Stabilization of BH$_4$ Group in Zinc Borohydride via Adduct of Ammonia towards a Pure Hydrogen Release

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Zn(BH$_4$)$_2$·2NH$_3$, a new ammine metal borohydride, has been synthesized via simply ball-milling a mixture of ZnCl$_2$·2NH$_3$/2LiBH$_4$. Structure analysis shows that the subsequent complex has a monoclinic structure with unit-cell parameters of $a = 6.392(4)$ Å, $b = 8.417(6)$ Å, $c = 6.388(4)$ Å and $\beta = 92.407(4)$ $^\circ$ and space group $P2_1$, in which Zn atoms coordinate with two BH$_4$ groups and two NH$_3$ groups. The interatomic distances reported herein show that Zn–H bonding in Zn(BH$_4$)$_2$·2NH$_3$ is shorter than Ca–H bonds in Ca(BH$_4$)$_2$·2NH$_3$ and Mg in Mg(BH$_4$)$_2$·2NH$_3$. This reduced bond contact leads to an increase in the ionic character of H. This study is able to show a good correlation between the reduced M–H distance and enhanced dehydrogenation behavior of the hydride material. Dehydrogenation results showed that this novel compound is able to release 8.9 wt. % hydrogen below 115 °C within 10 min without concomitant release of undesirable gases such as ammonia and/or boranes, thereby demonstrating the potential of Zn(BH$_4$)$_2$·2NH$_3$ to be used as a solid hydrogen storage material.

Introduction

Hydrogen is considered one of the environmentally clean energy carriers, as it achieves nearly zero emission of pollutants from power generators, such as fuel cells. However, efforts to make use of hydrogen as an on-board power source have been hampered by the safety concerns and volumetric constraints. In order for the wide-spread, practical use of hydrogen as an energy provider, it is necessary to store the gas in such a way as to achieve a high energy density, in addition it is important for storage materials to be easily produced and subsequently used. Meeting these criteria will allow the efficient use of hydrogen storage materials. There is no doubt that if the hydrogen economy is to meet the practical application requirements then fundamental and applied research must provide the breakthrough in identifying and understanding hydrogen-rich materials. Several metal borohydrdes are known to provide high H$_2$-capacity, however, issues such as: (1) high thermodynamic instability [e.g. high desorption temperature for LiBH$_4$ or Mg(BH$_4$)$_2$], (2) thermodynamic instability [as seen in Ti(BH$_4$)$_2$ and Cu(BH$_4$)$_2$], and (3) release of highly dangerous or toxic by-products, such as BeH$_2$, B$_2$H$_6$ [Be(BH$_4$)$_2$, Al(BH$_4$)$_3$ and Zn(BH$_4$)$_2$], have thus far limited their success as suitable hydrogen storage candidates. It has been shown that there are ways in which to overcome these challenges, such as utilizing doping or the identification of catalysis, etc. Nevertheless, the utilization of additive agents imposes a penalty on hydrogen capacity to a level that is unacceptable for practical application. Thermodynamic modification of metal hydrides is considered to be an appropriate approach to reduce the operating temperature due to the driving force of H$^+/\text{H}_2$ combination. In recent years, such an approach has been widely adopted by different research groups to destabilize the Li(Mg, Ca)–B–N–H system; this has resulted in a significant decrease in the reaction enthalpy and has resulted in a low dehydrogenation onset temperature compared to the individual constituent. Ammonia borane (AB) and its related compounds, are another series of materials generating intense interest as hydrogen sources. It is widely accepted that an attractive interaction between H$^+$ and H$^-$ is responsible for the hydrogen molecule being desorbed at low temperature. More recently, ammine metal borohydrdes (AMBs), another B-N-based hydride system, have been investigated with respect to their thermal decomposition properties, their crystalline structure and mechanism of H-evolution. In AMBs, the ammonia is coordinated with the metal cation of borohydrdes, which is similar to the ammine metal salts. The distinguished performance of AMBs regarding hydrogen storage can be ascribed to the combination of the NH$_3$ group and the BH$_4^-$ anion on a molecular level. NH$_3$ and BH$_4^-$ groups have a number of favorable attributes including, a high hydrogen capacity, 17.6 wt. % for NH$_3$ and 26.7 wt.% for BH$_4^-$; and highly mobile Hδ+/Hδ-atoms which may lead to a rapid generation of H$_2$ and subsequent desorption at low temperature. However, despite their promising characteristics, it has been observed that across a range of AMBs they display a variety of different thermal decomposition properties. LiBH$_4$·NH$_3$ and Ca(BH$_4$)$_2$·2NH$_3$ mainly release ammonia rather than hydrogen during decomposition in argon, which is attributed to the weak coordination between Li$^+$ (Ca$^{2+}$) with NH$_3$ in the material. In order to promote their dehydrogenation performance, chemical modification with various metal hydrides or metal chlorides or thermal decomposition under ammonia atmosphere are required. On the contrary, Mg(BH$_4$)$_2$·2NH$_3$ and Al(BH$_4$)$_3$·6NH$_3$ and its double cation complex show dominant hydrogen release upon heating. This is particularly true of the aluminum-based complexes, which are able to release over 10% hydrogen below 150 °C, exhibiting their potential as an advanced solid state hydrogen storage substrate. The above results strongly suggest that the dehydrogenation of AMBs is dependent on the central metal cation(s), which affect the bonding properties between BH$_4^-$ and NH$_3$ and thus lead to different dehydrogenation behavior. Therefore, development of AMBs requires a better understanding of the crystal and electronic structures of the materials in order attempt targeted design and to further improve characteristics such as the dehydrogenation temperature, purity of gas released, and
thermodynamic properties.

Along with Mg$^{2+}$ and Al$^{3+}$, Zn$^{2+}$ is also able to form strong coordination bonds with ammonia, which suggests potential for favorable dehydrogenation of ammonia complexes of the Zinc borohydride system.\textsuperscript{28-31} As early as 1959, zinc tetrahydroborate amines (Zn(BH$_4$)$_2$·4NH$_3$) could be obtained from aqueous-ammonia solutions at low temperature by exchange reaction between the metal salts and sodium tetrahydroborate.\textsuperscript{32} However, to the best of our knowledge, there have been no reports on the formation of Zn(BH$_4$)$_2$·2NH$_3$ and dehydrogenation properties of this class materials. In this paper, we report the synthesis and detailed structural, physical, and chemical characterization of the new ammine borohydride-based material Zn(BH$_4$)$_2$·2NH$_3$. Our results show that the dehydrogenation properties of Zn(BH$_4$)$_2$·2NH$_3$ are significantly improved in terms of dehydrogenation temperature, hydrogen capacity, and the purity of gas released compared to the other reported ammine metal borohydrides. In addition, density functional theory results relating to this compound are compared to results from similar calculations for Ca(BH$_4$)$_2$·2NH$_3$ and Mg(BH$_4$)$_2$·2NH$_3$ and hydrogen release properties of these materials are discussed.

**Experimental**

**Sample and equipments**

LiBH$_4$ (95%, J&K Co. Ltd), liquid anhydrous ammonia (99.999%, Sinopharm Chemical Reagent Co. Ltd) and anhydrous ZnCl$_2$ (99.99%, Sigma Aldrich Co. Ltd) were all sourced commercially. In order to produce pure ZnCl$_2$·2NH$_3$, ZnCl$_2$·6NH$_3$ was pre-fabricated by exposing ZnCl$_2$ powder in 1 atm ammonia for 24 hours and then thermally decomposing the product to ZnCl$_2$·2NH$_3$ and NH$_3$ under Ar flow at 150 °C. The composition of ZnCl$_2$·2NH$_3$ was identified by gravimetry. XRD results (Figure S1) revealed that the synthesized ZnCl$_2$·2NH$_3$ structure is orthorhombic (space group Imm) with lattice parameters $a = 7.7025(2)$ Å, $b = 8.1005(3)$ Å and $c = 8.5051(3)$ Å, which is consistent with that reported in literature.\textsuperscript{32} Zn(BH$_4$)$_2$·2NH$_3$ was prepared by milling the mixture of LiBH$_4$ and ZnCl$_2$·2NH$_3$ in a 2:1 molar ratio for 60 min (planetaryQM-1SP2) at 400 rpm under argon using stainless steel spheres with a BPR of 60:1. The milling process was carried out alternating 6 min of milling and 6 min of rest in order to avoid an unacceptable increase in the temperature of the powders in the vial. By way of comparison, ZnCl$_2$·2LiBH$_4$ was also processed under the same conditions as described above. All handling of the powders before and after milling were carried out in a glove box containing an argon atmosphere. Gas release property measurements were performed by thermogravimetry analysis connected to a mass spectrometer (TGA-MS), using a heating rate of 10 °C min$^{-1}$ under 1 atm Nitrogen with a purge rate of 200 cm$^3$ min$^{-1}$. To identify all possible gaseous products, survey scans in the mass range of 2-80 amu were recorded from the two samples. The temperature dependence of desorption/decomposition was monitored by a Sievert’s temperature-programmed-desorption (TPD) under 1 atm argon.

High-resolution X-ray powder diffraction data were collected from Zn(BH$_4$)$_2$·2NH$_3$ samples at the Australian Synchrotron powder diffraction beamline, using the Mythen-II detector.\textsuperscript{34} For phase identification and structure determination, the sample was loaded into a pre-dried 0.5 mm special-glass capillary whilst inside an Argon-filled glove box. The capillary was sealed with vacuum grease for X-ray diffraction measurements. High temperature in-situ XRD were conducted using a Cyberstar hot air blower at a heating rate of 3 °C min$^{-1}$; and data were collected over the temperature range 25 to 430 °C, in steps of 5 °C. For in-situ high temperature measurements, the sample was loaded into a 0.7 mm quartz capillary and mounted in a gas flow-cell in order to maintain an argon atmosphere over the sample throughout the experiment. Data were collected for all measurements at a wavelength of 0.8260 Å, determined through the use of NIST standard LaB$_6$ 660a. Solid-state infrared spectra of the samples (as Kbr pellets) were recorded on a Nicolet Nexus 470 in the range of 300 cm$^{-1}$ to 4000 cm$^{-1}$. During the IR measurement, samples were loaded into a sealed tube with CaF$_2$ windows. Solid-state $^{11}$B NMR data were recorded (DSX 300) using a Doty CP-MAS probe with no probe background. All of those solid samples were spun at 12 kHz, using 4 mm ZrO$_2$ rotors filled under a purified argon atmosphere within a glove box. A 0.55 µs single-pulse excitation was employed, with repetition times of 1.5 s. Differential scanning calorimetry (DSC) was performed by netzsch 204 HP DSC under argon with a gas flow of 20 ml min$^{-1}$ at a heating rate of 10 K min$^{-1}$. The N and H elemental analyses were performed using an Elementar Vario EL-III instrument. The isothermal dehydrogenation performances of the samples were examined by TPD apparatus with typical sample weigh of 90 mg. For comparison, the TG and TPD results relative to the pure Zn(BH$_4$)$_2$·2NH$_3$ are also showed in this study.

**Sample and equipments**

The geometries of Me(BH$_4$)$_2$·2NH$_3$ (Me = Zn, Ca or Mg) have been optimized by first principles calculations with the CASTEP code\textsuperscript{35, 36} based on density functional theory (DFT). The Perdew Burke Ernzerhof (PBE) functional was used with the generalized gradient approximation (GGA) for all calculations.\textsuperscript{37} The ultrasoft pseudopotentials that we used have the valence-electron configurations of 1s$^1$ (core radius 0.8 a. u.) for H, 2s$^2$2p$^1$ (core radius 1.4 a. u.) for B, 2s$^2$2p$^3$ (core radius 1.4 a. u.) for N, 3d$^{10}$4s$^2$ (core radius 2.0 a. u.) for Zn, 2p$^6$3s$^2$ (core radius 2.06 a. u.) for Mg and 3S$^2$2p$^4$4S$^2$ (core radius 1.6 a. u.) for Ca. The initial Me(BH$_4$)$_2$·2NH$_3$ structures for optimization were taken from the X-ray refinement data directly. We have used the plane-wave cutoff of 500 eV for representing the wave functions and 4 x 3 x 4 k-
point grid (i.e. 24 k-points) for the Brillouin zone sampling by the Monkhorst–Pack scheme. Geometry optimizations were performed using the BFGS procedure 38 at 0 K. The energy tolerance was $5 \times 10^{-6}$ eV/atom; the maximum tolerance for force and atom displacements along any Cartesian component was 0.01 eV/Å and $5 \times 10^{-4}$ Å, respectively. These parameters lead to a satisfactory convergence of the total energy. Geometry optimization was conducted in this study with the full optimization. The calculated structure files (ZnBNH-2-opt.cif) are attached in the supplementary information. The fully-optimized structure was selected for further exploration and was used to calculate density of states (DOS) and the electron localization function (ELF) information.

**Results and discussions**

**Synthesis and Crystal structure determination**

Our proposal to synthesize Zn(BH$_4$)$_2$(NH$_3$)$_2$ stems from the early report regarding Zn(BH$_4$)$_2$ preparation by solution chemistry. 22,39

\[ 2\text{MBH}_4 + \text{ZnCl}_2 \rightarrow \text{Zn(BH}_4)_2 + 2\text{MCl} \quad (1) \quad (\text{M}=\text{K, Li or Na}) \]

Given Zn$^{2+}$ in Zn(BH$_4$)$_2$ is a soft Lewis acid as compared to alternatives such as Li$^+$, and Na$^+$ which are hard acids, 22,39 the desired metathesis reaction should occur by substituting the starting material of ZnCl$_2$ in Eqn. (1) with ZnCl$_2$·2NH$_3$, as described in Eqn. (2).

\[ \text{ZnCl}_2 \cdot 2\text{NH}_3 + 2\text{LiBH}_4 \rightarrow \text{Zn(BH}_4)_2 + 2\text{LiCl} \quad (2) \]

The product of this reaction has been verified by XRD, FTIR and element analysis (N, H). Elemental analysis confirms that there is no appreciable change in the ratio of N to H (before ball milling, N:H=1.7; and after ball milling, N:H=1.665), indicating no loss of NH$_3$ sources during the ball milling. This study reports the structure of Zn(BH$_4$)$_2$·2NH$_3$ which has been solved by synchrotron radiation powder X-ray diffraction. (Structural data and atomic position are summarized in Table S1-S3, respectively). Bragg peaks in the room temperature diffraction patterns from the sample were indexed to a monoclinic unit cell using the program DICVOL. 40 The space group P2$_1$ and P2$_1$/m can be assigned based on systematic absences. The structure was subsequently solved in the space group of P2$_1$ (No. 4) by global optimization in direct space, using the program FOX. 41 Rietveld refinement was performed using TOPAS v4.2, 42 and the refined lattice parameters are $a = 6.392(4)$ Å, $b = 8.417$ (6) Å, $c = 6.388(4)$ Å, $\beta = 92.407(4)\,^\circ$. The diffraction profile fit using these parameters is shown in Figure S2; the Rietveld fit line and differences between the experimental and calculated values are visible.

The structure of Zn(BH$_4$)$_2$·2NH$_3$, as shown in Figure 1, can be described as comprising discrete units of Zn(BH$_4$)$_2$·2NH$_3$ where zinc cations are coordinated by 2NH$_3$ and 2BH$_4^-$, similar to the interactions observed in Mg(BH$_4$)$_2$·2NH$_3$ where the structure is described as essentially molecular. 20 The observed average Zn-N distance, of 2.13 Å, is a little longer than that in ZnCl$_2$·2NH$_3$ at 2.02 Å. The difference in the structures of these two complexes is evidently not caused by steric factors (the ionic radius of the BH$_4^-$ group is close to that of Cl$^-$) but rather the possible formation of Cl-N hydrogen bonds in the latter. 43 The Zn-B average distance of 2.32 Å is quite close to the corresponding contact in Mg(BH$_4$)$_2$·2NH$_3$ (2.39 Å) for the pseudotetrahedral coordinated Mg atom. 20 In addition, the packing of Zn(BH$_4$)$_2$·2NH$_3$ is highly consistent with that observed in Mg(BH$_4$)$_2$·2NH$_3$, the N$_2$ edge of one molecule faces one B atom of another molecule. These interactions lead to the arrangement of the Zn(BH$_4$)$_2$·2NH$_3$ molecules into pseudo-layers perpendicular to the $c$ axis. The Zn-H bonds in Zn(BH$_4$)$_2$·2NH$_3$, at 1.9 Å, are shorter by ca. 0.2 Å, than those reported for the...
The knowledge about the chemical bonding features pertaining to the structures. Regions of the spectra have been marked to denote relevant features pertaining to the structures.

![FTIR spectra](image)

**Fig. 2** FTIR spectra from reagents (a) ZnCl₂·2NH₃ and (b) pure LiBH₄. FTIR spectra from the product (c) post-milled ZnCl₂·2NH₃/2LiBH₄ and (d) post-heated ZnCl₂·2NH₃/2LiBH₄. The knowledge about the chemical bonding features pertaining to the structures.

![TG-MS profile](image)

**Fig. 3** TG-MS profiles for the as-prepared Zn(BH₄)₂·2NH₃ (a) and 2LiBH₄/ZnCl₂ (b). For comparison, the TG results relative to the Zn(BH₄)₂·2NH₃/2LiCl and pure Zn(BH₄)₂·2NH₃ are shown in (a), respectively.

Zn₄(BH₄)₆⁺ ion. This observation is supported by FTIR data as shown in Figure S3, which also shows a formed weakening of the Zn-H bond relative to the reported Zn-H bond in Zn(BH₄)₂. Such weakening may be caused by the steric effects of NH₃ group in Zn(BH₄)₂·2NH₃. Furthermore, the much shorter H-H distances (1.91–2.31 Å, Table S4) from Zn(BH₄)₂·2NH₃ suggest the formation of dihydrogen bonding as addressed in other AMBs compounds. As shown in Figure 1c, d, e, and f, Zn(BH₄)₂·2NH₃ comprises H⁺ from NH₃ units and H⁻ from BH₄⁻ units indicating the high possibility to possess of strongly hybridized valence electrons or closed shell bonds between B-H and between N-H, which can be primarily responsible for stability of this structure at room temperature. The strong NH···HB interaction in Zn(BH₄)₂·2NH₃ structure is also expected to have a great impact on improving the dehydrogenation performance.

It is reported that the preparation of neat Zn(BH₄)₂ using dry chemistry such as ball milling can be hindered by the tendency toward formation of mixed-cation (Zn-Li or Zn-Na) borohydrides. By analogy, it is also possible for the formation of LiZn(BH₄)₂·2NH₃ in the reaction of Eqn.(2). We tried to solve the structure on both LiZn(BH₄)₂·2NH₃ and Zn(BH₄)₂·2NH₃ chemical formula with all possible space groups with the relatively small volume (343.4 Å³). However, with LiZn(BH₄)₂·2NH₃ composition, the additional Li atom and BH₄⁻ group can not fit into the indexed monoclinic unit cell with overestimated density. In addition, if the final product is the formation of LiZn(BH₄)₂·2NH₃, ZnCl₂·2NH₃ would be excessive. However, form the XRD results, no ZnCl₂·2NH₃ can be identified after ball milling (Figure S2). These results indirectly confirm that the formed ammoniate is the Zn(BH₄)₂·2NH₃ rather than LiZn(BH₄)₂·2NH₃.

To improve the knowledge about the chemical bond information of Zn(BH₄)₂·2NH₃, we have carefully examined this new phase by FTIR spectroscopy, before and after heat treatment, and have also obtained FTIR data from the reagents, ZnCl₂·2NH₃ and LiBH₄, for comparison (Figure 2). Features in the spectra pertaining to the starting materials are evident in the spectrum recorded from the post-milled sample, suggesting that both B and N atoms are still in the integral ligation pattern BH₄⁻ and NH₃ group. Thus, although it is normally believed that it is not possible to locate H-atom positions from powder XRD data, this FTIR information, which is highly consistent with original NH₃ and BH₄⁻ ions, lend credence to the rigid body modeling of BH₄⁻ and NH₃ groups. Moreover, Zn-N bonding can be clearly observed in Figure 2c, following milling, at the same wavenumber as in ZnCl₂·2NH₃, implying that the Lewis acid to which NH₃ coordinates is still Zn²⁺. The bond length, as determined by powder diffraction is longer in Zn(BH₄)₂·2NH₃ (at ca. 2.13 Å) compared to that in ZnCl₂·2NH₃ (at 2.02 Å), agreeing well with the decreasing intensity of IR absorption following milling. Notably, after ball milling of ZnCl₂·2NH₃ and LiBH₄, the appearance of a weak peak observed in 1409 cm⁻¹ (nearly exactly the position of the reported Zn-H vibration, see Figure S3) suggests that, by mechanochemical reaction, BH₄⁻ transfers from LiBH₄ to combine with Zn²⁺ and engages in a substitution reaction with Cl⁻. The above results directly confirm some key information about Zn(BH₄)₂·2NH₃, namely, that both the BH₄⁻ ion.
spectrometry (MS) profiles compared to the as-prepared borohydride (ZnLi(BH$_4$)$_3$). Figure 3 shows the thermal decomposition performance of the as-prepared Zn(BH$_4$)$_2$·2NH$_3$ compared to the as-prepared ZnLi(BH$_4$)$_3$. As seen from the mass spectrometry (MS) profiles Figure 3a, the H$_2$ desorption from Zn(BH$_4$)$_2$·2NH$_3$ starts at around 90 °C and ends before 150 °C with one peak centered at 127 °C, and no ammonia, boranes and borazine impurities were detected throughout the heating. By contrast, the MS results of the ball milled ZnCl$_2$/2LiBH$_4$ confirm that a significant volume of diborane, B$_4$H$_{10}$, accompanies the evolution of H$_2$, leading to a large mass loss of 15.1 wt.%, (Figure 3b). Furthermore, the quantity of H$_2$ released (about 5.7 equiv., see Figure S5) before 200 °C determined by volumetric measurement agrees very well with the value calculated based upon the TGA result (ca. 5.74 mole H$_2$), which shows a weight loss of 8.9 wt.% for pure Zn(BH$_4$)$_2$·2NH$_3$ (accounting for 5.36 wt.% in Zn(BH$_4$)$_2$·2NH$_3$/2LiCl mixture). Clearly, the adduct of NH$_3$ plays a crucial role in ensuring the purity of H$_2$ and suppressing B$_4$H$_{10}$ release. Furthermore, the dehydrogenation of Zn(BH$_4$)$_2$·2NH$_3$ was investigated using isothermal volumetric hydrogen release measurements at various temperatures. As shown in Figure 4, approximately 5.5 equiv. hydrogen can be released within 35 min at 100 °C, suggesting favorable kinetics for this hydrogen storage material. Using increasing temperatures, from 115 °C to 135 °C, hydrogen release time can be reduced from 15 min to 10 min, respectively. This faster release is accompanied by an increase in the volume of hydrogen released, to ca. 5.7 equiv. hydrogen, corresponding to 8.9 wt.% at 115 °C.

The differential scanning calorimetry (DSC) results from the thermal decomposition of Zn(BH$_4$)$_2$·2NH$_3$ (Figure S6) reveal that the decomposition is preceded by one small endothermic signal which occurs without any mass loss between 72-90 °C, originating from the melting of Zn(BH$_4$)$_2$·2NH$_3$. This melt point was visually confirmed by heating Zn(BH$_4$)$_2$·2NH$_3$ in an Argon filled transparent vial. A maximum exothermic peak appeared at ca. 131 °C, corresponding to the release of hydrogen. Integration of the differential heat in the range of 90-160 °C yields a heat of decomposition of approximately -15 kJ mol$^{-1}$ H$_2$, which is lower than that of AB (-21 kJ mol$^{-1}$ H$_2$). Although the exothermic dehydrogenation of Zn(BH$_4$)$_2$·2NH$_3$ suggests that a direct reversibility of rehydrogenation from the decomposed products is infeasible, recent results on the reversible rehydrogenation via a chemical route conducted in AB system$^{46}$ illuminate the possibility of a more feasible chemical reversibility of Zn(BH$_4$)$_2$·2NH$_3$ due to its lower exothermicity than AB upon decomposition.

From the in-situ X-ray diffraction data shown in Figure 5, the changes undergone by the sample are reflected in the diffraction data and can be correlated to melting and H$_2$ desorption observed in the MS and DSC results. At 26 °C, the as-prepared Zn(BH$_4$)$_2$·2NH$_3$ can be clearly identified with intense and sharp Bragg diffraction peaks in the angle range of 5-30 degrees, indicative of long-range crystalline order of the material. Above the presence of LiCl, which is a by-product of Zn(BH$_4$)$_2$·2NH$_3$ synthesis, a number of peaks with relatively weak intensity relating to Zn are also observed; these suggest the fractional decomposition of Zn(BH$_4$)$_2$·2NH$_3$ due to the ball milling. Fractional decomposition is supported by $^1$H NMR results which show small B-N-H peaks (see Figure S7). As the temperature increases during the diffraction experiment the data reveal an abrupt absence of Zn(BH$_4$)$_2$·2NH$_3$ and the presence of

![Fig. 4 Isothermal curves for hydrogen desorption of Zn(BH$_4$)$_2$·2NH$_3$ at various temperatures. The results are calculated relative to the pure Zn(BH$_4$)$_2$·2NH$_3$.](image)

![Fig. 5 In-situ variable temperature high resolution powder XRD data collected from Zn(BH$_4$)$_2$·2NH$_3$. The compound was heated to selected temperatures at fine temperature steps. Asterisks (*) mark the position of Zn(BH$_4$)$_2$·2NH$_3$ diffraction peaks, peaks relating to impurities are also indicated.](image)

and the ligand NH$_3$ subunits remain intact in the new structure; and Zn$^{2+}$ is observed to have bonded with both the NH$_3$ and BH$_4^-$ groups.

**Dehydrogenation performance and pathway**

In order to emphasize the positive effect of the coordinated NH$_3$, ZnCl$_2$/2LiBH$_4$ was milled together under the same condition as ZnCl$_2$·2NH$_3$/2LiBH$_4$ and laboratory XRD data were acquired to confirm the identity of the synthesized phase (see Figure S4). According to the previous literatures, the ball milled products of ZnCl$_2$/2LiBH$_4$ turn out to be a mixed-metal (Zn-Li) borohydride (ZnLi(BH$_4$)$_3$).$^{34}$ Figure 3 shows the thermal decomposition performance of the as-prepared Zn(BH$_4$)$_2$·2NH$_3$ compared to the as-prepared ZnLi(BH$_4$)$_3$. As seen from the mass spectrometry (MS) profiles(Figure 3a), the H$_2$ desorption from Zn(BH$_4$)$_2$·2NH$_3$ starts at around 90 °C and ends before 150 °C with one peak centered at 127 °C, and no ammonia, boranes and borazine impurities were detected throughout the heating. By contrast, the MS results of the ball milled ZnCl$_2$/2LiBH$_4$ confirm that a significant volume of diborane, B$_4$H$_{10}$, accompanies the evolution of H$_2$, leading to a large mass loss of 15.1 wt.%, (Figure 3b). Furthermore, the quantity of H$_2$ released (about 5.7 equiv., see Figure S5) before 200 °C determined by volumetric measurement agrees very well with the value calculated based upon the TGA result (ca. 5.74 mole H$_2$), which shows a weight loss of 8.9 wt.% for pure Zn(BH$_4$)$_2$·2NH$_3$ (accounting for 5.36 wt.% in Zn(BH$_4$)$_2$·2NH$_3$/2LiCl mixture). Clearly, the adduct of NH$_3$ plays a crucial role in ensuring the purity of H$_2$ and suppressing B$_4$H$_{10}$ release. Furthermore, the dehydrogenation of Zn(BH$_4$)$_2$·2NH$_3$ was investigated using isothermal volumetric hydrogen release measurements at various temperatures. As shown in Figure 4, approximately 5.5 equiv. hydrogen can be released within 35 min at 100 °C, suggesting favorable kinetics for this hydrogen storage material. Using increasing temperatures, from 115 °C to 135 °C, hydrogen release time can be reduced from 15 min to 10 min, respectively. This faster release is accompanied by an increase in the volume of hydrogen released, to ca. 5.7 equiv. hydrogen, corresponding to 8.9 wt.% at 115 °C.

The differential scanning calorimetry (DSC) results from the thermal decomposition of Zn(BH$_4$)$_2$·2NH$_3$ (Figure S6) reveal that the decomposition is preceded by one small endothermic signal which occurs without any mass loss between 72-90 °C, originating from the melting of Zn(BH$_4$)$_2$·2NH$_3$. This melt point was visually confirmed by heating Zn(BH$_4$)$_2$·2NH$_3$ in an Argon filled transparent vial. A maximum exothermic peak appeared at ca. 131 °C, corresponding to the release of hydrogen. Integration of the differential heat in the range of 90-160 °C yields a heat of decomposition of approximately -15 kJ mol$^{-1}$ H$_2$, which is lower than that of AB (-21 kJ mol$^{-1}$ H$_2$). Although the exothermic dehydrogenation of Zn(BH$_4$)$_2$·2NH$_3$ suggests that a direct reversibility of rehydrogenation from the decomposed products is infeasible, recent results on the reversible rehydrogenation via a chemical route conducted in AB system$^{46}$ illuminate the possibility of a more feasible chemical reversibility of Zn(BH$_4$)$_2$·2NH$_3$ due to its lower exothermicity than AB upon decomposition.

From the in-situ X-ray diffraction data shown in Figure 5, the changes undergone by the sample are reflected in the diffraction data and can be correlated to melting and H$_2$ desorption observed in the MS and DSC results. At 26 °C, the as-prepared Zn(BH$_4$)$_2$·2NH$_3$ can be clearly identified with intense and sharp Bragg diffraction peaks in the angle range of 5-30 degrees, indicative of long-range crystalline order of the material. Aside from the presence of LiCl, which is a by-product of Zn(BH$_4$)$_2$·2NH$_3$ synthesis, a number of peaks with relatively weak intensity relating to Zn are also observed; these suggest the fractional decomposition of Zn(BH$_4$)$_2$·2NH$_3$ due to the ball milling. Fractional decomposition is supported by $^1$H NMR results which show small B-N-H peaks (see Figure S7). As the temperature increases during the diffraction experiment the data reveal an abrupt absence of Zn(BH$_4$)$_2$·2NH$_3$ and the presence of
a partial investigation relies on developments in the hydrogen release process of Zn(BH₄)₂·2NH₃, which indicates that any other decomposition products which may have formed could only be present as amorphous phases. FTIR results reveal that, all of the B-H bonds, including B-H bending and stretching modes, are almost undetectable for the decomposed Zn(BH₄)₂·2NH₃ (Figure 2), while the other signals, including Zn-H, N-H and Zn-N, occur at the same position but decrease in intensity. The surviving absorption peaks imply that the final amorphous compound should consist of Zn-H, N-H and Zn-N bonds. The solid-state ¹¹B NMR results provided some additional valuable hints in the composition evolution and hydrogen release process of Zn(BH₄)₂·2NH₃. Figure 6 shows ¹¹B NMR results for the as-prepared sample which reveal a primary boron species with a chemical shift of -44.1 ppm; this is assigned to the boron nucleus in the tetrahedral BH₄⁻ units. Meanwhile, one comparatively weak peak is observed at 0.4 ppm, indicating that detectable changes occurred in the chemical environment of the B atoms compared to the BH₄⁻ molecules derived through mechanical milling. This, again, suggests the possibility of partial decomposition of Zn(BH₄)₂·2NH₃ (see Figure S7). After heat treatment to 100 °C, one weak peak at 15.0 ppm was observed along with the peak of 0.4 ppm (see Figure S7). The appearance of these two weak peaks suggests that the chemical environment of fractional B atom shifts to the lower fields intensively compared to the tetrahedral BH₄⁻ since the formation of HBN₂ and/or BN₃⁻. In addition, the chemical shift, which is assigned to

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<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Zn(BH₄)₂·2NH₃</th>
<th>Mg(BH₄)₂·2NH₃</th>
<th>Ca(BH₄)₂·2NH₃</th>
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</thead>
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<td>Space-group</td>
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<td>P b c a (61)</td>
<td>P b c n (60)</td>
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<tr>
<td></td>
<td>b=8.8878 Å</td>
<td>b=17.9632 Å</td>
<td>b=8.2730 Å</td>
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<tr>
<td></td>
<td>c=6.4625 Å</td>
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<td>c=12.4126 Å</td>
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<tr>
<td></td>
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<tr>
<td>H-H</td>
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<td>2.081</td>
<td>2.026</td>
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<td></td>
<td>2.003</td>
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<tr>
<td></td>
<td>2.177</td>
<td>2.230</td>
<td>2.438</td>
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</table>
BH₄⁻ is still observed at -43.1 ppm. Upon further heating to 200 °C, the peaks corresponding to HBN₂ and/or BN₃ (observed at 17.4 ppm and -3.1 ppm) increased in intensity which coincides with the peak of BH₄⁻ diminishing totally (Figure 6c). By combination of the XRD, FTIR, NMR and elementary analysis of the end-products (N: H ratio is 1:1) results, as well as the thermolysis results, the dehydrogenation of Zn(BH₄)₂·2NH₃ can be speculated as:

\[2\text{Zn(BH}_4\text{)}_2\cdot2\text{NH}_3 \rightarrow \text{Zn} + \text{Zn(BNH)}_2 + 13\text{H}_2\]

The calculated weight loss of the Eqn. (2) is ca. 10 wt.%, 1.1 wt.% higher than the experimental result, which can be explained by a fraction of decomposition of Zn(BH₄)₂·2NH₃ during the ball-milling, demonstrated by the XRD and ¹¹B NMR results (Figure S2 and Figure S7). From the results above, it is concluded that the dehydrogenation mechanism of Zn(BH₄)₂·2NH₃ could be generally traced to the combination of the positive and negative H atoms from [NH] and [BH] sources, respectively. However, On condition that a balanced reaction of BH and NH occurs in the Zn(BH₄)₂·2NH₃, the final products should remain excessive BH groups. This is opposite to the IR results, which gives the evidence of residual NH groups but not BH groups. Therefore, a H transfer from B to N may occur in Zn(BH₄)₂·2NH₃ upon dehydrogenation. Anyhow, the dehydrogenation pathway of ammoniates of Zn-based borohydrides is somewhat different with the other reported AMBs, e.g. Mg(BH₄)₂·2NH₃, in which the metal cations in the dehydrogenated products are always bonded to the BN species.

**Electronic structure and chemical bonding analysis**

In order to gain a better understanding of the structure and dehydrogenation properties of Zn(BH₄)₂·2NH₃, we compare it with two other similar compounds, which are summarized in Table 1. By comparing the Me-H and Me-N (Me = Ca, Mg or Zn) interatomic distances of these materials, it is possible to correlate the structural features of these materials with the dehydrogenation performance. The average distance of Ca-H in Ca(BH₄)₂·2NH₃ is 2.414 Å. While in Mg(BH₄)₂·2NH₃, that distance is ca. 2.026 Å. In Zn(BH₄)₂·2NH₃, the average distance is significantly lower, at 1.887 Å. In each case the metal cation is similarly coordinated and the ionic radii of Ca²⁺, Mg²⁺, and Zn²⁺ are 100, 72 and 74 pm, respectively. Thus, the hydrogen atoms bonded to boron are expected to show increasing anionic character with decreasing Me-H bond distance, in the order of Ca(BH₄)₂·2NH₃, Mg(BH₄)₂·2NH₃ to Zn(BH₄)₂·2NH₃. Thereby, affording Zn(BH₄)₂·2NH₃ improved dehydrogenation capacity. The Zn-N and Mg-N average distances are comparable in Me(BH₄)₂·2NH₃ with distances of 2.078 Å and 2.142 Å, respectively. While the Ca-N distance is surprisingly long, at 2.517 Å, which may contribute to the ammonia detachment under inert atmosphere and therefore poor dehydrogenation performance.

The calculated electronic density of states (DOS) (Figure 7) show all structures have a similar finite energy gap in general (Zn 4.8 eV, Mg 4.9 eV, Ca 5.1 eV), therefore they all exhibit non-metallic features. All calculated DOSs show similar features. From the projected DOS plots, it can be seen that the lower valence band (VB, -16 to -10 eV) is dominated by N electrons and H electrons in all three compounds. The middle VB, (-10 to -5 eV) is dominated by N states, B states and H states in all three compounds, indicating effective overlapping and forming of very strong bonds. This is consistent with the following analysis of the electron localization function plots, i.e., the high ELF value near B-H and N-H atoms. Furthermore, in the upper VB region (-5 to 0 eV), metal (Mg, Ca, Zn), B, N and H electrons dominate, indicating strongly hybridized B-N-H states, which suggests that metal atoms have some interaction with the surrounding atoms.

Mg and Ca electrons have negligible contribution near the Fermi energy, while Zn electrons have a larger contribution. It should be noted that Zn has high states in the -5 to -3 eV VB range, which overlaps with B-N-H states, indicating that Zn forms bonds with surrounding atoms. This may explain the favorable dehydrogenating properties of Zn(BH₄)₂·2NH₃ comparing with Ca(BH₄)₂·2NH₃ and Mg(BH₄)₂·2NH₃. In the conduction band (CB), the main contributions are from metal, B and H atoms, while N contributes negligibly to the CB.

---

**Fig. 7** Electronic density of states for Zn(BH₄)₂·2NH₃, Mg(BH₄)₂·2NH₃ and Ca(BH₄)₂·2NH₃. Total DOS results are shown for each material, followed by DOS results for M, B, N, and H.
Fig. 8 Electron localization function (ELF η) for Zn(BH₄)₂:2NH₃, Mg(BH₄)₂:2NH₃ and Ca(BH₄)₂:2NH₃. An isosurface of η = 0.15 has been used in all figures, 2D cross section cut through M, B, N, and H atoms.

Table 2. Summary of dehydrogenation peak temperature (Dₚ), Pauling electronegativity (χₚ) and H₂ and NH₃ evolution for Zn(BH₄)₂:2NH₃, Mg(BH₄)₂:2NH₃, and Ca(BH₄)₂:2NH₃.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Zn(BH₄)₂:2NH₃</th>
<th>Mg(BH₄)₂:2NH₃</th>
<th>Ca(BH₄)₂:2NH₃</th>
</tr>
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<tbody>
<tr>
<td>χₚ</td>
<td>1.65</td>
<td>1.31</td>
<td>1.0</td>
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<tr>
<td>Dₚ (°C)</td>
<td>127</td>
<td>~200</td>
<td>~280</td>
</tr>
<tr>
<td>H₂ released (wt. %)</td>
<td>Observed 8.9⁶</td>
<td>12.3~13.1</td>
<td>12.3⁹</td>
</tr>
<tr>
<td></td>
<td>Calculated 10.8⁶</td>
<td>16</td>
<td>13.5</td>
</tr>
<tr>
<td>NH₃ released</td>
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<td>0~0.8</td>
<td>32.7</td>
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<tr>
<td></td>
<td>Calculated 26.4</td>
<td>38.6</td>
<td>32.7</td>
</tr>
<tr>
<td>References</td>
<td>This paper</td>
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<td>²⁰</td>
</tr>
</tbody>
</table>

⁶ Nearly no hydrogen releases from Ca(BH₄)₂:2NH₃ under the dynamic flow mode, and the listed value is obtained as the dehydrogenation of Ca(BH₄)₂:2NH₃ conducted in closed vessel under ammonia atmosphere.

²⁰ The H₂-evolution was estimated based on a pure Zn(BH₄)₂:2NH₃ sample.

In order to further analyse the chemical bonding of the materials, the electron localization function (ELF) has also been calculated as shown in Figure 8. ELF is based on the Hartree-Fock pair probability of parallel spin electrons and can be calculated in density functional theory from the excess kinetic energy density due to Pauli-repulsion.⁴⁹,⁵⁰ This function produces easily understandable, pictorially informative patterns of chemical bonding in molecules and solids.⁵⁰ As described earlier, in the case of Zn or Mg they each directly coordinates with 2 BH₄ groups and 2 NH₃ groups, while each Ca atom directly coordinates with 4 BH₄ groups and 2 NH₃ groups nearby. In Figure 8, the distribution of ELF in all structures shows the high ELF value near B-H and N-H atoms. This indicates strongly hybridized valence electrons or closed shell bonds between B and H and between N and H, i.e., covalent bonding. The spherical shell attractors around the H atoms are highly distorted, indicating H atoms are seen by the surrounding H atoms and have strongly localized electrons. The valence shell of the Mg and Ca atoms in the crystal structures is nearly spherical and with low ELF value, which indicates delocalized electrons, while the Zn shell is slightly distorted indicating interaction with nearby atoms. No additional attractors were found in between B and N atoms. This suggests there is no direct ionic bonding between B and N sites; BH₄ and NH₃ groups are only interacting through bonded H atoms. A feature of note is that an attractor can be seen in between metal and N atoms in all structures, which bias toward the N atom. This can be interpreted as ionic bonding characterization between NH₃ groups and metal atoms.

The decomposition behaviours of these three materials are summarized in Table 2. It can be seen that almost no hydrogen is released from Ca(BH₄)₂:2NH₃ under the dynamic flow mode, and the listed value is obtained as the dehydrogenation of Ca(BH₄)₂:2NH₃ conducted in closed vessel under ammonia atmosphere. Favorable dehydrogenation performance is observed in the Mg(BH₄)₂:2NH₃, which can release total of 13.1 wt % H₂ before 400 °C. Like Mg(BH₄)₂:2NH₃, the calcium analogue has an equivalent number of BH₄ and NH₃ groups. However, the decomposition of calcium borohydride diammoniate under a flow of inert gas only yields NH₃ and later Ca(BH₄)₂: no hydrogen is detected by mass spectroscopy.²¹ When conducting volumetric release measurement in a closed vessel, the Ca analogue releases...
H₂ instead of NH₃, after sample melting. It is proposed that in a closed vessel NH₃ remains in the vicinity of the Ca(BH₄)₂, and thus increases the chance of interaction with BH₄⁻ group. In the case of Zn(BH₄)₂·2NH₃, 8.9 wt.% hydrogen is released under isothermal conditions at 115 °C within 10 min without any undesirable NH₃ and/or B₂H₆ evolved during the decomposition. As summarized in Table 2, it shows that the dehydrogenation temperature of these AMBs is correlated to the Pauling electronegativity (χp) of metal cations, i.e. increased χp leads to lower decomposition temperature, suggesting that the χp of metal cations may play a crucial role in tuning the dehydrogenation temperature of AMBs. This may be due to more electronegativity of Zn atoms than that of Ca and Mg, which contributes to the increased anionic character of H in B-H and cationic character of H in B-H, and thus leading to easier NH···HB interaction.

Therefore, the fact that the Zn(BH₄)₂·2NH₃ exhibited even lower dehydrogenation temperature than Ca(BH₄)₂·2NH₃ and Mg(BH₄)₂·2NH₃ may attribute to its unique structure characteristic obtained by chemical alteration that incorporates NH₃ with BH₄⁻ on a molecular level, which can be detailed as the deliberately introduced dihydrogen bonds and tuned cations electronegativity to adjust the temperature and purity of dehydrogenation. The regularity discussed above may provide further insights into the development of new AMBs with more favourable dehydrogenation performance.

Conclusions

In summary, Zn(BH₄)₂·2NH₃ has been mechanically synthesized via a simple ball-milling method. The crystal structure of Zn(BH₄)₂·2NH₃ was solved by high resolution powder X-ray diffraction which has been supported by evidence from infra-red spectroscopy and B¹¹ NMR. It has been shown, through DSC and MS, that this novel compound is able to release 8.9 wt.% hydrogen at 115 °C within 10 min without any undesirable gas accompanying this release during decomposition, thereby demonstrating the potential of Zn(BH₄)₂·2NH₃ for onboard hydrogen storage. Promotion of H₂ evolution in Zn(BH₄)₂·2NH₃ compared to non-ammonia Zn-base borohydride can be ascribed to the bonded ligand ammonia which is crucial for the prevention of release of B₂H₆. Furthermore, by comparing the crystal structures of Me(BH₄)₂·2NH₃ (M = Zn, Ca, Mg), it has been shown that Zn-H bonding is remarkably shorter in the Zn analogue, thus leading to increased ionic character of H. A correlation between the decreasing of M-H distance and the enhanced dehydrogenation performance has been observed. The DFT calculations show that Mg and Ca electrons have negligible contribution near the Fermi energy, while Zn electrons have considerable contribution; indicating that Zn forms bonding with surrounding N and H(B) atoms, which leads to the increasing reactivity of H⁺ in Zn(BH₄)₂·2NH₃. The observations of this research demonstrate that the adduct of NH₃, which is close to BH₄⁻ in molecular level, is an effective chemical approach for lowering the dehydrogenation temperature and restraining the emission of borane from metal borohydrides. Our findings provide useful insights and guidelines for the design and synthesis of novel AMBs for hydrogen storage.

Acknowledgements

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Notes and references

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Electronic Supplementary Information (ESI) available: [Crystallographic details, XRD, MS, NMR, DSC, FTIR, and TPD results, including Figures S1-S7 and Tables S1-S4.]; See DOI: 10.1039/b0000000z

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