 2022, **92**, 393–417.
- 20 V. V. Avdeeva, E. A. Malinina and N. T. Kuznetsov, *Coord. Chem. Rev.*, 2022, **469**, 214636–214734.
- 21 P. Kaszynski, *Collect. Czech. Chem. Commun.*, 1999, **64**, 895–926.
- 22 V. I. Stanko, A. C. Yu, V. A. Brattsev and I. Z. Leonid, *Russ. Chem. Rev.*, 1965, **34**, 424.
- 23 U. B. Demirci, O. Akdim, J. Andrieux, J. Hannauer, R. Chamoun and P. Miele, *Fuel Cells*, 2010, **10**, 335–350.
- 24 T. D. Humphries, M. B. Ley, C. Frommen, K. T. Munroe, T. R. Jensen and B. C. Hauback, *J. Mater. Chem. A*, 2015, **3**, 691–698.
- 25 B. Richter, D. B. Ravnsbæk, N. Tumanov, Y. Filinchuk and T. R. Jensen, *Dalton Trans.*, 2015, **44**, 3988–3996.
- 26 G. L. Soloveichik, M. Andrus, Y. Gao, J. C. Zhao and S. Kniajanski, *Int. J. Hydrogen Energy*, 2009, **34**, 2144–2152.
- 27 K. Chłopek, C. Frommen, A. Léon, O. Zabara and M. Fichtner, *J. Mater. Chem.*, 2007, **17**, 3496–3503.
- 28 M. B. Ley, S. Boulineau, R. Janot, Y. Filinchuk and T. R. Jensen, *J. Phys. Chem. C*, 2012, **116**, 21267–21276.
- 29 R. Černý, N. Penin, V. D'Anna, H. Hagemann, E. Durand and J. Růžicka, *Acta Mater.*, 2011, **59**, 5171–5180.
- 30 C. Frommen, M. H. Sørby, P. Ravindran, P. Vajeeston, H. Fjellvåg and B. C. Hauback, *J. Phys. Chem. C*, 2011, **115**, 23591–23602.
- 31 L. H. Jepsen, M. B. Ley, Y. Filinchuk, F. Besenbacher and T. R. Jensen, *ChemSusChem*, 2015, **8**, 1452–1463.

- 32 N. A. Tumanov, D. A. Safin, B. Richter, Z. Łodziana, T. R. Jensen, Y. Garcia and Y. Filinchuk, *Dalton Trans.*, 2015, **44**, 6571–6580.
- 33 V. Makhaev, A. Borisov, T. Gnilomedova, É. Lobkovskii and A. Chekhlov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 1582–1586.
- 34 M. Bremer, H. Nöth and M. Warchhold, *Eur. J. Inorg. Chem.*, 2003, **2003**, 111–119.
- 35 P. Zanella, L. Crociani, N. Masciocchi and G. Giunchi, *Inorg. Chem.*, 2007, **46**, 9039–9041.
- 36 D. R. Lide, *CRC Handbook of Chemistry and Physics*, Taylor & Francis, 88th edn, 2007.
- 37 C. R. Cloutier, *Electrochemical recycling of sodium borohydride for hydrogen storage : physicochemical properties of sodium metaborate solutions*, University of British Columbia, 2006.
- 38 H. Nöth and B. Wrackmeyer, *Nuclear magnetic resonance spectroscopy of boron compounds*, Springer Science & Business Media, 1978.
- 39 R. M. Adams, *Boron, metallo-boron compounds and boranes*, Interscience Publishers, New York, 1964.
- 40 Rohm and Haas, *Sodium borohydride digest*, Rohm and Haas Company, 2003.
- 41 M. D. Banus, R. W. Bragdon and T. R. Gibb Jr, *J. Am. Chem. Soc.*, 1952, **74**, 2346–2348.
- 42 D. J. Raber, W. C. Guida and D. C. Shoenberger, *Tetrahedron Lett.*, 1981, **22**, 5107–5110.
- 43 A. Gigante, L. Duchêne, R. Moury, M. Pupier, A. Remhof and H. Hagemann, *ChemSusChem*, 2019, **12**, 4832–4837.
- 44 H. C. Brown, Y. M. Choi and S. Narasimhan, *Inorg. Chem.*, 1982, **21**, 3657–3661.
- 45 J. A. Heppert and D. F. Gaines, *Inorg. Chem.*, 1983, **22**, 3155–3161.
- 46 R. Černý, F. Murgia and M. Brighi, *J. Alloys Compd.*, 2022, **895**, 162659–162667.
- 47 L. Titov and L. Gavrilova, *Russ. J. Inorg. Chem.*, 1970, **15**, 1509.
- 48 R. R. Rietz, A. Zalkin, D. H. Templeton, N. M. Edelstein and L. K. Templeton, *Inorg. Chem.*, 1978, **17**, 653–658.
- 49 E. Petit, F. Salles, D. Alligier and U. B. Demirci, *Molecules*, 2022, **27**, 1975.
- 50 Z.-W. Pei, C. Wu, Y. Bai, X. Liu and F. Wu, *Int. J. Hydrogen Energy*, 2017, **42**, 14725–14733.
- 51 E. Roedern and T. R. Jensen, *Inorg. Chem.*, 2015, **54**, 10477–10482.
- 52 L. H. Rude, T. K. Nielsen, D. B. Ravnsbæk, U. Bösenberg, M. B. Ley, B. Richter, L. M. Arnbjerg, M. Dornheim, Y. Filinchuk, F. Besenbacher and T. R. Jensen, *Phys. Status Solidi A*, 2011, **208**, 1754–1773.
- 53 D. H. Souza, K. T. Möller, S. A. Moggach, T. D. Humphries, A. M. D'Angelo, C. E. Buckley and M. Paskevicius, *J. Mater. Chem. A*, 2021, **9**, 15027–15037.
- 54 H. Miller, N. Miller and E. Muetterties, *J. Am. Chem. Soc.*, 1963, **85**, 3885–3886.
- 55 R. Moury, A. Gigante and H. Hagemann, *Int. J. Hydrogen Energy*, 2017, **42**, 22417–22421.
- 56 J. M. H. Makhlof, W. V. Hough and G. T. Hefferan, *Inorg. Chem.*, 1967, **6**, 1196–1198.
- 57 V. V. Volkov and I. S. Posnaya, *Zh. Neorg. Khim.*, 1979, **24**, 2824–2826.
- 58 V. V. Volkov and I. S. Posnaya, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1979, **4**, 88–92.
- 59 J. Wang, T. Steenhaut, H.-W. Li and Y. Filinchuk, *Inorg. Chem.*, 2023, **62**, 2153–2160.
- 60 X. Chen, X.-R. Liu, X. Wang, X.-M. Chen, Y. Jing and D. Wei, *Dalton Trans.*, 2021, **50**, 13676–13679.
- 61 X.-M. Chen, N. Ma, Q.-F. Zhang, J. Wang, X. Feng, C. Wei, L.-S. Wang, J. Zhang and X. Chen, *J. Am. Chem. Soc.*, 2018, **140**, 6718–6726.
- 62 L. Wang, Y. Jiang, S. Duttwyler, F. Lin and Y. Zhang, *Coord. Chem. Rev.*, 2024, **516**, 215974–216007.
- 63 A. Grahame and K.-F. Aguey-Zinsou, *Inorganics*, 2018, **6**, 106–143.
- 64 W. H. Knoch, H. C. Miller, D. C. England, G. W. Parshall and E. L. Muetterties, *J. Am. Chem. Soc.*, 1962, **84**, 1056–1057.
- 65 W. H. Knoch, J. C. Sauer, D. C. England, W. R. Hertler and E. L. Muetterties, *J. Am. Chem. Soc.*, 1964, **86**, 3973–3983.
- 66 A. I. Wixtrom, Y. Shao, D. Jung, C. W. Machan, S. N. Kevork, E. A. Qian, J. C. Axtell, S. I. Khan, C. P. Kubiak and A. M. Spokoyny, *Inorg. Chem. Front.*, 2016, **3**, 711–717.
- 67 R. N. Grimes, *Carboranes*, Academic Press, 2016.
- 68 A. Berger, C. E. Buckley and M. Paskevicius, *Inorg. Chem.*, 2021, **60**, 14744–14751.
- 69 M. Brighi, F. Murgia and R. Černý, *Cell Rep. Phys. Sci.*, 2020, **1**, 100217–100233.
- 70 M. Brighi, F. Murgia and R. Černý, *Adv. Mater. Interfaces*, 2022, **9**, 2101254–2101260.
- 71 F. Murgia, M. Brighi and R. Černý, *Electrochem. Commun.*, 2019, **106**, 106534–106539.
- 72 M. Brighi, F. Murgia, Z. Łodziana, P. Schouwink, A. Wołczyk and R. Cerny, *J. Power Sources*, 2018, **404**, 7–12.
- 73 R. Asakura, D. Reber, L. Duchêne, S. Payandeh, A. Remhof, H. Hagemann and C. Battaglia, *Energy Environ. Sci.*, 2020, **13**, 5048–5058.
- 74 B. Brellochs, J. Bačkovský, B. Štíbr, T. Jelinek, J. Holub, M. Bakardjiev, D. Hnyk, M. Hofmann, I. Cisarová and B. Wrackmeyer, *Eur. J. Inorg. Chem.*, 2004, **2004**, 3605–3611.
- 75 S. Li, Y. Zhang, Y. Ma, P. Qiu and X. Chen, *Organometallics*, 2021, **40**, 3480–3485.
- 76 J. B. Grinderslev, L. N. Skov, D. R. Sørensen, I. Kantor, M. R. V. Jørgensen and T. R. Jensen, *Dalton Trans.*, 2022, **51**, 15806–15815.
- 77 A. Blake, MS, Pittsburg State University, 2015.
- 78 H. Miller, N. Miller and E. Muetterties, *Inorg. Chem.*, 1964, **3**, 1456–1463.
- 79 M. M. Green, MS, California State University, Northridge, 2023.
- 80 D. V. Peryshkov, A. A. Popov and S. H. Strauss, *J. Am. Chem. Soc.*, 2009, **131**, 18393–18403.

- 81 W. H. Knoth, H. Miller, J. C. Sauer, J. Balthis, Y. Chia and E. Muetterties, *Inorg. Chem.*, 1964, **3**, 159–167.
- 82 E. Muetterties, J. Balthis, Y. Chia, W. Knoth and H. Miller, *Inorg. Chem.*, 1964, **3**, 444–451.
- 83 T. Peymann, C. B. Knobler, S. I. Khan and M. F. Hawthorne, *J. Am. Chem. Soc.*, 2001, **123**, 2182–2185.
- 84 A. Garcia, G. Müller, R. Černý, D. Rentsch, R. Asakura, C. Battaglia and A. Remhof, *J. Mater. Chem. A*, 2023, **11**, 18996–19003.
- 85 V. V. Avdeeva, E. A. Malinina, A. V. Churakov, I. N. Polyakova and N. T. Kuznetsov, *Polyhedron*, 2019, **169**, 144–150.
- 86 V. Avdeeva, I. Polyakova, L. Goeva, G. Buzanov, E. Malinina and N. Kuznetsov, *Inorg. Chim. Acta*, 2016, **451**, 129–134.
- 87 L. Zakharkin, V. Guseva and P. Petrovskii, *Russ. J. Gen. Chem.*, 2001, **71**, 1017–1018.
- 88 M.-C. Bay, R. Grissa, K. V. Egorov, R. Asakura and C. Battaglia, *Mater. Futures*, 2022, **1**, 031001–031008.
- 89 O. Volkov, W. Dirk, U. Englert and P. Paetzold, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1193–1200.
- 90 A. N. Bridges, J. Liu, R. G. Kultyshev, D. F. Gaines and S. G. Shore, *Inorg. Chem.*, 1998, **37**, 3276–3283.
- 91 J. W. Johnson and J. F. Brody, *J. Electrochem. Soc.*, 1982, **129**, 2213–2219.
- 92 X. Zheng, Y. Yang, F. Zhao, F. Fang and Y. Guo, *Chem. Commun.*, 2017, **53**, 11083–11086.
- 93 A. Y. Bykov, A. Zhdanov, K. Y. Zhizhin and N. Kuznetsov, *Russ. J. Inorg. Chem.*, 2016, **61**, 1629–1648.
- 94 J. Forstner, T. Haas and E. Muetterties, *Inorg. Chem.*, 1964, **3**, 155–159.
- 95 N. Kuznetsov, L. Kulikova and S. Zhukov, *Zh. Neorg. Khim. (USSR)*, 1976, **21**, 96–99.
- 96 W. Preetz and G. Peters, *Eur. J. Inorg. Chem.*, 1999, **1999**, 1831–1846.
- 97 F. Klanberg, D. R. Eaton, L. J. Guggenberger and E. L. Muetterties, *Inorg. Chem.*, 1967, **6**, 1271–1281.
- 98 E. Muetterties, R. Wiersema and M. Hawthorne, *J. Am. Chem. Soc.*, 1973, **95**, 7520–7522.
- 99 F. Klanberg and E. Muetterties, *Inorg. Chem.*, 1966, **5**, 1955–1960.
- 100 M. J. Bayer and M. F. Hawthorne, *Inorg. Chem.*, 2004, **43**, 2018–2020.
- 101 W. H. Knoth, J. C. Sauer, J. H. Balthis, H. C. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, 1967, **89**, 4842–4850.
- 102 X. Mu, J. C. Axtell, N. A. Bernier, K. O. Kirlikovali, D. Jung, A. Umanson, K. Qian, X. Chen, K. L. Bay and M. Kirillos, *Chem*, 2019, **5**, 2461–2469.
- 103 M. A. Nelson and G. Kodama, *Inorg. Chem.*, 1981, **20**, 3579–3580.
- 104 V. Mustyatsa, N. Votinova, I. Dudenkov, K. Solntsev and N. Kuznetsov, *Russ. J. Coord. Chem.*, 1998, **24**, 847–850.
- 105 T. A. Hales, K. T. Møller, T. D. Humphries, A. M. D'Angelo, C. E. Buckley and M. Paskevicius, *J. Phys. Chem. C*, 2023, **127**, 949–957.
- 106 T. A. Hales, K. T. Møller, T. D. Humphries, A. M. D'Angelo, C. E. Buckley and M. Paskevicius, *Phys. Chem. Chem. Phys.*, 2023, **25**, 31249–31256.
- 107 Y. Li, U. Kusari, P. J. Carroll, M. G. Bradley and L. G. Sneddon, *Pure Appl. Chem.*, 2006, **78**, 1349–1355.
- 108 S. Li, H. Gao and J. N. M. Shreeve, *Angew. Chem.*, 2014, **126**, 3013–3016.
- 109 M. Büchner, A. M. T. Erle, H. Scherer and I. Krossing, *Chem. – Eur. J.*, 2012, **18**, 2254–2262.
- 110 N. Zhou, G. Zhao, K. Dong, J. Sun and H. Shao, *RSC Adv.*, 2012, **2**, 9830–9838.
- 111 R. T. Boéré, J. Derendorf, C. Jenne, S. Kacprzak, M. Keßler, R. Riebau, S. Riedel, T. L. Roemmele, M. Rühle, H. Scherer, T. Vent-Schmidt, J. Warneke and S. Weber, *Chem. – Eur. J.*, 2014, **20**, 4447–4459.
- 112 R. T. Boéré, S. Kacprzak, M. Keßler, C. Knapp, R. Riebau, S. Riedel, T. L. Roemmele, M. Rühle, H. Scherer and S. Weber, *Angew. Chem., Int. Ed.*, 2011, **50**, 549–552.
- 113 S. V. Ivanov, S. M. Miller, O. P. Anderson, K. A. Solntsev and S. H. Strauss, *J. Am. Chem. Soc.*, 2003, **125**, 4694–4695.
- 114 B. R. S. Hansen, M. Paskevicius, M. Jørgensen and T. R. Jensen, *Chem. Mater.*, 2017, **29**, 3423–3430.
- 115 E. V. Bukovsky, D. V. Peryshkov, H. Wu, W. Zhou, W. S. Tang, W. M. Jones, V. Stavila, T. J. Udovic and S. H. Strauss, *Inorg. Chem.*, 2017, **56**, 4369–4379.
- 116 J. H. Morris, H. J. Gysling and D. Reed, *Chem. Rev.*, 1985, **85**, 51–76.
- 117 A. Covington, *Physical chemistry of organic solvent systems*, Springer Science & Business Media, 2012.
- 118 B. Chamberland and E. Muetterties, *Inorg. Chem.*, 1964, **3**, 1450–1456.
- 119 V. Aftandilian, H. Miller, G. Parshall and E. Muetterties, *Inorg. Chem.*, 1962, **1**, 734–737.
- 120 L. Titov and P. Petrovskii, *Russ. J. Inorg. Chem.*, 2011, **56**, 1032–1033.
- 121 S. G. Shore and O. S. U. R. F. COLUMBUS, *Studies on Syntheses and Derivatives of Boron Hydride Systems*, 1988.
- 122 L. Titov, L. Gavrilova and P. Petrovskii, *Russ. J. Inorg. Chem.*, 2008, **53**, 565–567.
- 123 S. Pylypko, S. Ould-Amara, A. Zadick, E. Petit, M. Chatenet, M. Cretin and U. B. Demirci, *Appl. Catal., B*, 2018, **222**, 1–8.
- 124 G. B. Dunks, K. Barker, E. Hedaya, C. Hefner and P. Remec, *Inorg. Chem.*, 1981, **20**, 1692–1697.
- 125 A. C. Dunbar, J. A. Macor and G. S. Girolami, *Inorg. Chem.*, 2014, **53**, 822–826.
- 126 H. Beall and D. F. Gaines, *Inorg. Chim. Acta*, 1999, **289**, 1–10.
- 127 W. R. Hertler, F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, 1967, **6**, 1696–1706.
- 128 W. Knoth and E. Muetterties, *J. Inorg. Nucl. Chem.*, 1961, **20**, 66–72.
- 129 D. F. Gaines and T. V. Iorns, *J. Am. Chem. Soc.*, 1967, **89**, 3375–3376.

- 130 S. Payandeh, D. Rentsch, Z. Łodziana, R. Asakura, L. Bigler, R. Černý, C. Battaglia and A. Remhof, *Adv. Funct. Mater.*, 2021, **31**, 2010046.
- 131 D. H. Souza, A. M. D'Angelo, T. D. Humphries, C. E. Buckley and M. Paskevicius, *Dalton Trans.*, 2022, **51**, 13848–13857.
- 132 V. Brice, H. Johnson, D. Denton and S. G. Shore, *Inorg. Chem.*, 1972, **11**, 1135–1137.
- 133 M. R. Palacin, P. Johansson, R. Dominko, B. Dlugatch, D. Aurbach, Z. Li, M. Fichtner, O. Lužanin, J. Bitenc and Z. Wei, *J. Phys.: Energy*, 2024, **6**, 031501.
- 134 M. B. Amdisen, J. B. Grinderslev, L. N. Skov and T. R. Jensen, *Chem. Mater.*, 2023, **35**, 1440–1448.
- 135 Y. Yan, J. B. Grinderslev, M. Jørgensen, L. N. Skov, J. R. Skibsted and T. R. Jensen, *ACS Appl. Energy Mater.*, 2020, **3**, 9264–9270.
- 136 Y. Yan, W. Dononelli, M. Jørgensen, J. B. Grinderslev, Y.-S. Lee, Y. W. Cho, R. Černý, B. Hammer and T. R. Jensen, *Phys. Chem. Chem. Phys.*, 2020, **22**, 9204–9209.
- 137 L. N. Skov, J. B. Grinderslev, A. Rosenkranz, Y.-S. Lee and T. R. Jensen, *Batteries Supercaps*, 2022, **5**, e202200163.
- 138 W. Hertler and M. Raasch, *J. Am. Chem. Soc.*, 1964, **86**, 3661–3668.
- 139 E. V. Bukovsky, PhD, Colorado State University, 2015.
- 140 N. Miller, J. Forstner and E. Muetterties, *Inorg. Chem.*, 1964, **3**, 1690–1694.
- 141 H. Miller, W. Hertler, E. Muetterties, W. Knoth and N. Miller, *Inorg. Chem.*, 1965, **4**, 1216–1221.
- 142 W. Knoth, *J. Am. Chem. Soc.*, 1966, **88**, 935–939.
- 143 S. H. Lawrence, J. R. Wermer, S. K. Boocock, M. A. Banks, P. C. Keller and S. G. Shore, *Inorg. Chem.*, 1986, **25**, 367–372.