

# Analyzing Ammonia Bridges – and more about Bonding in Boron-rich Solids

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**Abstract:** Three types of boron-rich compounds in unusual bonding situations are described: First, salts that contain *closo*-hydroborate anions and exhibit hydrogen and dihydrogen bonds and a strong ammonia network; second, boron-rich metal borides with an unexpected metal–metal bond stabilized by Peierls distortion; and third, nanoscale metal borides that bind selectively to certain heptapeptides identified by the phage display technique.

**Keywords:** Ammoniates · Borides · Crystal structures · Hydroborates · Properties

## 1. Introduction

In 1893 Alfred Werner published his article ‘Beitrag zur Konstitution anorganischer Verbindungen’ and suggested an octahedral coordination of cobalt, for example in  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ .<sup>[1]</sup> At that time it seemed to be a revolutionary idea to place the ammonia molecules at six corners of a metal-centered octahedron (Fig. 1).

Werner’s idea caused a paradigm shift in coordination and inorganic chemistry that can easily be seen as significant as Kekulé’s dream of aromatic rings. Earlier, Christian Wilhelm Blomstrand had postulated chains of ammonia molecules<sup>[2]</sup> and his picture was well accepted by important scientists of that time, for example Sophus Mads Jørgensen, who apparently fought with Werner for the truth.<sup>[3]</sup>

Ammoniates and the role of ammonia as ligand or bridge remain an interesting research topic until today. Korber *et al.* investigated the role of ammonia molecules in a huge variety of complex inorganic solids that were synthesized in liquid ammonia, and they found several different roles of ammonia and types of linkages.<sup>[4]</sup> However, compared to hydrogen bridges in hydrated salts or biomolecules, the interaction of ammonia with cations, anions and other molecules in solids is much less

investigated and understood. Here, we will discuss ammonia molecules in *closo*-hydroborates with anions like  $\text{B}_6\text{H}_6^{2-}$ . Incidentally, such compounds are perfectly suited to discuss both features that excited Alfred Werner and his contemporaries: octahedrally and tetrahedrally arranged ammonia ligands – and chains of ammonia molecules! Boranes and hydroborates are molecular entities containing boron and hydrogen. They are extremely interesting in many ways. A very special bonding situation and a unique interplay between symmetry, molecular structure, electronic deficiency and properties have brought such boron compounds even to the attention of several Nobel-Prize winners like William N. Lipscomb (Nobel Prize 1976, borane structures), Herbert C. Brown (Nobel Prize 1979, boron compounds in organic

reactions), and Roald Hoffmann (Nobel Prize 1981, bonding theory). Nowadays, hydroborates are being discussed in the context of energy-related materials being potentially useful for hydrogen storage.<sup>[5]</sup>

We have synthesized, crystallized, and structurally analyzed many *closo*-hydroborates because they are fascinating as model compounds for comparison of molecular solids to solids with extended frameworks.<sup>[6,7]</sup> Boron-rich borides like  $\text{BaB}_6$  for example show structural ( $\text{B}_6$  octahedra) and bonding (electron deficiency) features that resemble the corresponding molecular salt with a  $\text{B}_6\text{H}_6^{2-}$  anion (Fig. 2). In our first section, we will present findings of topological analyses of selected hydroborates.

The second section presents a selection of boron-rich borides in unusual bonding situations. Typically, boron-rich borides

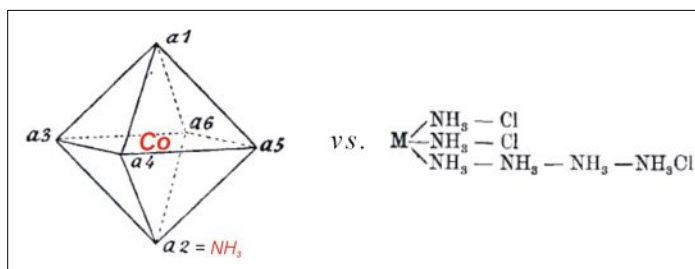


Fig. 1 Werner’s suggestion for the ammonia arrangement in  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  compared to Jørgensen’s model, according to ref. [1] (slightly modified).

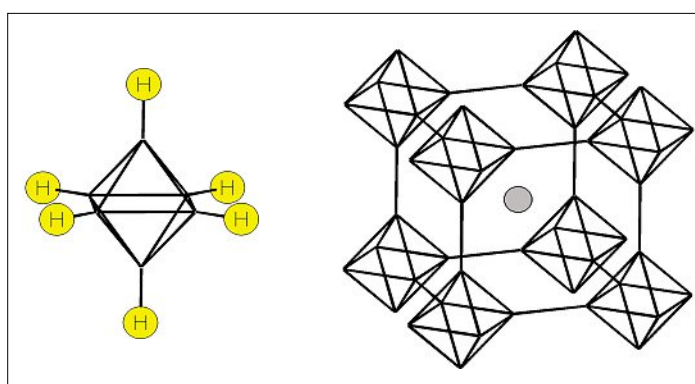


Fig. 2. *closo*-Hydroborate  $\text{B}_6\text{H}_6^{2-}$  (left) compared to barium hexaboride,  $\text{BaB}_6$  (right).

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exhibit crystal structures that are characterized by the motif of three-dimensionally interconnected polyhedra.<sup>[8]</sup> The example described here,  $\text{MnB}_4$ , takes us from polyhedral arrangements like the aforementioned octahedron of boron atoms to very unusual diamond-like boron atom frameworks.  $\text{BB}_4$  tetrahedra were found that resemble  $\text{CC}_4$  tetrahedra in lonsdaleite, a hexagonal diamond variant. An unexpected metal atom arrangement with a Mn–Mn bond was also observed.

Finally, a third and closing section will present new findings on nanoscale boride particles. Here, the bonding situation that is unique is that between a heptapeptide and nickel boride,  $\text{Ni}_3\text{B}$ . To our knowledge, this is the first description of selective binding between a boride and a peptide.

## 2. Ammonia Molecules in *closo*-Hydroborates – Multipole Refinements Based on Electron Density Distributions

Two of our synthetic procedures are novel for hydroborates and gave access to new compounds and their crystal structures: i) the reaction in liquid ammonia at very low temperatures,<sup>[5,9,10]</sup> and ii) the gel crystallization (Fig. 3).<sup>[11]</sup>

Formation and crystallization of hydroborates in liquid ammonia has led to unexpected compounds like  $\text{Cs}[\text{Na}(\text{NH}_3)_6]\text{B}_{10}\text{H}_{10} \cdot \text{NH}_3$ <sup>[9]</sup> or  $[\text{Li}(\text{NH}_3)_4]_2\text{B}_6\text{H}_6 \cdot 2\text{NH}_3$ .<sup>[10]</sup> These compounds exhibit strong ammonia networks that allow for an accurate localization of the atoms – including hydrogen – via X-ray data collected up to high angles. Conventional structure determination does not lead to deeper insights into the bonding situation of solids. But the experimental determination of the charge density followed by multipole refinements and topological analyses according to the atoms-in-molecules (AIM)-method by Bader *et al.*<sup>[12]</sup> permits a classification of the characteristics of interatomic areas of the electron density by means of critical points. Establishing bond critical point (BCP), ring critical points and cage critical points helps to better understand the bonding situation.

As can be seen in Fig. 4, lithium ions in  $[\text{Li}(\text{NH}_3)_4]_2\text{B}_6\text{H}_6 \cdot 2\text{NH}_3$  are tetrahedrally coordinated by ammonia molecules – Werner-like. In addition to that a hydrogen bond was observed between the ligands of neighboring complex cations, thus leading to a chain-like arrangement of ammonia molecules that reminds us of Jørgensen's theory. For  $[\text{Li}(\text{NH}_3)_4]_2\text{B}_6\text{H}_6 \cdot 2\text{NH}_3$ , charge density analysis further revealed multicenter bonds in the boron atom cluster of the anion, and a dihydrogen bond between  $\text{H}^-$  and  $\text{H}^+$  (Fig. 5). Such a visualization

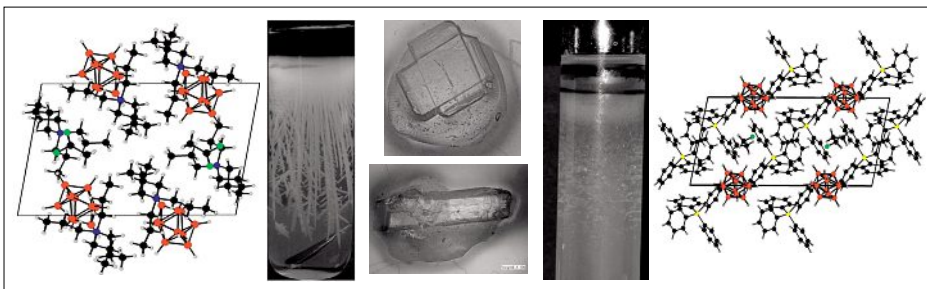


Fig. 3. Crystal growth in silica gel and structure determination: Unit cell of  $[(\text{C}_3\text{H}_7)_{7/4}]\text{B}_{10}\text{H}_{10} \cdot \text{CH}_3\text{COOH}$ , crystals of  $[(\text{C}_3\text{H}_7)_{7/4}]\text{B}_{10}\text{H}_{10} \cdot \text{CH}_3\text{COOH}$  and  $[\text{PPh}_4]_2\text{B}_{12}\text{H}_{12} \cdot \text{C}_3\text{H}_7\text{OH}$ , unit cell of  $[\text{PPh}_4]_2\text{B}_{12}\text{H}_{12} \cdot \text{C}_3\text{H}_7\text{OH}$  (from left to right).<sup>[11]</sup>

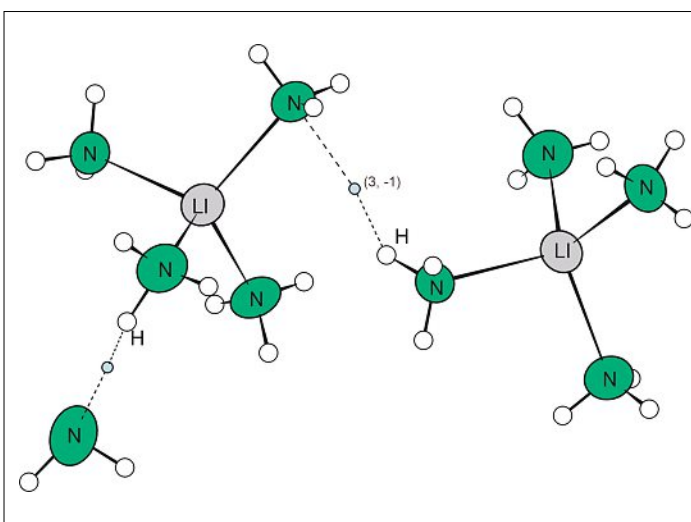


Fig. 4 Both Werner-like tetrahedral coordination of lithium ions and Jørgensen-like chain formation between ammonia ligands, the latter emphasized by an experimentally derived bond critical point with the (3,-1) signature.<sup>[10]</sup>

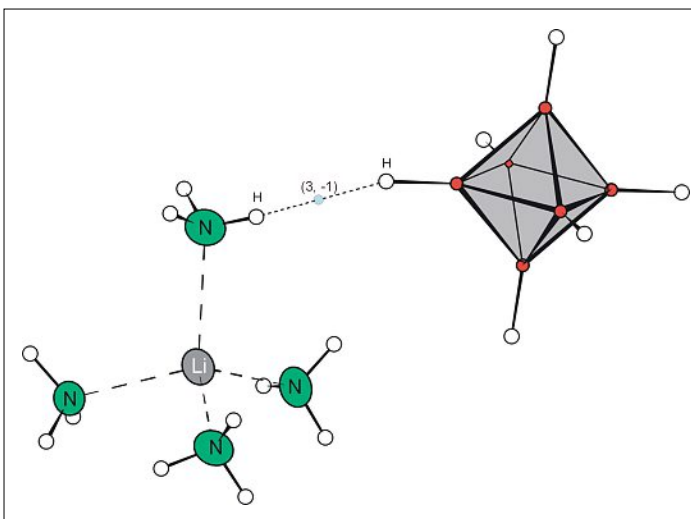


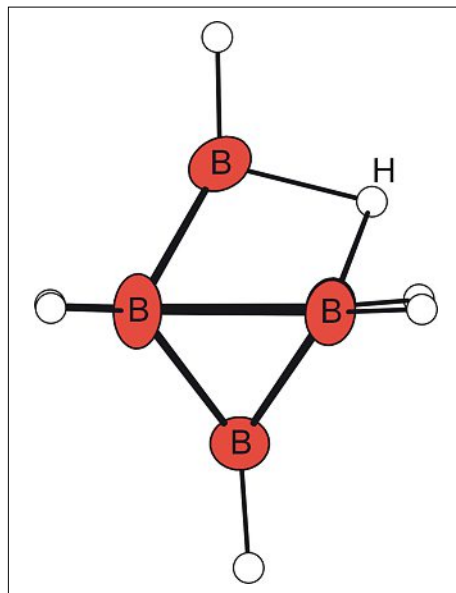
Fig. 5. Dihydrogen bond between  $\text{B}_6\text{H}_6^{2-}$  cage (red) with  $\text{H}^-$  and a  $[\text{Li}(\text{NH}_3)_4]^+$  tetrahedron with  $\text{H}^+$ , visualized by a bond critical point with the (3,-1) signature.<sup>[10]</sup>

of a dihydrogen bond using bond critical points derived from experimentally determined electron density maps is rather unique in literature.

We obtained another hydroborate,  $\text{N}(\text{C}_4\text{H}_9)_4\text{B}_6\text{H}_7$ , by a different synthetic procedure, and again performed a topological analysis of charge densities.<sup>[13]</sup> The anion can be seen as a product of a Brønsted acid-base reaction between a  $\text{B}_6\text{H}_6^{2-}$  anion and a  $\text{H}^+$  cation. The detailed electron density analysis of this compound allowed us to identify a rhomboid BBBH ring and a new type of a 4c–2e bond (Fig. 6).

## 3. Unexpected Mn–Mn Bond in a Refractory Material, $\text{MnB}_4$

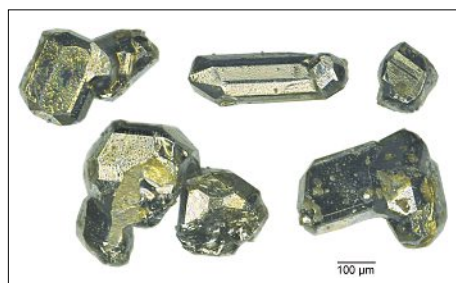
Boron-rich borides are hard and refractory compounds that are very versatile concerning their structural arrangements and their properties.<sup>[8]</sup> Semiconducting, superconducting, ferromagnetic and thermoelectric properties have been described for metal borides with varying boron content. We recently found boron-rich scandium and europium borides with excellent thermoelectric properties at very high temperatures. As mentioned above, typical


 Fig. 6. BBBH ring in  $N(C_4H_9)_4B_6H_7$ .

boron-rich borides are characterized by a framework of electron-deficient boron atom polyhedra like octahedra, bipyramids or icosahedra that are three-dimensionally interconnected – and metal atoms nestling in the interstices of the boron atom framework.

On the other hand, manganese tetraboride,  $MnB_4$ , has an unusual boron atom arrangement with distorted  $BB_4$  tetrahedra that are corner- and edge-connected in all three directions – similar to what is known from the carbon atom arrangement in diamond. Such a framework is known also from the chromium variant, but otherwise very untypical for borides. The metal atoms are located in a twelve-membered cage of boron atoms that is formed by two boat-like  $B_6$ -rings. Similar boat-like hexagons are known from the layered structure of ultra-hard osmium diboride,  $OsB_2$ . We obtained single crystals (Fig. 7) of this grey-metallic compound by reacting the elements at high-temperatures in the presence of iodine as mineralizer, and investigated its crystal structure and properties in detail.<sup>[14]</sup> X-ray powder patterns confirmed the samples to be mono-phasic.

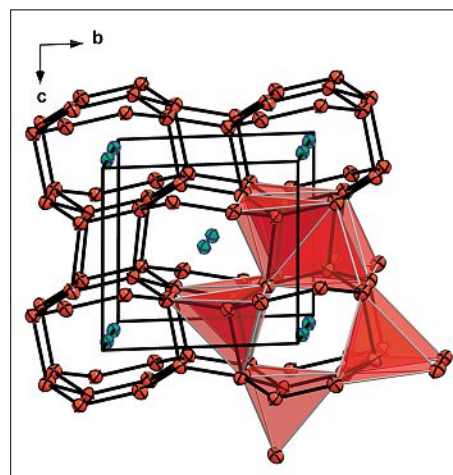
Unexpectedly, the crystal structure determination (Fig. 8) revealed two different


 Fig. 7. Crystals of  $MnB_4$ .

$Mn-Mn$  distances. One of them is very short with 269.61(7) pm, which is astonishing compared to other Mn-containing solids like  $MnP_4$  ( $Mn-Mn$  distances are  $>292.1$  pm<sup>[15]</sup>) or  $Mn_2(CO)_{10}$  (292.3 pm<sup>[15]</sup>). In  $MnP_4$ , an oxidation state of Mn(II), non-metallic properties and diamagnetism was observed.<sup>[16]</sup> For  $MnB_4$  we measured a very small band-gap (0.04 eV), and paramagnetism. According to theoretical calculations the oxidation state Mn(I) is very probable and the  $Mn-Mn$  bond in  $MnB_4$  may be described as a double bond. It is caused by a Peierls distortion. The distorted variant was calculated to be energetically more stable than an undistorted structure. In addition to that manganese tetraboride was found to be a hard material ( $H \approx 15(3)$  GPa), and the oxidation state Mn(I) was confirmed by  $^{55}Mn$  solid state NMR spectroscopy.<sup>[17]</sup>

#### 4. Bonding between Nickel Boride and Heptapeptides

Usually, metal borides are obtained by high-temperature synthesis routes. A


 Fig. 8. Unit cell of  $MnB_4$  (red: boron atoms; blue: manganese atoms).

rather unusual method of preparation is to precipitate nanoscale boride particles from solvents. The method has been shown to be successful for metal-rich borides of iron, cobalt, and nickel:  $M_3B$ ,  $M_2B$ ,  $MB$  ( $M = Fe, Co, Ni$ ). Here,  $Ni_3B$  nanoparticles were obtained by a precipitation route using nickel salts and sodium tetrahydroborate,  $NaBH_4$ , in water.<sup>[18]</sup> Earlier, we applied a similar preparation technique using non-aqueous solvents to obtain nanoscale powders of ferromagnetic iron boride,  $FeB$ , which is a compound far more water-sensitive than the Ni variant. For  $FeB$ , the metal atom coordination in amorphous precipitates was investigated by X-ray absorption spectroscopy as well as other properties, for example the size- and crystallinity dependence of the magnetism.<sup>[19]</sup>

Very little is known about the interaction between organic materials and borides. By screening M13 phage display peptide libraries we found best binders that are specific and selective for  $Ni_3B$  nanoparticles.<sup>[20]</sup> Biopanning, binding and competitive assays allowed for identification of peptides and a unique set of sequences that bind to the amorphous and crystalline nickel boride nanoparticles from a random peptide library. Certain strong binders proved to be selective for nickel boride, for example the heptamer peptide with the sequence LGFREKE. The specific binding affinity was confirmed by fluorescence microscopy and atomic force microscopy. The heptapeptides that were identified by phage display technique were then used as surfactants during the synthesis of  $Ni_3B$  nanoparticles. Thus bio-borides can be generated by genetic engineering. Using best-binding peptides it was now for the first time possible to synthesize peptide-coated, otherwise phase-pure  $Ni_3B$  in absence of traces of metallic, ferromagnetic nickel.<sup>[21]</sup> This established unambiguously and for the first time experimentally the compound to be paramagnetic (Fig. 9), as predicted by theory.<sup>[22]</sup>

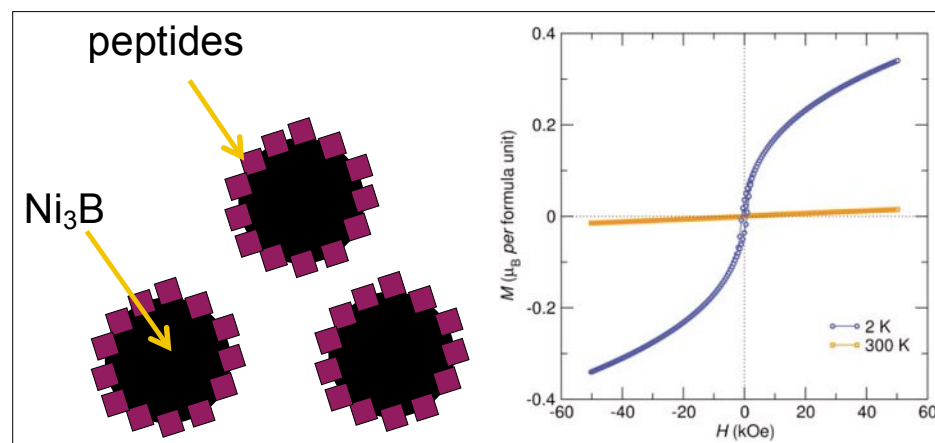


Fig. 9. Schematic presentation of peptide-protected nickel boride particles (left) and magnetic measurement of a corresponding sample (right).

## 5. Summary

Metal borides are a class of inorganic solids that is much less known and investigated than for example metal oxides or intermetallics. At the same time it is a highly versatile and interesting class of substances in terms of structures, physical and chemical properties, like conductivity, magnetism, or catalytic activity. This makes these solids interesting for detailed analyses of the electronic structure and bonding situation – and also attractive for the generation of new types of materials. On the other hand metal hydroborates represent an important group of compounds that are both model compounds for boron-rich borides and exhibit bonding features considered to be rather unique in inorganic chemistry. Their crystallization from liquid ammonia has led to new insights into the details of electron density distribution that still follow Werner's train of thought, even 100 years after he received the Nobel Prize for his revolutionary theory of coordination.

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