Towards hydrogen-rich ionic \((\text{NH}_4)\)(\text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_3)\) and related molecular \(\text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_3\)\#

Rafal Owczaryn\#*, Tomasz Jarofi\#, Krysztof Kazimierczuk\#*, Przemyslaw J. Malinowski\#*, Wojciech Grochala\# and Karol J. Fijalkowski\#*

Attempts of synthesis of ionic \((\text{NH}_4)\)(\text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_3)\) using metathetical approach resulted in a mixture of the target compound and a partly dehydrogenated molecular \(\text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_3\) product. The mixed specimen was characterized by NMR and vibrational spectroscopies, and the crystal structure of their cocrystal was solved from powder x-ray diffraction data, and supplemented by theoretical density functional theory calculations. Despite their impressive hydrogen content, and similarly to ammonia borane, both title compounds release hydrogen substantially polluted with borazine, and traces of ammonia and diborane.

Introduction

Protic-hydridic compounds constitute one important family of solid-state hydrogen storage materials with the potential to be applied as onboard fuel systems required in the hydrogen economy. The presence of both positively and negatively charged hydrogen atoms results in the formation of a network of dihydrogen bonds governing the crystal structure and facilitating the process of thermal decomposition.\(^1\) These features were observed and thoroughly described for ammonia borane,\(^2\) metal amidoboranes,\(^3\) and further explored for \(\text{NH}_3\text{BH}_4.\(^4\)

Ammonia borane \((\text{AB})\) is one of the best-researched materials in this group, being an air and water insensitive solid and containing ca. 19.6% of hydrogen by weight.\(^5\) Unfortunately, \(\text{AB}\) releases only 1/3 of the stored hydrogen below 120°C.\(^6\) Moreover, the hydrogen released is contaminated with ammonia, diborane, borazine, aminoborane and aminodiborane, which excludes its use as a direct \(\text{H}_2\) source for low-temperature fuel cells.\(^7\) Such high gravimetric H content, however, provides significant room for modifications – even if the relatively heavy elements are introduced, the system still should be able to fulfill the gravimetric DOE requirements for \(\text{H}\) storage materials.\(^8\)

Among the derivatives of \(\text{AB}\), amidoborane salts of a general formula \(\text{M(NH}_3\text{BH}_4)_n\) [abbreviated here as MAB or M(AB)_n] constitute the largest group.\(^9,10\) Two dozens of mono- and bimetallic amidoborane salts have been reported. Some of them \([\text{e.g.} \text{KAB},\text{11 RbAB},\text{12,13 CsAB},\text{12,13 Mg(AB)}_2,\text{14 Ba(AB)}_2,\text{15 Al(AB)}_2,\text{16 LiAl(AB)}_2,\text{17 Li}_2\text{Mg(AB)}_2,\text{18} \] evolve pure \(\text{H}_2\) upon thermal decomposition at ca. 100°C. Nonetheless, all these materials suffer from a lack of reversibility and relatively low hydrogen content available at moderate temperatures.\(^9,10\)

Recently, a novel group of ammonia borane derivatives containing five-membered chain anions of a general formula \(\text{M(BH}_3\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_3\text{)}\) [abbreviated here as M(B3N2)] have been reported.\(^19–23\) Among them, one can list two allotropes of Verkade’s base salt,\(^20,21\) five alkali metal salts,\(^19,21,22,24,25\) and four ionic liquids.\(^23\) Although three of them \([\text{e.g.} \text{Li(B3N2)},\text{21,22 (Bu}_3\text{N)}(\text{B3N2}),\text{23 (Et}_3\text{N)}(\text{B3N2})\text{23]\ meet the target H wt% content and release pure hydrogen below 150°C, yet none of them fulfils all the DOE targets simultaneously.\(^8\)

---

\# This work is dedicated to Prof. Roald Hoffmann at his 85th birthday

Electronic Supplementary Information (ESI) available: synthesis, NMR, FTIR, Raman, PXD, crystal structures, TGA/DSC/MS, EIS, and comparison with other ammonia borane derivatives. See DOI: 10.1039/x0xx00000x
Results and discussion

2.1 Synthesis

Synthesis of (NH₄)[B₃N₂] was attempted employing Jaron’s et al. metathetic approach mediated by the precursors containing weakly coordinating ions 26–28. The reaction was conducted in dry THF similarly to the previous syntheses of all alkali metal M[B₃N₂] salts21 according to Equation 1:

\[(\text{VBH})[\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_2] + (\text{NH}_4)\text{][B(C}_6\text{H}_{12}]\rightarrow (\text{NH}_4)[\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_2] + (\text{VBH})[\text{B(C}_6\text{H}_{12}]\text{] (1)}

Unexpectedly, during the reaction, we observed the evolution of a small amount of gas which should not occur in a metathetic reaction. Since the expected main product contains ammonium cation and B₃N²⁻ anion (essentially, a derivative of a borohydride anion) we assumed that — similarly to what is observed for NH₄BH₄ — hydrogen might be evolved upon reaction of these ions according to Equation 2:

\[(\text{NH}_4)[\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_2] \rightarrow \text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_3 + \text{H}_2\uparrow \text{ (2)}

Confirmation that this surmise is correct is presented below.

Synthesis led to a mixture of well THF-soluble products, which were separated by precipitation of the side product (VBH)[B(C₆H₁₂)] in dry DCN. Both products were subjected to spectroscopic analyses (Fig. 2) and powder X-ray diffraction (Fig. 3) to demonstrate successful ion exchange according to Eq. 1. Indeed, FTIR spectra (Fig. 2) of the products show that the target product contains the NH and BH groups, while the side product contains the CH groups. Unfortunately, complete separation of the main product and side product was not achieved, as documented by very weak CH bands at ca. 3000 cm⁻¹ from B(C₆H₁₂)₄ anions for the former, and very weak BH bands at ca. 2400 cm⁻¹ from (B₃N₂)²⁻ anions for the latter product. X-ray diffraction points to the same conclusion, showing that two new distinct crystalline species formed during the reaction (Fig. 3).

The diffraction patterns of the products are free from reflections coming from the substrates which suggests at least 95% purity of the former.

2.2 NMR spectra

A detailed ¹¹B NMR investigation of the main product dissolved in THF-d₄ was performed (Fig. 4). A typical spectrum of M[B₃N₂] salt consists of a triplet at ca. –8.5 ppm from [BH₂] groups and a quartet at ca. –22.5 ppm from [BH₃] groups, having a relative intensity of 1:2. Here, the spectrum of the main product is more complicated and contains two triplets (δ = –10.4 ppm, J = 101 Hz; δ = –12.3 ppm, J = 102 Hz) and a quartet (δ = –22.2 ppm, J = 91 Hz) in an intensity ratio that varies from batch to batch (in average ca. 4:3:5). These features altogether suggest that the main product formed according to (Eq. 1) partially undergoes a subsequent dehydrogenation reaction (Eq. 2). Variation in the observed intensity ratio of the signals may be caused by the partial decomposition of the main product thus changing the ratio between the components of the product. We note that a 1:3 mixture of (NH₄)[B₃N₂] and NH₄BH₂NH₂BH₃NH₂BH₃ (abbreviated as N3B3) would yield 4 BH₂ triplets units coordinated by two NH₂ groups, 3 BH₂ triplets from units coordinated by NH₂ and NH₃, and 5 BH₃ quartets altogether. This result would suggest that ca. ½ of (NH₄)[B₃N₂] decomposed to N3B3 while dissolved in THF.

To get more insights into the processes occurring during the synthesis, we conducted in situ ¹¹B(H) NMR measurements in THF-d₄ to monitor signals of the products and substrates (Fig. 5). The monitoring showed that all three signals from the product(s) (marked with #) arise simultaneously, testifying to the simultaneous progress of reactions described by Eq.1 and Eq.2. Apart from the signals assigned to the substrates and the main product, numerous additional signals which do not change during the reaction are present. These signals come from the moieties that do not play a direct role in the formation of the main product, e.g. [B(C₆H₁₂)]⁺, in which the chemical neighbourhood of boron atom does not change during the synthesis. The monitored reaction (Fig. 4) was not completed (i.e. signals of the substrates were still intense) because of the local depletion of the substrates (no mixing was applied in an NMR test tube inside the spectrometer).
products and substrates. Ewing observed in Table of successful synthesis of B3N3, however, all signals observed groups present in the molecule (two BH signals observed were assigned to three boron). The reaction, performed in glyme solution, was accompanied by ammonium chloride, according to the following equation:

$$\text{Na(BH}_3\text{NH}_2\text{BH}_3\text{NH}_2\text{BH}_3 \text{H}) \rightarrow \text{NH}_2\text{BH}_3\text{NH}_2\text{BH}_3\text{NH}_2\text{BH}_3 + \text{H}_2 \uparrow + \text{NaCl} \downarrow$$

(3)

The reaction, performed in glime solution, was accompanied by evolution of hydrogen gas, which is similar to our observations.

Ewing et al. assumed that the solid product obtained was B3N3 based only on an NMR study of this material. Three signals observed were assigned to three boron-containing groups present in the molecule (two BH2, one BH3). In the case of successful synthesis of B3N3, however, all signals observed should be equally intense (1:1:1) while their intensity ratio was clearly different (Fig. 4). Our analysis suggest that the reaction towards B3N3 is in fact a two-step process (Eqn. 1 and 2) and some (NH2)(B3N2) intermediate (i.e. our main target compound) remains. The resulting assignment of NMR signals for both products is given in Table 1.

To further support our claim, we performed further characterisation of the reaction product.

### 2.3 FTIR and Raman analysis

Two preeminent sets of bands in the vibrational (IR absorption and Raman scattering) spectra of the main product (Fig. 6, Fig. 7), originate from stretching vibrations of NH (3000–3400 cm⁻¹) and BH (2150–2400 cm⁻¹) groups. They are accompanied by bands coming from deformation vibrations of NH₂ moieties (1400–1600 cm⁻¹) as typical of M(B3N2) salts and by BH stretching. BH deformation modes fall below 1350 cm⁻¹.

Aside from the bands typical for M(B3N2) salts, the NH stretching region of Raman spectrum (Fig. 7) contains a relatively low frequency band (peaking at 3041 cm⁻¹) originating from ammonium cations. The ammonium cations are known to give strong Raman at much lower energies than the [NH₃] and [NH₂] groups, e.g. ammonium chloride gives a single band at 3052 cm⁻¹, while ammonium borohydride yields two bands at somewhat higher energies of 3118 cm⁻¹ and 3178 cm⁻¹.

In the higher energy part of NH stretching region, in both FTIR and Raman spectra, we observe at least 6 distinct bands, four of which (3306 cm⁻¹, 3288 cm⁻¹, 3259 cm⁻¹, 3239 cm⁻¹) in IR; 3307 cm⁻¹, 3288 cm⁻¹, 3260 cm⁻¹, 3240 cm⁻¹ in Raman) form a doublet of doublets seen for heavy alkali metal M(B3N2) salts; it is characteristic for M(B3N2) salts that that the higher energy doublet is more intense in FTIR spectra, while the lower-wavenumber one is stronger in Raman spectra. In contrast, the lower energy one is more intensive in Raman spectra. The presence of such doublets is caused by Davydov splitting, i.e. the interaction of NH₂ groups coexisting within one crystallographic unit cell (the resonance of the corresponding oscillators removing their degeneration). A similar split of NH band was observed in the spectra of Rb(B3N2) and Cs(B3N2), which contain gauche-form of (B3N2)⁻ anions, unlike the lighter analogues featuring straight anions and not showing Davidov.

---

### Table 1. Chemical shifts, J-coupling values and assignment of the signals observed in ¹¹B NMR spectra of the main product, sample reported by Ewing et al.²² Data for alkali metal M(B3N2) salts²³ given as reference.

| compound | NH₂–BH₂–NH₂ | NH₂–BH₂–NH₂ | BH₂–NH₂ | | |
| --- | --- | --- | --- | --- | --- |
| δ [ppm] | J [Hz] | δ [ppm] | J [Hz] | δ [ppm] | J [Hz] |
| main product | –10.4 | 101 | –12.3 | 102 | –22.2 | 91 |
| Ewing et al.²² | –10.5 | 95 | –12.4 | 104 | –22.3 | 95 |
| (VBH)(B3N2)²¹ | –8.2 | 100 | – | – | –21.6 | 91 |
| Li(B3N2)²¹ | –8.4 | 103 | – | – | –22.6 | 90 |
| Na(B3N2)²¹ | –8.7 | 99 | – | – | –22.4 | 91 |
| K(B3N2)²¹ | –8.6 | 101 | – | – | –22.0 | 89 |
| Rb(B3N2)²¹ | –8.4 | 100 | – | – | –21.7 | 90 |
| Cs(B3N2)²¹ | –8.4 | 101 | – | – | –21.2 | 94 |

---

### Fig. 5.

The sequence of ¹¹B(NH) NMR spectra collected in situ upon synthesis according to Eq. 1. The bottom spectrum shows the mixture of substrates (t=60s). The top spectrum shows to final mixture of products and substrates (t=6060s). @ indicates signals from substrates. # indicates signals of the main product. * indicates [B(C₆H₅)₄]²⁻ anions.

### Fig. 6.

Comparison of FTIR absorption (top in each bracket) and Raman scattering (bottom in each bracket) spectra of the main product of the synthesis according to Eq. 1 (magenta) and the spectra of alkali metal M(B3N2) salts. Regions magnified in Fig. 7 (NH stretching and NH bending) are marked with grey fields.
split. The split observed here equals ±9 cm⁻¹, which is intermediate between those of ±4 cm⁻¹ and ±14 cm⁻¹ seen for Rb(B3N2) and Cs(B3N2), respectively. Two remaining bands observed in NH stretching region (3224 cm⁻¹ and 3268 cm⁻¹ in IR), are weaker than the doublets of doublets, and they must originate from vibrations of terminal [NH₄] groups of B3N3. Indeed, they fall in a spectral region typical for terminal [NH₃] groups of ammonia borane (3196 cm⁻¹, 3253 cm⁻¹ and 3311 cm⁻¹). Naturally, it is expected that signals originating from the terminal [NH₃] of B3N3 are weaker than those from more numerous [NH₄] groups present in both (NH₄)(B3N2) and B3N3.

The region of the IR absorption spectrum associated with deformations of the NH₄ moieties (Figure 7) is consistent with these conclusions. One can clearly distinguish signals at ca. 1530–1600 cm⁻¹, typical for [NH₄] and [NH₃] groups, from the signals at ca. 1250–1500 cm⁻¹, characteristic for ammonium cations (cf. 1402 cm⁻¹ for NH₄Cl). It is worth to notice, that the IR spectra in the 1350–1500 cm⁻¹ region show five bands (1374 cm⁻¹, 1392 cm⁻¹, 1415 cm⁻¹, 1427 cm⁻¹, 1479 cm⁻¹), and this agrees with the number of deformation modes expected for NH₄ cation in a low-symmetry environment.

The spectroscopic analysis clearly shows that both (NH₄)(B3N2) and B3N3 moieties constitute the main product, thus confirming the reactions according to Eq. 1 and Eq. 2.

2.4 Crystal structure of the side product

The chemical composition of the side product of metathesis was confirmed by single crystal x-ray diffraction measurements (cf. ESI). This compound contains protonated Verkade’s base cations and tetraphenylborate anions, ([VBH][B(C₆H₄)₄]), proving successful ion exchange in reaction according to Eq. 1. The compound crystallises in P1 space group with the constituent ions of different polarities showing no significant interactions, as expected for large ions with small charge smeared over the entire ion.

2.5 Crystal structure of the main product

As we could not obtain a single crystal of the main product, we were forced to use powder X-ray diffraction (PXRD), supported by DFT calculations and the results of spectroscopic analysis described above.

Indexing of the PXRD pattern leads to a P2₁/c unit cell with the refined lattice parameters of: a = 13.391(10) Å, b = 13.195(8) Å, c = 17.822(12) Å, β = 125.86(4)° and V = 2552(3) Å³. Assuming (NH₄)(B3N2) as a product, such unit cell volume would suggest Z = 16 (multiplicity of the general atomic position) and V/Z = 159.5 Å³. However, this V/Z value is too small as the values for K and Rb analogues are larger (167.7 Å³ and 174.3 Å³ respectively) while the size of NH₄⁺ falls between these two alkali metal cations. Somewhat The smaller than expected V/Z volume suggests that the crystalline phase should contain also the partially dehydrogenated molecules of the product of condensation presented in Eq. 2.

To test such scenario, structural models were derived for (NH₄)(B3N2), B3N3 and the (NH₄)(B3N2)-3(B3N3) cocrystal with the components in the 1:3 molar ratio as indicated by NMR data. Initial positions of heavy atoms came from simulated annealing using the experimental diffraction data. The models were then fully optimized using periodic DFT calculations (Table 2 and S1). The theoretical unit cell volume calculated for (NH₄)(B3N2) is significantly larger than those for the models containing B3N3 moieties and the latter are only 4.0–4.5% larger than the experimental value. This degree of overestimation is rather typical for the GGA calculations. Importantly, the closest H···H contacts in the optimized structure of (NH₄)(B3N2) remain unreasonably short (1.40 Å), and outside the distribution observed experimentally for the dihydrogen bonds (usually >1.80 Å), Fig. 9. This reconfirms that the main product is not a pure (NH₄)(B3N2). The minimum H···H contacts in the optimized crystal structures containing B3N3 are significantly longer (1.60–1.68 Å), and closer to typical values for very strong dihydrogen interactions. Therefore, we have used a theoretical model of the (NH₄)(B3N2)-3(B3N3) cocrystal to refine its crystal structure using the best experimental dataset, Figure 8 and Figure S9.3 (S1).

The obtained structural model of (NH₄)(B3N2)-3(B3N3) contains four formula units in the unit cell (Z = 4) with one asymmetric unit (Z’ = 1).

![Fig. 7. Comparison of NH stretching (3000–3400 cm⁻¹) and NH bending (1300–1700 cm⁻¹) regions of FTIR absorption (top in each bracket) and Raman scattering (bottom in each bracket) spectra of the main product of the synthesis according to Eq. 1 (magenta) and alkali metal M(B3N2) salts. Full spectra presented in Fig. 6.](image)

![Fig. 8. Visualisation of the unit cell (left) and the asymmetric unit (right) of the crystal structure of the cocrystal comprising one unit of (NH₄)(B3N2) salt and three independent units of B3N3 molecules. Atom code: nitrogen – blue, boron – green, hydrogen – white.](image)
The structure is stabilized by strong dihydrogen interactions. Two B3N3 chains adopt gauche geometry, and resemble the B3N2 anions in the heavier M(B3N2) salts, M = Rb, Cs.21 The third B3N3 moiety and (B3N2)– anion are more straight, closer to the geometry of anionic moieties in the light M(B3N2) salts, M = Li–K.21,22 The B–N distances of 1.56(2)–1.58(2) Å remain within range observed in other compounds from this group. Further improvements of our preliminary experimental structure model, and in particular positions of hydrogen atoms, would require application of neutron diffraction methods, and is beyond the scope of this work.

2.6 Thermal decomposition

The theoretical gravimetric hydrogen content of the 1:3 cocrysats is very large, 16.4%. We have studied thermal decomposition of this new compound to assess its hydrogen storage properties. In Fig. 10 we present the results of a simultaneous thermogravimetric and calorimetric analysis of the main product together with gas evolution curves (hydrogen, ammonia, diborane, borazine) acquired in mass spectrometry experiment of the evolved gases.

The main product is thermally stable below 50°C. At higher temperatures, one can observe a multistep exothermic decomposition preceded by an endothermic process. During decomposition, a mixture of gases containing borazine, hydrogen, diborane and ammonia is being evolved. Close analysis of TGA/DSC/MS curves suggests that decomposition proceeds in at least 3 steps below 200°C, but each of them seems to have a similar profile of evolved gases. Interestingly, borazine is the main gaseous product of thermal decomposition, just as in the case of NH4BH3,6 but dissimilarly to alkali metal M(B3N2) salts.21,22 Facile evolution of borazine may be related to stoichiometry of two components of the main product. (NH4)2(B3N2) and B3N3, both contain 3 boron atoms and 3 nitrogen atoms, just like borazine molecules. Dehydrogenation of B3N3 molecule proceeds with formation of a new B–N bond at [BH3] and [NH3] terminals according to Eq. 4. This reaction was also proposed as the final step of borazine evolution during thermal decomposition of ammonia borane.34 Formation of pseudo-aromatic borazine is accompanied by dehydrogenation of the elusive head-to-tail cyclohexane-like intermediates, according to Equation 4.

\[
\text{NH}_4\text{BH}_3 \rightarrow \text{NH}_3\text{BH}_3 \rightarrow \text{NH}_4\text{B}_6\text{H}_{12} + \text{H}_2 \rightarrow \text{B}_9\text{H}_{22} + 4\text{H}_2
\]

We also observed the formation of B3H6 and NH3, similarly as in decomposition of Na(B3N2),21,22 K(B3N2),21 Rb(B3N2)21 and Cs(B3N2),22 which come from fragmentation of (B3N2)– anions.

As mentioned above, the thermal decomposition of the main product is preceded by an endothermic process. Analogies to ammonia borane6 and amidoboranes10 might suggest melting of the sample. However, direct visual observations ruled out this possibility. Endothermic event is related either to an intermolecular reorganization or a structural phase transition.

Depending on the heating rate, decomposition temperature reaches the fastest rate at ca. 145°C ca. 152°C for 1 K/min and 5 K/min scans, respectively. The observed mass loss upon thermal decomposition in the range up to 200°C, equals ca. 45% and surpasses those of alkali metal M(B3N2) salts21 and parent ammonia borane.6 Such large observed mass loss may be attributed to the evolution of borazine and other volatiles. The
Solid residue is amorphous, and consists of boron nitride and polymeric B₄N₆H₁₂ phases as deduced from FTIR analysis (cf. ES1).

The observations discussed above lead to the following overall equations describing thermal decomposition of the two components of the main product:

\[
\begin{align*}
(\text{NH}_4)(\text{BH}_3\text{NH}_2\text{BH}_3\text{NH}_2\text{BH}_3) & \rightarrow \text{B}_3\text{N}_3\text{H}_6 + \text{N}_2 + \text{H}_2 + 14(\text{BHNH}) + \text{BN} \quad (5) \\
\text{NH}_3\text{BH}_3\text{NH}_2\text{BH}_3\text{NH}_2\text{BH}_3 & \rightarrow \text{B}_3\text{N}_3\text{H}_6 + + \text{H}_2 + 14(\text{BHNH}) + \text{BN} \quad (6)
\end{align*}
\]

Theoretical mass loss of Eq. 5 and Eq.6 equal 43% and 42%, respectively, which reasonably agree with the observed experimental mass loss of ca. 45%.

Conclusions

Synthesis of hydrogen-rich (NH₄)(B₃N₂) salt was attempted in metathetic approach using precursors which contained weakly coordinating ions. The obtained product, however, corresponds to a mixture of ionic (NH₄)(B₃N₂) and neutral B₃N₃ forming co-crystals in molar ratio of 1:3. Based on available ¹¹B NMR data, the main product was found to be very similar to the samples reported earlier by Ewing et al., as B₃N₃.

The compound crystallizes in P2₁/c unit cell with the lattice parameters of: a = 13.401(11) Å, b = 13.196(8) Å, c = 17.828(12) Å, β = 128.83(4)°, V = 2556(3) Å³ and Z = 4. The expected side product of a metathetic reaction, (VBH)[(C₆H₅)₄], crystallises in P2₁ unit cell with the lattice parameters of a = 11.7376(3) Å, b = 19.5388(5) Å, c = 20.5479(4) Å, α = 61.751(2)°, β = 73.618(2)°, γ = 89.605(2)°, V = 3937.71 Å³ and Z = 4.

Although its high hydrogen content of 16.4%, the new compound cannot act as a self-standing solid-state hydrogen reservoir as it decomposes via a set of exothermic events while evolving mixture of volatile gaseous products such as borazine, diborane, and ammonia, aside from hydrogen. However, it is possible that templating our product in porous matrices could result in substantial improvement of purity of the evolved hydrogen, similarly as it was observed for ammonia borane.

Experimental

Reagents: All operations were performed under inert Ar atmosphere inside gloveboxes, MBRAUN Labmaster DP or Vigor SG1200 (O₂, H₂O < 1.0 ppm). Commercially available reagents and solvents were used: NH₃BH₃ (98%, JSC Aviabor), NH₃B(C₆H₅)₄ (99%, Sigma-Aldrich (later denoted as SA)), C₂H₅O (99%, SA), CH₃Cl₂ (99%, SA). The synthesis of (C₆H₅N=PH)(BH₃NH₂BH₃NH₂BH₃) was performed according to the route described in our earlier paper. For NMR measurements we used THF-d₈ (99.5 atom% D, SA).

Infrared absorption spectroscopy: FTIR spectra were measured in the standard range of 400–4000 cm⁻¹ using Fourier Transform IR spectrometer Vertex 80v from Bruker. Samples were examined using KBr pallets prepared using anhydrous KBr (99%, SA) additionally dried in 150°C for 24h.

Raman spectroscopy: Raman scattering measurements were done using Raman microscopy setup from Jobin Yvon T64000 with Si CCD detector and Kr-Ar gas laser from Spectrophysics. We used green 514.5 nm excitation line. For the measurements small doses of samples were placed in 0.5 mm thick quartz capillaries sealed under inert gas atmosphere.

Nuclear Magnetic Resonance: ¹¹B NMR spectra with and without ¹⁴N decoupling were obtained using Agilent 700 MHz spectrometer with Direct Drive 2 console and 5 mm room-temperature broadband probe. We used deuterated tetrahydrofuran (d₄-THF) as a solvent. The number of scans has been set to 256, the interscan delay to 1 s and the acquisition time to 200 ms. The spectra were acquired at 25°C. The exponential apodization has been used during processing (line broadening of 5 Hz).

Thermogravimetrical Analysis: Thermal decomposition was investigated using STA 410 thermal analyser from Netzsch, in the temperature range from -10°C to +200°C. STA 449 allows simultaneous thermogravimetric analysis, differential scanning calorimetry and evolved gas analysis by means of mass spectrometer. The samples were loaded into alumina crucibles inside a glovebox. Helium was used as a carrier gas. Evolved gases were analysed with a QMS 403C Aëolos MS from Pfeiffer–Vacuum. Transfer line was preheated to 100°C to avoid condensation of residues.

Powder X-ray diffraction: PXRD measurements were conducted on samples sealed in 0.5 mm thick quartz capillaries under inert atmosphere. Two diffractometers were used: Panalytical X’Pert Pro with linear PIXcel Medipix2 detector (parallel beam; the CoKα₂ radiation); and Bruker D8 Discover with 2D Vantec detector (parallel beam; the CuKα₁ radiation).

Crystal structure solution of the main product: Diffraction signals have been indexed using X-cell and the initial structural model has been obtained using FOX software, while the Rietveld refinement has been performed in Jana2006. Pseudovoltage functions with Berrar-Baldinnozzi asymmetry have been used for modeling of diffraction profiles. The restraints were used during refinement for the N–H and B–H distances at 0.900(10) Å and 1.100(10) Å, respectively, Fig. S59.2). The angles related to hydrogen atoms (to 109.47° with tolerance of ca. 0.5°). The N–B distances were set to the value 1.57(1) Å. The atomic displacement parameters of B and N atoms were set equal, while those of H atoms were constrained according to the riding model. The bottom constraint of 1.91 Å for B–H distances was applied. Further details on the crystal structure may be obtained from CCDC/FIZ Karlsruhe on quoting the CSD deposition No. 2193624.

Crystal structure solution of the side product: Crystal of the compound were covered with perfluorinated oil (Krytox 1531). Data collection and reduction was performed with Agilent Supernova X-ray diffractometer with Ka-Cu radiation (microsource) with data reduction performed by CrysAlisPro software (v. 40.99). Structure solution: SHELXT, refinement against F² in Shelxi-2018, with ShelXle as GUI software. The disorder of the –OC(CF₃)₁ group was resolved using DSR. Further details on the crystal structure may be obtained from CCDC/FIZ Karlsruhe on quoting the CSD deposition No. XXX.

Density Functional Theory (DFT) calculations were performed using CASTEP. Generalized Gradient Approximation (GGA) was used with PBE functional and
Tkatchenko-Scheffler dispersive correction. The cutoff value of 500 eV was applied to achieve good energy convergence. The density of the k-point grid was set below 0.1 Å⁻¹ and ultrasoft, generated on the fly pseudopotentials were used as they provide more accurate lattice parameters.

Graphical presentation of crystal structures has been performed with Vesta.

Conflicts of interest
There are no conflicts of interests to declare.

Acknowledgements
This research was funded by Polish National Science Centre within the projects Preludium 13 (UMO/2017/25/N/ST5/01977) and Sonata Bis 8 (UMO/2018/30/E/ST5/00854). Research was carried out with the use of CePT infrastructure financed by the European Union – the European Regional Development Fund within the Operational Programme "Innovative economy" for 2007–2013 (POIG.02.01.00-14/024/08-00).

Notes and references
Supplementary Information (ESI) contains detailed data for the main product and reference data for \(M(BH_xNH_yBH_zNH_zBH_z)\) salts.

1. T. Richardson, S. de Gala, R. H. Crabtree and P. E. M. Siegbahn, J Am Chem Soc, 1995, 117, 12875–12876.

2. W. T. Klooster, T. F. Koetzle, P. E. M. Siegbahn, T. B. Richardson and R. H. Crabtree, J Am Chem Soc, 1999, 121, 6337–6343.

3. E. Magos-Palasyuk, T. Palasyuk, P. Zaleski-Ejgierd and K. Fijalkowski, CrystEngComm, 2014, 16, 10367–10370.

4. S. Filipov, J. B. Grinderslev, M. S. Andersson, J. Armstrong, M. Karlsson, T. R. Jensen, J. Klarbring, S. I. Simak and U. Häussermann, The Journal of Physical Chemistry C, 2019, 123, 28631–28639.

5. U. B. Demirci, Energies (Basel), 2020, 13, 3071.

6. F. Baitalow, J. Baumann, G. Wolf, K. Jaenicke and G. Palm, Thermochimica Acta, 2002, 391, 159–168.

7. A. Al-Kukhun, H. T. Hwang and A. Varma, International Journal of Hydrogen Energy, 2013, 38, 169–179.

8. DOE Technical Targets for Onboard Hydrogen Storage for Light-Duty Vehicles.

9. Y. S. Chua, P. Chen, G. Wu and Z. Xiong, Chemical Communications, 2011, 47, 5116.

10. R. Owarzany, P. Leszczyński, K. Fijalkowski and W. Grochala, Crystals (Basel), 2016, 6, 88.

11. H. V. K. Diyabalanage, T. Nakagawa, R. P. Shrestha, T. A. Semelsberger, B. L. Davis, B. L. Scott, A. K. Burrell, W. I. F. David, K. R. Ryan, M. O. Jones and P. P. Edwards, J Am Chem Soc, 2010, 132, 11836–11837.

12. I. v. Kazakov, A. v. Butlak, P. A. Shelyganov, V. v. Suslono and A. Y. Timoshkin, Polyhedron, 2017, 127, 186–190.

13. R. Owarzany, T. Jaroń, P. J. Leszczyński, K. J. Fijalkowski and W. Grochala, Dalton Transactions, 2017, 46, 16315–16320.

14. J. Luo, X. Kang and P. Wang, Energy and Environmental Science, 2013, 6, 1018–1025.

15. N. A. Shcherbina, I. v. Kazakov and A. Y. Timoshkin, Russian Journal of General Chemistry, 2017, 87, 2875–2877.

16. M. F. Hawthorne, S. S. Jalisañi, A. v. Safronov, H. B. Lee and J. Wu, Chemical Hydrogen Storage Using Polyhedral Borane Anions and Aluminum-Ammonia-Borane Complexes, 2010.

17. G. Xia, Y. Tan, X. Chen, Z. Guo, H. Liu and X. Yu, J Mater. Chem. A, 2013, 1, 1810–1820.

18. N. Biliškov, A. Borschgulte, K. Užarević, I. Halasz, S. Lukin, S. Milošević, I. Milanovic and I. G. Novaković, Chemistry – A European Journal, 2017, 23, 16274–16282.

19. W. C. Ewing, P. J. Carroll and L. G. Sneddon, Inorganic Chemistry, 2013, 52, 10690–10697.

20. W. C. Ewing, A. Marchione, D. W. Himmelberger, P. J. Carroll and L. G. Sneddon, J Am Chem Soc, 2011, 133, 17093–17099.

21. K. J. Fijalkowski, T. Jaroń, P. J. Leszczyński, Ł. Dobrzycki, M. K. Cyrański and W. Grochala, Inorganic Chemistry, 2016, 55, 37–45.

22. R. Owarzany, K. J. Fijalkowski, T. Jaroń, P. J. Leszczyński, T. Kukhun, H. T. Hwang and A. Varma, Inorganic Chemistry, 2016, 80, 1–3.

23. A. Starobrat, M. J. Tyszkiewicz, W. Wegner, D. Pancerz, P. A. Orlowski, P. J. Leszczyński, K. J. Fijalkowski, T. Jaroń and W. Grochala, Dalton Transactions, 2015, 44, 19469–19477.

24. T. Jaroń, W. Wegner, K. J. Fijalkowski, P. J. Leszczyński and W. Grochala, Chemistry - A European Journal, 2015, 21, 5689–5692.

25. T. Jaroń, P. A. Orlowski, W. Wegner, K. J. Fijalkowski, P. J. Leszczyński and W. Grochala, Angewandte Chemie - International Edition, 2015, 54, 1236–1239.

26. R. W. Parry, D. R. Schultz and P. R. Girardot, J Am Chem Soc, 1988, 110, 734–735.

27. R. S. Krishnan, Proceedings of the Indian Academy of Sciences - Section A, 1947, 47, 432.

28. A. Karkamkar, S. M. Kathmann, G. K. Schenter, D. J. Heldebrant, N. Hess, M. Gutowski and T. Autrey, Chemistry of Materials, 2009, 21, 4356–4358.

29. A. S. Davydov, Theory of Molecular Excitons, Springer, 1971.

30. W. E. Wallace, in NIST Standard Reference Database Number 69, eds. P. Linstron and W. Mallard, National Institute of Standards and Technology, 2018.

31. H. Wu, W. Zhou and T. Yildirim, J Am Chem Soc, 2008, 130, 14834–14839.

32. A. Gutowska, L. Li, Y. Shin, C. M. Wang, X. S. Li, J. C. Linehan, R. S. Smith, B. D. Kay, B. Schmid, W. Shaw, M. Gutowski and T. Autrey, Angewandte Chemie International Edition, 2005, 44, 3578–3582.

33. M. A. Neumann, Journal of Applied Crystallography, 2003, 36, 356–365.

34. V. Favre-Nicolin and R. Černý, Journal of Applied Crystallography, 2002, 35, 734–743.

35. V. Petiček, M. Dušek and L. Palatinus, Zeitschrift für Kristallographie - Crystaline Materials, 2014, 229, 345–352.

36. Agilent, 2014.

37. G. M. Sheldrick, Acta Crystallographica Section A Foundations and Advances, 2015, 71, 3–8.
41  C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *Journal of Applied Crystallography*, 2011, 44, 1281–1284.

42  D. Kratzert, J. J. Holstein and I. Krossing, *Journal of Applied Crystallography*, 2015, 48, 933–938.

43  S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. J. Probert, K. Refson and M. C. Payne, *Zeitschrift fur Kristallographie*, 2005, 220, 567–570.

44  A. Tkatchenko and M. Scheffler, *Physical Review Letters*, 2009, 102, 073005.

45  K. Momma and F. Izumi, *Journal of Applied Crystallography*, 2011, 44, 1272–1276.
“Towards hydrogen-rich ionic \((\text{NH}_4)\text{(BH}_3\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_3)\) and related molecular \(\text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_3\)”

R. Owarzany, T. Jaroń, K. Kazimierczuk, P. J. Malinowski, W. Grochala, K. J. Fijalkowski

Contents:

1. Records of reports on novel amidoborane and \(\text{M(B}_3\text{N}_2)\) salts and related compounds:

2. Synthesis of \(\text{M(B}_3\text{N}_2)\) salts of the products obtained:
   \((\text{NH}_4)\text{(B}_3\text{N}_2)\cdot3(\text{B}_3\text{N}_3)\) Li(\(\text{B}_3\text{N}_2\)) Na(\(\text{B}_3\text{N}_2\)) K(\(\text{B}_3\text{N}_2\)) Rb(\(\text{B}_3\text{N}_2\)) Cs(\(\text{B}_3\text{N}_2\)) \(\text{NH}_3\text{BH}_3\)

3. Table of \(^{11}\text{B}\) NMR @ THF-\(d_8\) chemical shifts of \(\text{M(B}_3\text{N}_2)\) salts and ammonia borane:
   \((\text{NH}_4)\text{(B}_3\text{N}_2)\cdot3(\text{B}_3\text{N}_3)\) Li(\(\text{B}_3\text{N}_2\)) Na(\(\text{B}_3\text{N}_2\)) K(\(\text{B}_3\text{N}_2\)) Rb(\(\text{B}_3\text{N}_2\)) Cs(\(\text{B}_3\text{N}_2\)) \(\text{NH}_3\text{BH}_3\) VBH(B(\(\text{B}_3\text{N}_2)\))

4. Table of bands appearing in the FTIR spectra of \(\text{M(B}_3\text{N}_2)\) salts and ammonia borane:
   \((\text{NH}_4)\text{(B}_3\text{N}_2)\cdot3(\text{B}_3\text{N}_3)\) Li(\(\text{B}_3\text{N}_2\)) Na(\(\text{B}_3\text{N}_2\)) K(\(\text{B}_3\text{N}_2\)) Rb(\(\text{B}_3\text{N}_2\)) Cs(\(\text{B}_3\text{N}_2\)) \(\text{NH}_3\text{BH}_3\)

5. Table of bands appearing in the Raman spectra of \(\text{M(B}_3\text{N}_2)\) salts and ammonia borane:
   \((\text{NH}_4)\text{(B}_3\text{N}_2)\cdot3(\text{B}_3\text{N}_3)\) Li(\(\text{B}_3\text{N}_2\)) Na(\(\text{B}_3\text{N}_2\)) K(\(\text{B}_3\text{N}_2\)) Rb(\(\text{B}_3\text{N}_2\)) Cs(\(\text{B}_3\text{N}_2\)) \(\text{NH}_3\text{BH}_3\)

6. Comparison FTIR and Raman spectra of \(\text{M(B}_3\text{N}_2)\) salts:
   \((\text{NH}_4)\text{(B}_3\text{N}_2)\cdot3(\text{B}_3\text{N}_3)\) Li(\(\text{B}_3\text{N}_2\)) Na(\(\text{B}_3\text{N}_2\)) K(\(\text{B}_3\text{N}_2\)) Rb(\(\text{B}_3\text{N}_2\)) Cs(\(\text{B}_3\text{N}_2\))

7. Thermal decomposition (TGA curves) of \(\text{M(B}_3\text{N}_2)\) salts:
   \((\text{NH}_4)\text{(B}_3\text{N}_2)\cdot3(\text{B}_3\text{N}_3)\) Li(\(\text{B}_3\text{N}_2\)) Na(\(\text{B}_3\text{N}_2\)) K(\(\text{B}_3\text{N}_2\)) Rb(\(\text{B}_3\text{N}_2\)) Cs(\(\text{B}_3\text{N}_2\))

8. FTIR spectra of the products of thermal decomposition of \(\text{M(B}_3\text{N}_2)\) salts:
   \((\text{NH}_4)\text{(B}_3\text{N}_2)\cdot3(\text{B}_3\text{N}_3)\) Li(\(\text{B}_3\text{N}_2\)) Na(\(\text{B}_3\text{N}_2\)) K(\(\text{B}_3\text{N}_2\)) Rb(\(\text{B}_3\text{N}_2\)) Cs(\(\text{B}_3\text{N}_2\))

9. Experimental crystal structure and Rietveld fit for \((\text{NH}_4)\text{(B}_3\text{N}_2)\cdot3(\text{B}_3\text{N}_3)\):
   \((\text{NH}_4)\text{(B}_3\text{N}_2)\cdot3(\text{B}_3\text{N}_3)\)

10. Table with the closest H···H distances in the crystal structure of \((\text{NH}_4)\text{(B}_3\text{N}_2)\cdot3(\text{B}_3\text{N}_3)\):
    \((\text{NH}_4)\text{(B}_3\text{N}_2)\cdot3(\text{B}_3\text{N}_3)\)

11. Experimental and modelled NMR spectra for various possible compositions of the main product:
    \((\text{NH}_4)\text{(B}_3\text{N}_2)\cdot3(\text{B}_3\text{N}_3)\) \((\text{NH}_4)\text{(B}_3\text{N}_2)\) \((\text{B}_3\text{N}_3)\)

12. Results of DFT optimisation of modelled crystal structures:
    \((\text{NH}_4)\text{(B}_3\text{N}_2)\cdot3(\text{B}_3\text{N}_3)\) \((\text{NH}_4)\text{(B}_3\text{N}_2)\) \((\text{B}_3\text{N}_3)\)

13. Crystal structure (VBH)[\text{B(C}_6\text{H}_5)_4]\n    (VBH)[\text{B(C}_6\text{H}_5)_4]
1. Records of reporting synthesis of novel amidoborane and M(B3N2) salts and related compounds:

Fig. S1.1. Hydrogen content of monometallic amidoboranes (black), bimetallic amidoboranes (grey), M(B3N2) salts (magenta) and as a function of reporting date. Hydrogen content of NH3BH3 (19.6%), polymeric NH3BH3 (14.0%) and DOE ultimate target (6.5%) given as a reference. Reports and theses marked with hollow circles.

References:
01 NaAB (9.5%) – H. I. Schlesinger, A.B. Burg, J. Am. Chem. Soc. 60 (1938) 290–299.
02 α-LiAB (13.7%), NaAB (9.5%) – P. M. Niedenzu, Ph.D. Thesis, Ohio State University, 1990.
03 NaAB (9.54%) – T. Salupo, Ph.D. Thesis, Ohio State University, 1993.
04 α-LiAB (13.7%), NaAB (9.5%), KAB (7.3%), Mg(AB)2 (12.0%), Zn(AB)2 (8.1%) – A. L. DeGraffenreid, Ph.D. Thesis, Ohio State University, 1995.
05 α-LiAB (13.7%) – A. G. Myers, et al., Tetrahedron Lett. 37 (1996) 3623–3626.
06 α-LiAB (13.70%), NaAB (9.54%) – Z. Xiong, et al., Nature Mater. 7 (2008) 138–141.
07 Ca(AB)2 (10.10%) – J. Spielmann, et al., Angew. Chem. Int. Ed. 47 (2008) 6290–6295.
08 Sr(AB)2 (6.84%) – Q. Zhang, et al., J. Phys. Chem. C 114 (2010) 1709–1714.
09 β-LiAB (13.70%) – C. Wu, et al., Inorg. Chem. 49 (2010) 4319–4323.
10 Y(AB)2 (8.47%) – R. V. Genova, et al., J. Alloys Compd. 499 (2010) 144–148.
11 Al(AB)2 (12.97%) – M. F. Hawthorne, et al., Final Report, University of Missouri 2010.
12 KAB (7.31%) – H. V. K. Diyabalanage, et al., J. Am. Chem. Soc. 132 (2010) 11836–11837.
13 Mg(AB)2 (12.00%) – J. Luo, J. et al., Energy Environ. Sci. 6 (2013) 1018–1025.
14 Zn(AB)2 (8.06%) – R. Owarzany, M.Sc. Thesis, University of Warsaw, 2013.
15 LT-RbAB (4.37%), LT-CSA (3.1%) – I. V. Kazakov, et al., Polyhedron 127 (2017) 186–190.
16 Ba(AB)2 (5.12%) – N. A. Shcherbina, et al., Russ. Gen. Chem. 87 (2017) 2875–2877.
17 HT-RbAB (4.37%), HT-CSA (3.1%) – R. Owarzany, et al., Dalton Trans. 46 (2017) 16315–16320.
18 NaMg(AB)2 (10.63%) – H. Wu, et al., Chem. Commun. 47 (2011) 4102–4104.
19 NaMg(AB)2 (11.05%) – X. Kang, et al., Dalton Trans. 40 (2011) 3799–3801.
20 LiNa(AB)2 (11.24%) – K. J. Fijałkowski, et al., Dalton Trans. 40 (2011) 4407–4413.
21 KMg(AB)2 (9.88%) – RbMg(AB)2 (7.58%) – X. Kang, et al., Int. J. Hydrog. Energy 37 (2012) 4259–4266.
22 K,Mg(AB)2 (9.08%) – Y. S. Chua, et al., Chem. Mater. 24 (2012) 3574–3581.
23 LiAl(AB)2 (11.15%) – C. Wu, et al., Mater. Chem. A 1 (2013) 1810–1820.
24 NaAl(AB)2 (11.9%) – I. Dovydkul et al., Chem. Eur. J. 21 (2015) 14562–14570.
25 Li3Mg(AB)2 (12.79%) – N. Bilikov et al., Chem. Eur. J. 23 (2017) 16274–16282.
26 KAl(AB)2 (10.87%) – K. T. Möller, et al., Int. J. Hydrog. Energy 43 (2018) 311–321.
27 Li3Ca(AB)2 (11.63%), Na3Ca(AB)2 (9.81%) – I. Milanovic, et al., ACS Sustainable Chem. Eng. 9 (2021) 2089–2099.
28 Li(B3N2)2 (15.22%), Na(B3N2)2 (12.66%) – I. C. Evans, Ph.D. Thesis, University of Birmingham, 2011.
29 Li(B3N2)2 (15.22%) – K. R. Ryan, Ph.D. Thesis, University of Oxford, 2011.
30 α-VB(B3N2)2 (3.15%) – W. C. Ewing, et al., J. Am. Chem. Soc. 133 (2011) 17093–17099.
31 Na(B3N2)2 (12.66%), (NH4)2B3N2/3(B3N3) (16.4%) – W. C. Ewing, et al., Inorg. Chem. 52 (2013) 10690–10697.
32 Li(B3N2)2 (15.22%), Na(B3N2)2 (12.66%) – K. J. Fijałkowski, et al., Phys. Chem. Chem. Phys. 16 (2014) 23340–23346.
33 K(B3N2)2 (10.83%), Rb(B3N2)2 (7.65%), Cs(B3N2)2 (5.89%), β-VB(B3N2)2 (3.15%) – R. Owarzany, et al., Inorg. Chem. 55 (2016) 37.
34 (Bu,N)2(B3N2)2 (3.80%), (Et,N)2(B3N2)2 (6.00%), (C(Ni,H)4)2(B3N2)2 (13.70%), (C(Ni,H,CH)4)(B3N2)2 (11.7%) – X. M. Chen, Chem Asian J. 16 (2021) 1–7.
35 (NH4)2(B3N2)2/3(B3N3) (16.4%) – this study.
2. Synthesis of alkali metal M(B3N2) salts:
All operations were performed under inert Ar atmosphere inside gloveboxes, MBRAUN Labmaster DP or Vigor SG1200 (O₂, H₂O < 1.0 ppm). Commercially available reagents and solvents were used: NH₃BH₃ (98%, JSC Aviabor), NH₄B(C₆H₅)₄ (99%, Sigma-Aldrich (later denoted as SA), C₄H₈O (99%, SA), CH₂Cl₂ (99%, SA).

**Metathetic synthesis** was performed using (C₁₈H₃₉N₄P(HBH₃NH₂BH₂NH₂BH₃) and NH₄[B(C₆H₅)₄] in anhydrous THF at room temperature under argon atmosphere:

(C₁₈H₃₉N₄P)(BH₃NH₂BH₂NH₂BH₃) + NH₄[B(C₆H₅)₄] → (NH₄)(BH₃NH₂BH₂NH₂BH₃) + (C₁₈H₃₉N₄P)(B(C₆H₅)₄)

A follow-up process of dehydrogenation of NH₄(BH₃NH₂BH₂NH₂BH₃) occurs leading to neutral linear molecule NH₃BH₂NH₂BH₂NH₂BH₃:

(NH₄)(BH₃NH₂BH₂NH₂BH₃) → NH₃BH₂NH₂BH₂NH₂BH₃ + H₂↑

Obtained mixture of products was well soluble in THF. Side product (C₁₈H₃₉N₄P)(B(C₆H₅)₄] was precipitated by washing with anhydrous DCM.

The main product crystallises in P2₁/c unit cell with the lattice parameters of: a = 13.401(11) Å, b = 13.196(8) Å, c = 17.828(12) Å, β = 128.83(4)°, V = 2556(3) Å³ and Z = 16. The crystalline product contains two compounds: NH₄(BH₃NH₂BH₂NH₂BH₃) and NH₃BH₂NH₂BH₂NH₂BH₃ in molar ratio 1:3. In the manuscript, the product is denoted as “main product” or “(NH₄)(B3N2)-3(B3N3)

The synthesis of (C₁₈H₃₉N₄P)(BH₃NH₂BH₂NH₂BH₃) was performed according to the route described in our earlier paper (R. Owarzany, et al., Inorg. Chem. 55 (2016) 37/) in a direct reaction of Verkade’s Base with 3 equivalents of ammonia borane in toluene at room temperature:

C₁₈H₃₉N₄P + 3NH₃BH₃ → (C₁₈H₃₉N₄P)(BH₃NH₂BH₂NH₂BH₃) + H₂↑ + NH₃↑

**Different route of metathetic synthesis** between Na(BH₃NH₂BH₂NH₂BH₃) and NH₄Cl in glyme at room temperature for 24 hours was reported earlier (W. C. Ewing et al. Inorg. Chem. 52 (2013) 10690.), however, the authors were aiming NH₃BH₂NH₂BH₂NH₂BH₃ according to the following equation:

Na(BH₃NH₂BH₂NH₂BH₃) + NH₄Cl → NH₃BH₂NH₂BH₂NH₂BH₃ + H₂↑ + NaCl↓

Judging from the comparison of NMR data presented by Ewing et al. to our own data we strongly believe that this process leads to (NH₄)(B3N2)-3(B3N3) according to the following reaction equations:

Na(BH₃NH₂BH₂NH₂BH₃) + NH₄Cl → (NH₄)(BH₃NH₂BH₂NH₂BH₃) + NaCl↓

(NH₄)(BH₃NH₂BH₂NH₂BH₃) → NH₃BH₂NH₂BH₂NH₂BH₃ + H₂↑
3. Table of $^{11}$B NMR @ THF-d$_8$ chemical shifts of M(B3N2) salts and ammonia borane:

Table S3. Chemical shifts, positions of multiplets, excitation frequencies and $J$-coupling values observed in $^{11}$B NMR spectra in deuterated THF solution (δ [ppm]) of (NH$_4$)(B3N2)-3(B3N3) at room temperature. Results for ammonia borane [AB], precursor [β-VBH(B3N2)] and alkali metal M(B3N2) salts: [Li(B3N2), Na(B3N2), K(B3N2), Rb(B3N2), Cs(B3N2)] at RT are shown for comparison.

|                  | NH$_3$BH$_3$ | VBH(B3N2) | M(B3N2) salts | (NH$_4$)(B3N2)·3(B3N3) |
|------------------|--------------|------------|----------------|-------------------------|
|                  |              |            | Li(B3N2) | Na(B3N2) | K(B3N2) | Rb(B3N2) | Cs(B3N2) |            |            |
| BH$_2$ triplet   | –            | –6.590     | –6.743   | –7.155   | –7.499   | –7.410   | –7.792   | –9.95     | –11.78    |
|                  | –            | –8.184     | –8.360   | –8.582   | –8.568   | –8.424   | –8.384   | –10.40    | –12.26    |
|                  | –            | –9.716     | –9.966   | –10.227  | –9.591   | –9.491   | –9.042   | –10.85    | –12.70    |
| position        | –            | –8.163     | –8.356   | –8.654   | –8.553   | –8.442   | –8.406   | –10.4      | –12.3     |
| $^1J$ (B,H)      | –            | 100 Hz     | 103 Hz   | 99 Hz    | 101 Hz   | 100 Hz   | 101 Hz   | 101 Hz    | 102 Hz    |
| freq.            | 96.32 MHz    | 64.16 MHz  | 96.32 MHz| 96.32 MHz| 96.32 MHz| 96.32 MHz| 160.48 MHz| 224.62 MHz|

|                  | NH$_3$BH$_3$ | VBH(B3N2) | M(B3N2) salts | (NH$_4$)(B3N2)·3(B3N3) |
|------------------|--------------|------------|----------------|-------------------------|
|                  |              |            | Li(B3N2) | Na(B3N2) | K(B3N2) | Rb(B3N2) | Cs(B3N2) |            |            |
| BH$_3$ quartet   | –18.184      | –19.462    | –20.465   | –20.264   | –20.613   | –20.294   | –20.279   | –21.60     |            |
|                  | –19.632      | –20.933    | –21.836   | –21.693   | –21.556   | –21.226   | –20.902   | –22.01     |            |
|                  | –21.144      | –22.342    | –23.314   | –23.202   | –22.499   | –22.168   | –21.479   | –22.42     |            |
|                  | –22.610      | –23.752    | –24.634   | –24.582   | –23.382   | –23.105   | –22.025   | –22.83     |            |
| position        | –20.393      | –21.622    | –22.562   | –22.435   | –22.013   | –21.698   | –21.171   | –22.21     |            |
| $^1J$ (B,H)      | 95 Hz        | 91 Hz      | 90 Hz     | 91 Hz     | 89 Hz     | 90 Hz     | 94 Hz     | 91 Hz      |            |
| freq.            | 96.32 MHz    | 64.16 MHz  | 96.32 MHz | 96.32 MHz | 96.32 MHz | 96.32 MHz | 160.48 MHz| 224.62 MHz |            |
4. Table of bands appearing in the FTIR spectra of M(B3N2) salts and ammonia borane:

**Table S4.** Absorption bands detected in IR spectra (wavenumber [cm\(^{-1}\)]) of NH\(_4\)B(B3N2)-3(B3N3) at room temperature. Results for ammonia borane [AB] and alkali metal M(B3N2) salts: [Li(B3N2), Na(B3N2), K(B3N2), Rb(B3N2), Cs(B3N2)] at RT. Absorption bands of ammonia borane at RT are shown for comparison. (ν = stretching, δ = deformation: bending and torsional modes).

| Band | NH\(_4\)BH\(_3\) | M(B3N2) salts | (NH\(_4\))(B3N2)·3(B3N3) |
|------|-----------------|---------------|-----------------------------|
| v(NH) | 3311 vs | 3310 s | 3308 m | 3306 vs |
| | 3302 vs | 3295 m | 3287 m | 3288 vs |
| | 3305 vs | 3313 w | 3268 sh | 3268 sh |
| | 3273 m | 3261 w | 3259 m | 3259 m |
| | 3256 m | 3252 w | 3239 m | 3239 m |
| | 3261 m | 3235 m | 3223 sh | 3223 sh |
| v(BH) | 2347 vs | 2350 vs | 2390 sh | 2439 sh |
| | 2322 s | 2364 s | 2394 vs | 2407 s |
| | 2315 s | 2352 m | 2363 s | 2357 s |
| | 2304 s | 2294 vs | 2302 sh | 2317 vs |
| | 2282 vs | 2279 s | 2291 vs | 2302 sh |
| | 2245 s | 2259 s | 2248 s | 2260 m |
| | 2118 m | 2210 sh | 2204 sh | 2204 sh |
| δ(NH) | 1611 m | 1571 vs | 1579 vw | 1604 sh |
| | 1576 w | 1562 sh | 1564 w | 1572 w |
| | 1556 m | 1557 m | 1557 vw | 1564 m |
| | 1568 m | 1557 m | 1556 m | 1556 m |
| | 1557 m | 1557 m | 1557 m | 1557 m |
| δ(BH) | 1283 m | 1248 m | 1244 m | 1262 s |
| | 1248 m | 1244 m | 1244 m | 1262 s |
| | 1244 m | 1244 m | 1244 m | 1262 s |
| | 1262 s | 1262 s | 1262 s | 1262 s |
| | 1226 s | 1202 s | 1202 s | 1244 s |
| | 1199 vs | 1199 vs | 1199 vs | 1203 vs |
| | 1175 m | 1175 m | 1175 m | 1175 m |
| | 1148 s | 1148 s | 1148 s | 1179 s |
| | 1135 m | 1135 m | 1135 m | 1168 sh |
| | 1129 vw | 1129 vw | 1129 vw | 1134 m |
| | 1074 m | 1074 m | 1074 m | 1118 w |
| | 1073 w | 1073 w | 1073 w | 1078 w |
| | 1044 m | 1044 m | 1044 m | 1056 w |
| | 1055 m | 1055 m | 1055 m | 1056 w |
| | 1056 m | 1056 m | 1056 m | 1056 w |
| v(BN) and other | 916 w | 893 vw | 901 vw | 861 w |
| | 874 vw | 875 w | 873 vw | 804 vw |
| | 799 vw | 804 vw | 804 vw | 791 w |
| | 785 vw | 811 vw | 811 vw | 791 w |
| | 781 vw | 727 vw | 727 vw | 723 vw |
5. Table of bands appearing in the RAMAN spectra of M(B3N2) salts and ammonia borane:

Table S5. Absorption bands detected in Raman spectra (wavenumber [cm\(^{-1}\)]) of NH\(_4\)(B3N2)-3(B3N3) at room temperature. Results for ammonia borane [AB] and alkali metal M(B3N2) salts: [Li(B3N2), Na(B3N2), K(B3N2), Rb(B3N2), Cs(B3N2)] at RT. Absorption bands of ammonia borane at RT are shown for comparison. (\(\nu\) = stretching, \(\delta\) = deformation: bending and torsional modes).

| Band  | NH\(_4\)BH\(_3\) | M(B3N2) salts | (NH\(_4\))(B3N2) -3(B3N3) |
|-------|----------------|----------------|--------------------------|
| \(\nu(\text{NH})\) |               |                |                          |
| 3314 m | 3314 m | 3304 sh | 3307 sh | 3307 m | 3288 m |
| 3253 vs | 3272 s | 3265 vs | 3263 vs | 3256 m | 3258 m | 3260 vs | 3241 vs |
| 3177 m | 3250 s | 3243 s | 3214 sh | 3245 m | 3232 m | 3261 s |
| \(\nu(\text{BH})\) |               |                |                          |
| 2378 vs | 2418 vw | 2403 w | 2379 m | 2379 m | 2475 sh | 2442 w | 2394 m |
| 2284 vs | 2282 m | 2275 s | 2274 s | 2243 vs | 2250 vs | 2261 s |
| \(\delta(\text{NH})\) |               |                |                          |
| 1598 m | 1597 m | 1539 w | 1569 vw | 1585 vw | 1565 w | 1566 w | 1578 s |
| 1583 m | 1519 vw | 1550 w | 1534 w |
| \(\delta(\text{BH})\) |               |                |                          |
| 1206 m | 1212 w | 1227 w | 1207 w | 1206 sh | 1201 w |
| 1190 sh | 1193 w | 1188 m | 1183 m | 1184 w |
| 1168 m | 1162 w | 1155 w | 1153 m | 1173 w | 1155 w |
| 1069 vw | 1132 w | 1122 vw | 1056 vw | 1036 vw |
| 1010 w | 1019 vw | 1004 vw | 993 w |
| \(\nu(\text{BN})\) and other |               |                |                          |
| 895 vw | 892 vw | 895 w | 915 w | 899 vw |
| 873 w | 871 w | 862 w | 876 w | 851 w |
| 806 w | 856 vw | 847 w | 851 w | 857 w |
| 785 m | 785 m | 749 w | 779 w | 783 vw |
| 729 w | 778 w | 721 w | 724 w | 715 vw |
| 614 vw | 614 vw | 653 w | 643 vw | 667 m |
| 604 s | 639 vw | 618 w | 604 s |
6. Comparison of FTIR and Raman spectra of alkali metal M(B3N2) salts:

FTIR and Raman spectra of NH₄(B3N2)/3(B3N3) and alkali metal M(B3N2) salts: [Li(B3N2), Na(B3N2), K(B3N2), Rb(B3N2), Cs(B3N2)]. NH and BH stretching and NH bending regions highlighted and magnified in separate figures.

**Fig. S6.1.** Comparison of FTIR spectra of M(B3N2) salts.

**Fig. S6.2.** Comparison of Raman spectra of M(B3N2) salts.

**Fig. S6.3.** Comparison of NH and BH stretching and NH bending regions of FTIR spectra of M(B3N2) salts.

**Fig. S6.4.** Comparison of NH and BH stretching and NH bending regions of Raman spectra of M(B3N2) salts.
7. Thermal decomposition (TGA curves) of M(B3N2) salts:
The thermal decomposition of NH₄(B3N2)/3(B3N3) and alkali metal M(B3N2) salts occurs at the temperature range of 120–180°C.

**Fig.S7.1.** TGA/DSC experiments of (NH₄)(B3N2)-3(B3N3) with scanning rates (1 K/min -black, 5 K/min -grey).

**Fig.S7.2.** TGA/DSC experiments of Li(B3N2) sample with different scanning rates (1 K/min -black, 10 K/min -grey).

**Fig.S7.3.** TGA/DSC experiments of Na(B3N2) sample with different scanning rates (1 K/min -black, 10 K/min -grey).

**Fig.S7.4.** TGA/DSC experiments of K(B3N2) sample with different scanning rates (1 K/min -black, 10 K/min -grey).

**Fig.S7.5.** TGA/DSC experiments of Rb(B3N2) sample with different scanning rates (1 K/min -black, 10 K/min -grey).

**Fig.S7.6.** TGA/DSC experiments of Cs(B3N2) sample with different scanning rates (1 K/min -black, 10 K/min -grey).
8. FTIR spectra of the products of thermal decomposition of M(B3N2) salts:
The thermal decomposition of (NH4)(B3N2) leads to formation of boron nitride while decomposition of alkali metal M(B3N2) salts leads to formation of respective borohydrides.

Fig. S8.1. FTIR spectra of the product of thermal decomposition of (NH4)(B3N2)-3(B3N3) sample.

Fig. S8.2. FTIR spectra of the product of thermal decomposition of Li(B3N2) sample.

Fig. S8.3. FTIR spectra of the product of thermal decomposition of Na(B3N2) sample.

Fig. S8.4. FTIR spectra of the product of thermal decomposition of K(B3N2) sample.

Fig. S8.5. FTIR spectra of the product of thermal decomposition of Rb(B3N2) sample.

Fig. S8.6. FTIR spectra of the product of thermal decomposition of Cs(B3N2) sample.
9. Experimental crystal structure and Rietveld fit for (NH$_4$)(B$_3$N$_2$)·3(B$_3$N$_3$):

Fig. S9.1. Visualisation of the unit cell and formula unit of the main product: (NH$_4$)(B$_3$N$_2$)·3(B$_3$N$_3$)

Fig. S9.2. Distribution of N-H and B-H distances in systems comprising both [NH$_x$] and [BH$_x$] groups found in structures in CSD database. Value of N-H and B-H distances in (NH$_4$)(B$_3$N$_2$)·3(B$_3$N$_3$) marked with a dot.

Fig. S9.3. Rietveld analysis of (NH$_4$)(B$_3$N$_2$)/3(B$_3$N$_3$) powder pattern. CoK$_{α1,2}$, $\lambda = 1.78901$ Å.
10. Table with the closest H···H distances in the crystal structure of (NH₄)(B₃N₂)·3(B₃N₃):

Table S10. List of the closest H···H distances in experimental crystal structure of (NH₄)(B₃N₂)·3(B₃N₃). Listed only strong dihydrogen bonds, < 2 Å.

| H atom1 | H atom2 | Length [Å] | Length-VdW [Å] | Neighboring groups |
|---------|---------|------------|-----------------|-------------------|
| H8      | H39     | 1.927      | -0.473          | B–H···H–N         |
| H12     | H29     | 1.928      | -0.472          | B–H···H–N         |
| H6      | H52     | 1.931      | -0.469          | B–H···H–N         |
| H12     | H53     | 1.935      | -0.465          | B–H···H–N         |
| H15     | H34     | 1.948      | -0.452          | B–H···H–N         |
| H54     | H42     | 1.949      | -0.451          | B–H···H–N         |
| H1      | H51     | 1.951      | -0.449          | B–H···H–N         |
| H50     | H64     | 1.971      | -0.429          | N–H···H–N         |
| H19     | H31     | 1.984      | -0.416          | B–H···H–N         |
| H52     | H64     | 1.987      | -0.413          | N–H···H–N         |
| H17     | H47     | 1.993      | -0.407          | B–H···H–N         |
11. Experimental and modelled NMR spectra for various possible compositions of the main product:
NMR spectra were simulated for various discussed possible compositions of the main product to ease
visual examination of the experimental spectra obtained by us and reported earlier by Ewing et al.,
*Inorganic Chemistry* 52 (2013) 10690.

**Fig. S11.1.** Comparison of the experimental $^{11}$B NMR spectra obtained here and reported by Ewing et al. (*Inorganic Chemistry* 52 (2013) 10690) with spectra simulated for various possible compositions of the main product: \((\text{NH}_4)(B3N2)\cdot 3(B3N3)\), \((\text{NH}_4)(B3N2)\) and \((B3N3)\).

**Fig. S11.2.** Comparison of the experimental $^{11}$B $\{^{1}H\}$ NMR spectra obtained here and reported by Ewing et al. (*Inorganic Chemistry* 52 (2013) 10690) with spectra simulated for various possible compositions of the main product: \((\text{NH}_4)(B3N2)\cdot 3(B3N3)\), \((\text{NH}_4)(B3N2)\) and \((B3N3)\).
12. Results of DFT optimisation of modelled crystal structures:

\[\text{NH}_4(\text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_3)\cdot 3(\text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_3\text{NH}_2\text{BH}_3)\] unit cell optimised

data_31_500eV\{fine+cell

|_audit_creation_date | 2022-03-22 |
|_audit_creation_method | 'Materials Studio' |
|_symmetry_space_group_name_H-M | 'P21/C' |
|_symmetry_Int_Tables_number | 14 |
|_symmetry_cell_setting | monoclinic |

| _symmetry_equiv_pos_as_xyz |
| x,y,z |
| -x,y+1/2,-z+1/2 |
| -x,-y,\text{z} |
| x,-y+1/2,z+1/2 |

| _cell_length_a | 13.2114 |
| _cell_length_b | 13.9512 |
| _cell_length_c | 19.0116 |
| _cell_angle_alpha | 90.0000 |
| _cell_angle_beta | 130.4617 |
| _cell_angle_gamma | 90.0000 |

|_atom_site_label |
|_atom_site_type_symbol |
|_atom_site_fract_x |
|_atom_site_fract_y |
|_atom_site_fract_z |
|_atom_site_U_iso_or_equiv |
|_atom_site_occupancy |

| B1 B | 0.70821 0.11494 0.70797 0.05000 Uiso 1.00 |
| N1 N | 0.76629 0.14302 0.80732 0.05000 Uiso 1.00 |
| B2 B | 0.77307 0.25603 0.82169 0.05000 Uiso 1.00 |
| N2 N | 0.88332 0.27855 0.92649 0.05000 Uiso 1.00 |
| B3 B | 0.90995 0.38672 0.95751 0.05000 Uiso 1.00 |
| H1 H | 0.60523 0.15758 0.65051 0.05000 Uiso 1.00 |
| H2 H | 0.79337 0.12973 0.70200 0.05000 Uiso 1.00 |
| H3 H | 0.71177 0.11450 0.82381 0.05000 Uiso 1.00 |
| H4 H | 0.86071 0.11477 0.85440 0.05000 Uiso 1.00 |
| H5 H | 0.80153 0.29445 0.77863 0.05000 Uiso 1.00 |
| H6 H | 0.66525 0.28348 0.79429 0.05000 Uiso 1.00 |
| H7 H | 0.97286 0.25206 0.94872 0.05000 Uiso 1.00 |
| H8 H | 0.86665 0.24060 0.96452 0.05000 Uiso 1.00 |
| H9 H | 0.7588 0.38896 1.04154 0.05000 Uiso 1.00 |
| H10 H | 0.80194 0.42592 0.91975 0.05000 Uiso 1.00 |
| H11 H | 0.9700 0.42553 0.93710 0.05000 Uiso 1.00 |
| H12 H | 0.41303 0.33205 0.60553 0.05000 Uiso 1.00 |
| N3 N | 0.27925 0.35690 0.50627 0.05000 Uiso 1.00 |
| B4 B | 0.15136 0.33856 0.49619 0.05000 Uiso 1.00 |
| N4 N | 0.15353 0.41316 0.55956 0.05000 Uiso 1.00 |
| B5 B | 0.06225 0.39383 0.58541 0.05000 Uiso 1.00 |
| H13 H | 0.42249 0.24605 0.61536 0.05000 Uiso 1.00 |
| H14 H | 0.42037 0.37241 0.66568 0.05000 Uiso 1.00 |
| H15 H | 0.27593 0.42579 0.48531 0.05000 Uiso 1.00 |
| H16 H | 0.27253 0.31420 0.45908 0.05000 Uiso 1.00 |
| H17 H | 0.15917 0.25731 0.52314 0.05000 Uiso 1.00 |
| H18 H | 0.05145 0.35051 0.41580 0.05000 Uiso 1.00 |
| H19 H | 0.13000 0.48023 0.52964 0.05000 Uiso 1.00 |
| H20 H | 0.25125 0.41791 0.61940 0.05000 Uiso 1.00 |
| H21 H | 0.25125 0.41791 0.61940 0.05000 Uiso 1.00 |
| Atom | Type | X      | Y      | Z      | Temperature | Uiso | Uiso Notes |
|------|------|--------|--------|--------|-------------|------|------------|
| H22  | H    | -0.05515 | 0.39939 | 0.51583 | 0.05000 | 1.00 |            |
| H23  | H    | 0.08380  | 0.45473 | 0.64012 | 0.05000 | 1.00 |            |
| H24  | H    | 0.08547  | 0.31319 | 0.61846 | 0.05000 | 1.00 |            |
| B7   | B    | 0.35945  | 0.56131 | 0.01225 | 0.05000 | 1.00 |            |
| N5   | N    | 0.39871  | 0.66288 | -0.00050 | 0.05000 | 1.00 |            |
| B8   | B    | 0.35089  | 0.76107 | 0.01297 | 0.05000 | 1.00 |            |
| N6   | N    | 0.43801  | 0.78284 | 0.11929 | 0.05000 | 1.00 |            |
| B9   | B    | 0.43903  | 0.89230 | 0.14365 | 0.05000 | 1.00 |            |
| H25  | H    | 0.40686  | 0.49856 | -0.00341 | 0.05000 | 1.00 |            |
| H26  | H    | 0.39674  | 0.31319 | 0.61846 | 0.05000 | 1.00 |            |
| H28  | H    | 0.50119  | 0.66593 | 0.04116 | 0.05000 | 1.00 |            |
| H29  | H    | 0.36881  | 0.82505 | -0.02191 | 0.05000 | 1.00 |            |
| H30  | H    | 0.36881  | 0.82505 | -0.02191 | 0.05000 | 1.00 |            |
| H31  | H    | 0.23334  | 0.75618 | -0.02405 | 0.05000 | 1.00 |            |
| H32  | H    | 0.35513  | 0.76316 | 0.15269 | 0.05000 | 1.00 |            |
| H33  | H    | 0.40908  | 0.74092 | 0.14813 | 0.05000 | 1.00 |            |
| H34  | H    | 0.50214  | 0.93738 | 0.12797 | 0.05000 | 1.00 |            |
| H35  | H    | 0.32535  | 0.92289 | 0.14813 | 0.05000 | 1.00 |            |
| H36  | H    | 0.49200  | 0.89920 | 0.22589 | 0.05000 | 1.00 |            |
| B10  | B    | 1.12914  | 0.99464 | 0.79230 | 0.05000 | 1.00 |            |
| N7   | N    | 1.08247  | 0.88703 | 0.78744 | 0.05000 | 1.00 |            |
| B11  | B    | 0.92947  | 0.86664 | 0.70636 | 0.05000 | 1.00 |            |
| N8   | N    | 0.88287  | 0.77045 | 0.72226 | 0.05000 | 1.00 |            |
| B12  | B    | 0.72463  | 0.75969 | 0.65604 | 0.05000 | 1.00 |            |
| H37  | H    | 1.08482  | 1.04747 | 0.81782 | 0.05000 | 1.00 |            |
| H38  | H    | 1.25109  | 0.98199 | 0.84578 | 0.05000 | 1.00 |            |
| H39  | H    | 1.08213  | 1.01873 | 0.71408 | 0.05000 | 1.00 |            |
| H40  | H    | 1.10997  | 0.87212 | 0.85076 | 0.05000 | 1.00 |            |
| H41  | H    | 1.13739  | 0.84084 | 0.78158 | 0.05000 | 1.00 |            |
| H42  | H    | 0.90914  | 0.85943 | 0.63407 | 0.05000 | 1.00 |            |
| H43  | H    | 0.86774  | 0.93227 | 0.70464 | 0.05000 | 1.00 |            |
| H44  | H    | 0.92197  | 0.71094 | 0.71553 | 0.05000 | 1.00 |            |
| H45  | H    | 0.91808  | 0.76911 | 0.78909 | 0.05000 | 1.00 |            |
| H46  | H    | 0.68750  | 0.80414 | 0.69155 | 0.05000 | 1.00 |            |
| H47  | H    | 0.67311  | 0.79488 | 0.58006 | 0.05000 | 1.00 |            |
| H48  | H    | 0.69326  | 0.67556 | 0.64739 | 0.05000 | 1.00 |            |
| N9   | N    | 0.53664  | 0.37064 | 0.61627 | 0.05000 | 1.00 |            |
| H50  | H    | 0.54045  | 0.44470 | 0.61701 | 0.05000 | 1.00 |            |
| H51  | H    | 0.54125  | 0.34734 | 0.56683 | 0.05000 | 1.00 |            |
| H52  | H    | 0.62319  | 0.34723 | 0.67920 | 0.05000 | 1.00 |            |
| N10  | N    | 0.20232  | 0.54959 | -0.06080 | 0.05000 | 1.00 |            |
| H53  | H    | 0.15399  | 0.57777 | -0.03889 | 0.05000 | 1.00 |            |
| H54  | H    | 0.17501  | 0.47816 | -0.07588 | 0.05000 | 1.00 |            |
| H55  | H    | 0.15962  | 0.57929 | -0.12419 | 0.05000 | 1.00 |            |
| N11  | N    | 0.67472  | 0.00314 | 0.69163 | 0.05000 | 1.00 |            |
| H57  | H    | 0.65387  | -0.01839 | 0.63157 | 0.05000 | 1.00 |            |
| H58  | H    | 0.75445  | -0.03858 | 0.74368 | 0.05000 | 1.00 |            |
| H59  | H    | 0.59194  | -0.01451 | 0.68348 | 0.05000 | 1.00 |            |
| N12  | N    | 0.23793  | 0.07365 | 0.68214 | 0.05000 | 1.00 |            |
| H61  | H    | 0.21085  | 0.01630 | 0.63715 | 0.05000 | 1.00 |            |
| H62  | H    | 0.19238  | 0.13480 | 0.64331 | 0.05000 | 1.00 |            |
| H63  | H    | 0.34093  | 0.08208 | 0.72959 | 0.05000 | 1.00 |            |
| H64  | H    | 0.20121  | 0.05757 | 0.71582 | 0.05000 | 1.00 |            |
\( \text{NH}_3(\text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_3\text{BH}_3) \) unit cell optimised

data 30 from 00 noH Hadd 500 eV fine + cell

audit creation date 2022-03-22
audit creation method Materials Studio
symmetry space group name H-M P21/C
symmetry Int Tables number 14
symmetry cell setting monoclinic

loop_
  symmetry equiv pos as xyz
  x, y, z
  -x, y+1/2, z+1/2
  -x, -y, z
  x, y+1/2, z+1/2
  cell length a 15.1296
  cell length b 14.0974
  cell length c 18.5157
  cell angle alpha 90.0000
  cell angle beta 134.1837
  cell angle gamma 90.0000

loop_
  atom site label
  atom site type symbol
  atom site frac x
  atom site frac y
  atom site frac z
  atom site U iso or equiv
  atom site adp type
  atom site occupancy

B1 B 0.66514 0.10694 0.69465 0.05000 Uiso 1.00
N1 N 0.71546 0.20346 0.75835 0.05000 Uiso 1.00
B2 B 0.85400 0.20822 0.86832 0.05000 Uiso 1.00
N2 N 0.91110 0.30099 0.95489 0.05000 Uiso 1.00
B3 B 1.01642 0.24767 1.06367 0.05000 Uiso 1.00
B4 B 0.58384 0.42106 0.65635 0.05000 Uiso 1.00
N3 N 0.48530 0.38527 0.65775 0.05000 Uiso 1.00
N4 N 0.30905 0.43511 0.64480 0.05000 Uiso 1.00
N5 N 0.29779 0.30927 0.65775 0.05000 Uiso 1.00
B5 B 0.43120 0.46721 0.67502 0.05000 Uiso 1.00
B6 B 0.53044 0.47321 0.65635 0.05000 Uiso 1.00
N6 N 0.30421 0.43511 0.64480 0.05000 Uiso 1.00
N7 N 0.25779 0.30927 0.65775 0.05000 Uiso 1.00
B7 B 0.43371 0.55157 0.67502 0.05000 Uiso 1.00
B8 B 0.30421 0.43511 0.64480 0.05000 Uiso 1.00
N8 N 0.25779 0.30927 0.65775 0.05000 Uiso 1.00
B9 B 0.43371 0.55157 0.67502 0.05000 Uiso 1.00
N9 N 0.30421 0.43511 0.64480 0.05000 Uiso 1.00
B10 B 0.19360 0.77848 0.05771 0.05000 Uiso 1.00
N10 N 0.29779 0.79874 0.14552 0.05000 Uiso 1.00
N11 N 0.40411 0.78172 0.53724 0.05000 Uiso 1.00
B11 B 0.67184 0.78858 0.24664 0.05000 Uiso 1.00
N12 N 0.89991 0.89287 0.23582 0.05000 Uiso 1.00
N13 N 0.40411 0.78172 0.53724 0.05000 Uiso 1.00
N14 N 0.16159 0.34399 0.59474 0.05000 Uiso 1.00
H25 H 0.57587 0.08165 0.67916 0.00000 Uiso 1.00
H26 H 0.74209 0.04326 0.74155 0.00000 Uiso 1.00
H27 H 0.63368 0.12074 0.61368 0.00000 Uiso 1.00
H28 H 0.65741 0.21604 0.76811 0.00000 Uiso 1.00
H29 H 0.69738 0.25979 0.71420 0.00000 Uiso 1.00
H30 H 0.92670 0.20886 0.85760 0.00000 Uiso 1.00
H31 H 0.87080 0.13194 0.90858 0.00000 Uiso 1.00
| H32 | H | 0.84498 | 0.34518 | 0.96014 | 0.00000 | Uiso | 1.00 |
| H33 | H | 0.96760 | 0.36208 | 0.95162 | 0.00000 | Uiso | 1.00 |
| H34 | H | 1.08626 | 0.28808 | 1.12530 | 0.00000 | Uiso | 1.00 |
| H35 | H | 1.05800 | 0.19576 | 1.05622 | 0.00000 | Uiso | 1.00 |
| H36 | H | 0.97446 | 0.21306 | 1.08218 | 0.00000 | Uiso | 1.00 |
| H37 | H | 0.54476 | 0.49423 | 0.60574 | 0.00000 | Uiso | 1.00 |
| H38 | H | 0.60038 | 0.36151 | 0.61857 | 0.00000 | Uiso | 1.00 |
| H39 | H | 0.67976 | 0.43811 | 0.66769 | 0.00000 | Uiso | 1.00 |
| H40 | H | 0.52471 | 0.33553 | 0.71369 | 0.00000 | Uiso | 1.00 |
| H41 | H | 0.41727 | 0.34701 | 0.59332 | 0.00000 | Uiso | 1.00 |
| H42 | H | 0.40227 | 0.53202 | 0.61842 | 0.00000 | Uiso | 1.00 |
| H43 | H | 0.51021 | 0.49321 | 0.76251 | 0.00000 | Uiso | 1.00 |
| H44 | H | 0.28544 | 0.48737 | -0.06386 | 0.00000 | Uiso | 1.00 |
| H45 | H | 0.32357 | 0.37640 | 0.68540 | 0.00000 | Uiso | 1.00 |
| H46 | H | 0.10247 | 0.39780 | 0.51231 | 0.00000 | Uiso | 1.00 |
| H47 | H | 0.21701 | 0.48714 | 0.48003 | 0.00000 | Uiso | 1.00 |
| H48 | H | 0.23580 | 0.69217 | 0.06386 | 0.00000 | Uiso | 1.00 |
| H49 | H | 0.28267 | 0.81830 | 0.07846 | 0.00000 | Uiso | 1.00 |
| H50 | H | 0.12202 | 0.80402 | 0.07375 | 0.00000 | Uiso | 1.00 |
| H51 | H | 0.24488 | 0.76892 | 0.06495 | 0.00000 | Uiso | 1.00 |
| H52 | H | 0.29626 | 0.80402 | 0.07375 | 0.00000 | Uiso | 1.00 |
| H53 | H | 0.43438 | 0.67496 | 0.13879 | 0.00000 | Uiso | 1.00 |
| H54 | H | 0.46301 | 0.78204 | 0.22402 | 0.00000 | Uiso | 1.00 |
| H55 | H | 0.51767 | 0.88032 | 0.14098 | 0.00000 | Uiso | 1.00 |
| H56 | H | 0.51530 | 0.78744 | 0.08665 | 0.00000 | Uiso | 1.00 |
| H57 | H | 0.73769 | 0.83551 | 0.24300 | 0.00000 | Uiso | 1.00 |
| H58 | H | 0.69524 | 0.70472 | 0.25101 | 0.00000 | Uiso | 1.00 |
| H59 | H | 0.69072 | 0.81080 | 0.32069 | 0.00000 | Uiso | 1.00 |
| H60 | H | 0.98211 | 1.02676 | 0.62065 | 0.00000 | Uiso | 1.00 |
| H61 | H | 1.15010 | 0.96615 | 0.72509 | 0.00000 | Uiso | 1.00 |
| H62 | H | 1.06616 | 1.01664 | 0.76417 | 0.00000 | Uiso | 1.00 |
| H63 | H | 1.03969 | 0.84687 | 0.74802 | 0.00000 | Uiso | 1.00 |
| H64 | H | 1.00510 | 0.83410 | 0.64268 | 0.00000 | Uiso | 1.00 |
| H65 | H | 0.79154 | 0.90640 | 0.53074 | 0.00000 | Uiso | 1.00 |
| H66 | H | 0.83251 | 0.93665 | 0.65811 | 0.00000 | Uiso | 1.00 |
| H67 | H | 0.83316 | 0.76230 | 0.68178 | 0.00000 | Uiso | 1.00 |
| H68 | H | 0.81562 | 0.73071 | 0.58623 | 0.00000 | Uiso | 1.00 |
| H69 | H | 0.61644 | 0.70373 | 0.54393 | 0.00000 | Uiso | 1.00 |
| H70 | H | 0.60103 | 0.79436 | 0.45185 | 0.00000 | Uiso | 1.00 |
| H71 | H | 0.61714 | 0.84255 | 0.56348 | 0.00000 | Uiso | 1.00 |
| H72 | H | 0.23237 | 1.01081 | 0.84819 | 0.00000 | Uiso | 1.00 |
| H73 | H | 0.37678 | 0.98260 | 0.95540 | 0.00000 | Uiso | 1.00 |
| H74 | H | 0.33389 | 1.09739 | 0.93189 | 0.00000 | Uiso | 1.00 |
| H75 | H | 0.27302 | 1.02156 | 0.95924 | 0.00000 | Uiso | 1.00 |
| H76 | H | 0.92845 | 0.34726 | 0.29651 | 0.00000 | Uiso | 1.00 |
| H77 | H | 0.85564 | 0.34756 | 0.17184 | 0.00000 | Uiso | 1.00 |
| H78 | H | 0.83467 | 0.43444 | 0.22113 | 0.00000 | Uiso | 1.00 |
| H79 | H | 0.97006 | 0.42799 | 0.25162 | 0.00000 | Uiso | 1.00 |
| H80 | H | 0.40974 | -0.08366 | 0.57357 | 0.00000 | Uiso | 1.00 |
| H81 | H | 0.40191 | -0.05445 | 0.48091 | 0.00000 | Uiso | 1.00 |
| H82 | H | 0.32424 | 0.01191 | 0.49763 | 0.00000 | Uiso | 1.00 |
| H83 | H | 0.47946 | 0.01857 | 0.58567 | 0.00000 | Uiso | 1.00 |
| H84 | H | 0.17156 | -0.02595 | 0.56907 | 0.00000 | Uiso | 1.00 |
| H85 | H | 0.08359 | 0.07275 | 0.53422 | 0.00000 | Uiso | 1.00 |
| H86 | H | 0.14981 | 0.01190 | 0.64117 | 0.00000 | Uiso | 1.00 |
| H87 | H | 0.23755 | 0.07955 | 0.63623 | 0.00000 | Uiso | 1.00 |
\( \text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_3 \), unit cell optimised

data 32_500eV\fine+cell

\_audit_creation_date 2022-04-05
\_audit_creation_method 'Materials Studio'
\_symmetry_space_group_name_H-M 'P21/C'
\_symmetry_Int_Tables_number 14
\_symmetry_cell_setting monoclinic

loop_
\_symmetry_equiv_pos_as_xyz
x,y,z
-x,y+1/2,-z+1/2
-x,-y,-z
x,-y+1/2,z+1/2
\_cell_length_a 14.0521
\_cell_length_b 12.5784
\_cell_length_c 19.2528
\_cell_angle_alpha 90.0000
\_cell_angle_beta 128.7292
\_cell_angle_gamma 90.0000

loop_
\_atom_site_label
\_atom_site_type_symbol
\_atom_site_fract_x \_atom_site_fract_y \_atom_site_fract_z
\_atom_site_U_iso_or_equiv
\_atom_site_occupancy
B1 B 0.61234 0.14161 0.69593 0.05000 Uiso 1.00
N1 N 0.74985 0.13798 0.78118 0.05000 Uiso 1.00
B2 B 0.80335 0.24827 0.83148 0.05000 Uiso 1.00
N2 N 0.94601 0.24008 0.90513 0.05000 Uiso 1.00
B3 B 1.00612 0.33672 0.97390 0.05000 Uiso 1.00
H1 H 0.54946 0.17792 0.71315 0.05000 Uiso 1.00
H2 H 0.60187 0.18975 0.63663 0.05000 Uiso 1.00
H4 H 0.76311 0.08260 0.82641 0.05000 Uiso 1.00
H5 H 0.80196 0.11174 0.76378 0.05000 Uiso 1.00
H6 H 0.78333 0.31438 0.77695 0.05000 Uiso 1.00
H7 H 0.75652 0.27053 0.86549 0.05000 Uiso 1.00
H8 H 0.98548 0.23333 0.87482 0.05000 Uiso 1.00
H9 H 0.97069 0.17067 0.94111 0.05000 Uiso 1.00
H10 H 1.00173 0.31692 1.03399 0.05000 Uiso 1.00
H11 H 0.95188 0.41887 0.93541 0.05000 Uiso 1.00
H12 H 1.11486 0.34492 1.00700 0.05000 Uiso 1.00
B4 B 0.50969 0.43569 0.71360 0.05000 Uiso 1.00
N3 N 0.46702 0.38819 0.62292 0.05000 Uiso 1.00
B5 B 0.33020 0.34237 0.55254 0.05000 Uiso 1.00
N4 N 0.25702 0.34528 0.59044 0.05000 Uiso 1.00
B6 B 0.17134 0.44485 0.56525 0.05000 Uiso 1.00
H13 H 0.50674 0.36814 0.75773 0.05000 Uiso 1.00
H15 H 0.45024 0.51405 0.70061 0.05000 Uiso 1.00
H16 H 0.47623 0.44544 0.58905 0.05000 Uiso 1.00
H17 H 0.52384 0.32667 0.63483 0.05000 Uiso 1.00
H18 H 0.33803 0.24984 0.53711 0.05000 Uiso 1.00
H19 H 0.27691 0.39738 0.48626 0.05000 Uiso 1.00
H20 H 0.31598 0.33436 0.65830 0.05000 Uiso 1.00
H21 H 0.20393 0.27761 0.56705 0.05000 Uiso 1.00
H22 H 0.22991 0.52690 0.58489 0.05000 Uiso 1.00
H23 H 0.12913 0.44167 0.60495 0.05000 Uiso 1.00
|      |    X    |    Y    |    Z    |  Uiso |  Uiso |
|------|---------|---------|---------|-------|-------|
|H24  | 0.08772 | 0.44511 | 0.48540 | 0.05000 | 1.00  |
|B7   | 0.27345 | 0.57022 | -0.00885| 0.05000 | 1.00  |
|N5   | 0.26635 | 0.66818 | -0.06284| 0.05000 | 1.00  |
|B8   | 0.22211 | 0.77997 | 0.05360 | 0.05000 | 1.00  |
|N6   | 0.26635 | 0.66818 | -0.06284| 0.05000 | 1.00  |
|B9   | 0.44363 | 0.86757 | 0.03827 | 0.05000 | 1.00  |
|H25  | 0.31804 | 0.49323 | -0.01834| 0.05000 | 1.00  |
|H26  | 0.33068 | 0.59327 | 0.06945 | 0.05000 | 1.00  |
|H28  | 0.34950 | 0.68144 | -0.04834| 0.05000 | 1.00  |
|H29  | 0.20852 | 0.64938 | -0.12983| 0.05000 | 1.00  |
|H30  | 0.19464 | 0.83592 | -0.11562| 0.05000 | 1.00  |
|H31  | 0.13695 | 0.76681 | -0.05285| 0.05000 | 1.00  |
|H32  | 0.36163 | 0.78334 | 0.08860 | 0.05000 | 1.00  |
|H33  | 0.29991 | 0.89825 | 0.04691 | 0.05000 | 1.00  |
|H34  | 0.41205 | 0.94339 | -0.01110| 0.05000 | 1.00  |
|H35  | 0.53224 | 0.88970 | 0.11504 | 0.05000 | 1.00  |
|H36  | 0.47107 | 0.79357 | 0.01180 | 0.05000 | 1.00  |
|B10  | 1.01084 | 1.09682 | 0.78046 | 0.05000 | 1.00  |
|N7   | 1.00571 | 0.98490 | 0.81574 | 0.05000 | 1.00  |
|B11  | 0.89496 | 0.91200 | 0.74411 | 0.05000 | 1.00  |
|N8   | 0.88698 | 0.81275 | 0.79116 | 0.05000 | 1.00  |
|B12  | 0.76080 | 0.75282 | 0.73529 | 0.05000 | 1.00  |
|H37  | 0.91116 | 1.14046 | 0.73976 | 0.05000 | 1.00  |
|H38  | 1.08492 | 1.15370 | 0.84346 | 0.05000 | 1.00  |
|H39  | 1.03831 | 1.08470 | 0.73181 | 0.05000 | 1.00  |
|H40  | 1.00795 | 0.99774 | 0.86972 | 0.05000 | 1.00  |
|H41  | 1.08598 | 0.94429 | 0.84318 | 0.05000 | 1.00  |
|H42  | 0.90823 | 0.88165 | 0.69059 | 0.05000 | 1.00  |
|H43  | 0.79993 | 0.96281 | 0.70640 | 0.05000 | 1.00  |
|H44  | 0.95736 | 0.76075 | 0.81376 | 0.05000 | 1.00  |
|H45  | 0.90141 | 0.83918 | 0.84788 | 0.05000 | 1.00  |
|H46  | 0.68411 | 0.81054 | 0.72636 | 0.05000 | 1.00  |
|H48  | 0.76990 | 0.66919 | 0.77091 | 0.05000 | 1.00  |
|N9   | 0.64892 | 0.47383 | 0.77073 | 0.05000 | 1.00  |
|H50  | 0.65955 | 0.53699 | 0.74190 | 0.05000 | 1.00  |
|H51  | 0.70708 | 0.41277 | 0.78183 | 0.05000 | 1.00  |
|H52  | 0.68082 | 0.49842 | 0.83280 | 0.05000 | 1.00  |
|H53  | 0.13759 | 0.54192 | -0.04916| 0.05000 | 1.00  |
|H54  | 0.10005 | 0.59620 | -0.03170| 0.05000 | 1.00  |
|H55  | 0.12833 | 0.46828 | -0.02971| 0.05000 | 1.00  |
|N11  | 0.56770 | 0.02149 | 0.66238 | 0.05000 | 1.00  |
|H57  | 0.48257 | 0.01895 | 0.60065 | 0.05000 | 1.00  |
|H58  | 0.62717 | -0.02152| 0.65896 | 0.05000 | 1.00  |
|H59  | 0.55927 | -0.01953| 0.70490 | 0.05000 | 1.00  |
|N12  | 0.27916 | 0.22761 | 0.86024 | 0.05000 | 1.00  |
|H61  | 0.36599 | 0.19486 | 0.90001 | 0.05000 | 1.00  |
|H63  | 0.28219 | 0.29363 | 0.89304 | 0.05000 | 1.00  |
|H64  | 0.22046 | 0.17569 | 0.85841 | 0.05000 | 1.00  |
13. Crystal structure (VBH)[B(C₆H₅)₄]

Table 13.1. Crystal structure parameters of (C₁₈H₃₉N₄P₂)[B(C₆H₅)₄].

| Compound                                      | (C₁₈H₃₉N₄P₂)[B(C₆H₅)₄] |
|-----------------------------------------------|--------------------------|
| Kα(Å)                                        | 1.54184 (Cu)             |
| Temperature (K)                               | 100(2)                   |
| Space group                                   | P₁                       |
| Z                                             | 4                        |
| a (Å)                                        | 11.7376(3)               |
| b (Å)                                        | 19.5388(5)               |
| c (Å)                                        | 20.5479(4)               |
| α (°)                                        | 61.751(2)                |
| β (°)                                        | 73.618(2)                |
| γ (°)                                        | 89.605(2)                |
| V (Å³)                                       | 3937.71(18)              |
| $\rho_{\text{calc}}$ (g cm⁻³)                | 1.118                    |
| $\mu_{\text{exp}}$ (mm⁻¹)                    | 0.856                    |
| $\theta_{\text{max}}$ (°)                    | 75.2030                  |
| $R_1$                                         | 0.0695                   |
| w$R_2$                                       | 0.2094                   |
| Goof                                         | 1.048                    |
| Crystal size (mm×mm×mm)                      | 0.06 x 0.16 x 0.20       |
| Crystal colour                                | colorless                |
| CCDC No.                                      | Fig. S13.2.             |

Fig. S13.2. Visualisation of the unit cell of the side product: (C₁₈H₃₉N₄P₂)[B(C₆H₅)₄].