

Article

Synthesis, Structural Characterization, and Hydrogen Release of Al-Based Amidoboranes Derived from $\text{MAI}H_4$ (Li, Na)- $\text{BH}_3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{BH}_3$

Ting Zhang ¹ , Xiao Li ^{1,2} , Hai-Wen Li ³ , Michel Devillers ¹ and Yaroslav Filinchuk ^{1,*}

¹ Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Place Louis Pasteur 1, 1348 Louvain-la-Neuve, Belgium; tingzhang9101@foxmail.com (T.Z.); lixiao_hgmri@163.com (X.L.)

² Hefei General Machinery Research Institute, Hefei 230031, China

³ School of Advanced Energy, Sun Yat-Sen University, Shenzhen 518107, China; lihw76@mail.sysu.edu.cn

* Correspondence: yaroslav.filinchuk@uclouvain.be

Abstract: Over the past two decades, the high hydrogen content and favorable dehydrogenation conditions of multi-metallic amidoboranes have gained significant attention for their potential in hydrogen storage. Among them, Al-based complex hydrides have shown promise because of their high polarizing power, light weight, and abundant natural presence. In this work, we successfully synthesized two novel tetrahedrally coordinated Al-based amidoboranes, namely, $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ and $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, using $\text{BH}_3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{BH}_3$ (EDAB) as a precursor. The structure of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ was determined through modeling based on synchrotron powder X-ray diffraction. Additionally, the formation of the Al-N bond in $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ and $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ was confirmed with IR spectra. $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ is more stable in air than $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$. Importantly, thermal gravimetric analysis and mass spectroscopic characterization confirmed that both compounds release hydrogen without the presence of ammonia, diborane, or ethylenediamine. Our work represents the first example of Al-based amidoboranes with chelation coordination geometry, which provides an essential foundation for understanding the relationship of complex multi-metallic amidoboranes in terms of synthesis, structure, and properties.

Keywords: Al-based amidoboranes; multi-metallic amidoboranes; thermal dehydrogenation; hydrogen release



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1. Introduction

As global energy consumption continues to rise toward its peak, fossil fuel resources are being depleted worldwide, resulting in escalating energy costs and increased greenhouse gas emissions [1]. Hydrogen has emerged as a promising alternative energy source, characterized by its high energy density (120 MJ/kg), sustainability, and environmentally friendly profile. It can be produced [2,3] from both renewable and non-renewable sources and is widely applicable in transportation, power generation, and industrial sectors. Despite these advantages, the commercialization of hydrogen energy is significantly constrained by its low volumetric density under standard conditions [4], which complicates storage and transportation. Conventional approaches, such as high-pressure gas storage and cryogenic liquid storage [5], partially address this issue but are associated with high energy consumption, safety risks, and system complexity. In recent years, solid-state hydrogen storage [6–10] has gained considerable attention as a viable alternative, offering

advantages such as high storage capacity, enhanced safety, stability, and operation under moderate temperature and pressure conditions, thereby presenting a potential solution to the limitations of traditional storage methods.

Compounds based on boron–nitrogen–hydrogen (B–N–H) [11,12] have emerged as promising solid-state hydrogen storage materials due to the lightweight nature of boron and nitrogen, as well as their ability to accommodate multiple hydrogen atoms. This is attributed to the hydridic and protic characteristics of the B–H and N–H bonds, which facilitate the release of hydrogen. One representative example of B–N–H material is ammonia borane [13,14] (NH_3BH_3 or AB), which can release up to 19.6 wt.% of hydrogen, exhibits low toxicity, and demonstrates good stability under ambient conditions.

However, the thermal decomposition of NH_3BH_3 occurs in multiple steps, typically at around 120 °C, 200 °C, and above 500 °C, leading to the generation of toxic volatile by-products such as B_2H_6 , NH_3 , and $\text{N}_3\text{B}_3\text{H}_6$. The decomposition process is often accompanied by severe foaming and volume expansion. Various strategies [15,16] have been explored to address these limitations, including the chemical modifications of NH_3BH_3 molecules to create derivatives. This approach has resulted in the synthesis of novel compounds like alkali amidoboranes [17–20], alkaline earth amidoboranes [21–25], and multi-metallic amidoboranes [26–37], which exhibit improved characteristics for hydrogen storage applications. For instance, KNH_2BH_3 releases approximately 5.8 wt.% of pure hydrogen from room temperature up to 160 °C [18]. $\text{Mg}(\text{NH}_2\text{BH}_3)_2$ can release approximately 10 wt.% of high-purity H_2 upon heating to 300 °C [25]. Furthermore, $\text{Na}_2\text{Mg}(\text{NH}_2\text{BH}_3)_4$ has the ability to release 8.4 wt.% of predominantly hydrogen, with minor amounts of ammonia and borazine [28].

Compared to monometallic amidoboranes, multi-metallic amidoboranes offer greater versatility in forming new compounds. So far, multi-metallic amidoboranes have been categorized into Li-, Mg-, Ca-, and Al-based amidoboranes according to the central coordination metals. Our works focus on the synthesis and chemical modification of Al-based amidoboranes, driven by the high polarizing power defined by the exceptional charge-to-radius ratio, low weight, and high natural abundance of Al.

Our initial investigation on Al-based amidoboranes led to the discovery of $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ [34], which exhibits a two-step hydrogen release process (at 120 °C and 168 °C), releasing approximately 9 wt.% of high-purity hydrogen. Furthermore, the amorphous residue obtained after the thermal decomposition of $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ demonstrated the ability to reversibly absorb around 27% of the released hydrogen at 250 °C and a hydrogen pressure of 150 bar. Subsequently, we conducted a study on the formation, structure, and hydrogen release properties of its derivative, $\text{Na}[\text{Al}(\text{CH}_3\text{NHBH}_3)_4]$ [37]. This compound was synthesized from NaAlH_4 and $\text{CH}_3\text{NH}_2\text{BH}_3$ (MeAB), and the introduction of a methyl group ($-\text{CH}_3$) on the nitrogen of NH_3BH_3 stabilized an intermediate compound, $\text{Na}[\text{AlH}(\text{CH}_3\text{NHBH}_3)_3]$, shedding light on the formation process of amidoboranes. Notably, the energy input required for the formation of $\text{Na}[\text{Al}(\text{CH}_3\text{NHBH}_3)_4]$ was lower than that of the unsubstituted $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$. $\text{Na}[\text{Al}(\text{CH}_3\text{NHBH}_3)_4]$ does not release high-purity hydrogen during its thermal decomposition but forms reactive hydride composites with NaH and NaNH_2 , desorbing pure H_2 under relatively mild conditions.

To further advance the development of Al-based amidoboranes and gain a deeper understanding of the relationships between synthesis, structure, and hydrogen release properties, we conducted additional modifications to $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$. In this paper, we introduce the new Al-based amidoboranes, namely, $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ and $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, providing comprehensive details about their synthesis, structural characterization, and thermal dehydrogenation properties.

For the synthesis of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ and $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, we employed $\text{BH}_3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{BH}_3$ (EDAB) as one of the precursors. EDAB offers greater accessibility than NH_3BH_3 , as it can be obtained from commercially available and cost-effective precursors. Additionally, the presence of the weak electron-donating ethylene substituent influences the coordination bonds between the nitrogen and aluminum atoms in the final complex, similar to the behavior observed in $\text{Na}[\text{Al}(\text{CH}_3\text{NHBH}_3)_4]$. EDAB exhibits a dimer-like structure derived from $\text{CH}_3\text{NH}_2\text{BH}_3$, facilitating the formation of a chelate complex with aluminum. This characteristic contributes to the creation of a more stable framework for Al-based amidoboranes, suppressing the release of significant fragments during thermal decomposition, as observed in $\text{Na}[\text{Al}(\text{CH}_3\text{NHBH}_3)_4]$ [37].

2. Results

2.1. Synthesis of $M[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ ($M = \text{Li}$ and Na)

2.1.1. Synthesis of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$

The crystal structures of the reported Al-based amidoborane complexes in a tetrahedral coordination geometry include $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ [34], $\text{K}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ [36], $\text{Na}[\text{AlH}(\text{CH}_3\text{NHBH}_3)_3]$ [37], and $\text{Na}[\text{Al}(\text{CH}_3\text{NHBH}_3)_4]$ [37]. These complexes can be synthesized by ball-milling NaAlH_4 or KAlH_4 with four equivalents of NH_3BH_3 or $\text{CH}_3\text{NH}_2\text{BH}_3$. Mechanochemical synthesis is preferred over wet chemical methods for the synthesis of hydrides used for hydrogen storage materials, as it avoids the use of coordinating or high-boiling-point solvents, which can increase the costs and the environmental impact.

It has been reported that the reaction between one equivalent of LiAlH_4 and four equivalents of NH_3BH_3 under ball milling conditions is excessively violent [34]. Furthermore, the lower melting point of $\text{CH}_3\text{NH}_2\text{BH}_3$ (58 °C) [38] compared to NH_3BH_3 (112–114 °C) [39] results in NaAlH_4 -4 $\text{CH}_3\text{NH}_2\text{BH}_3$ composites, exhibiting higher reactivity than NaAlH_4 -4 NH_3BH_3 . As a result, ball milling may not be suitable for the synthesis of $\text{Li}[\text{Al}(\text{CH}_3\text{NHBH}_3)_4]$. In contrast, $\text{BH}_3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{BH}_3$ (EDAB) demonstrates higher thermal stability and a slightly higher melting point (119 °C) [40] compared to NH_3BH_3 and $\text{CH}_3\text{NH}_2\text{BH}_3$. Therefore, the reaction between LiAlH_4 and EDAB is expected to go easier than between LiAlH_4 and $\text{CH}_3\text{NH}_2\text{BH}_3$ and/or NH_3BH_3 . Thus, we attempted the ball-milling synthesis of a novel Al-based amidoborane complex with Li using LiAlH_4 and EDAB.

Initially, we conducted ball milling experiments using LiAlH_4 -2 EDAB composites under the same conditions as for the synthesis of $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$; however, the analysis of the powder X-ray diffraction (PXRD) pattern revealed that the reaction between LiAlH_4 and 2 EDAB could not reach completion under these milling conditions (details shown in Section 3.2, Sample Li-A). To enhance the yield of the new product from the post-milled LiAlH_4 -2 EDAB composites, we optimized the milling conditions (details shown in Section 3.2, Sample Li-B) and obtained a higher yield for $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ (Figure 1, Sample Li-B).

Variable-temperature PXRD measurements were conducted to determine the number of phases associated with the newly observed peaks in Sample Li-B (Figure 1). Interestingly, all the peaks observed in the PXRD pattern of Sample Li-B (Figure 1) vanished simultaneously at approximately 130 °C (Figure 2). This indicates that these peaks correspond to a single phase. The pressure and temperature were carefully monitored throughout the milling process of LiAlH_4 -2 EDAB (refer to Section 3.2 and Table 1). The results revealed the

release of approximately 3.3 equivalents of gas per mole of LiAlH_4 , which closely matches the expected gas quantity (four equivalents) based on the equation below.

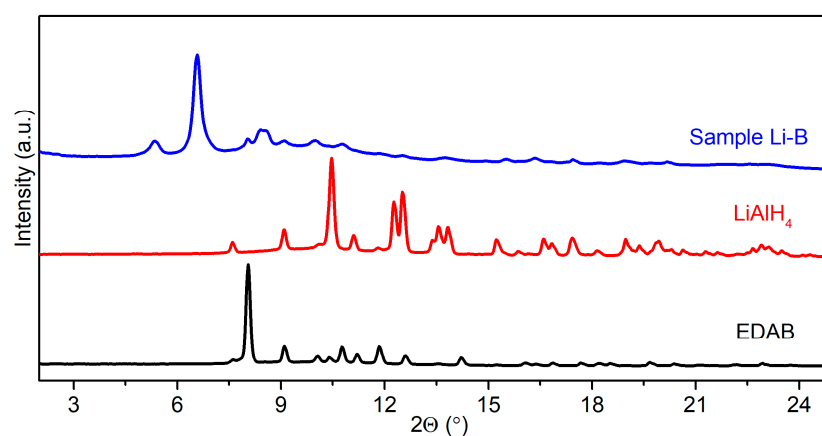
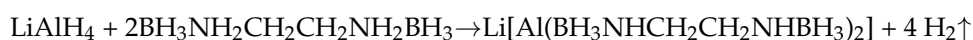


Figure 1. PXRD patterns of EDAB, LiAlH_4 , and Sample Li-B ($\lambda = 0.71073 \text{ \AA}$).

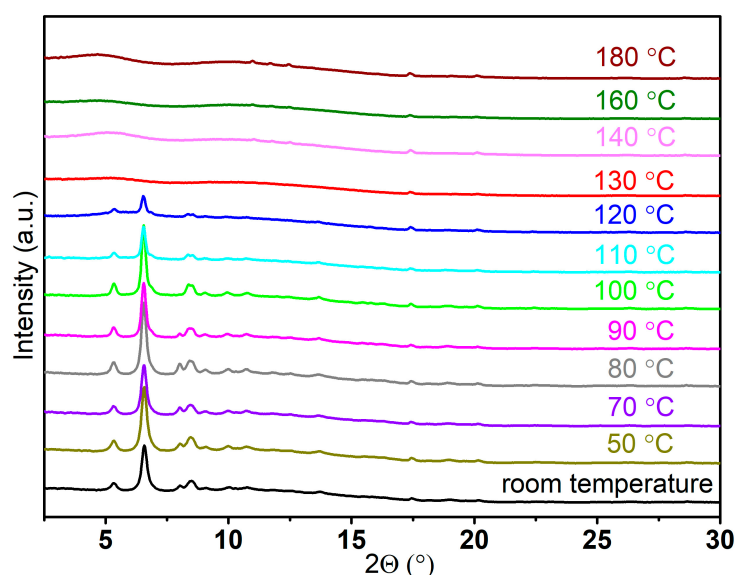


Figure 2. Temperature ramp followed by PXRD for Sample Li-B ($\lambda = 0.71073 \text{ \AA}$).

Table 1. Pressure and temperature at the start and at the end of synthesis, and the amount of released gas during synthesis of Sample **Li-B** using the Easy-GTM system.

P_{start} (bar)	T_{start} ($^{\circ}\text{C}$)	P_{end} (bar)	T_{end} ($^{\circ}\text{C}$)	Δn_{Gas} (mmol)	$\frac{\Delta n_{\text{Gas}}}{n_{\text{LiAlH}_4}}$
1.0	23.6	1.7	23.1	2.4	3.3

We also performed an IR spectra analysis of the $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ (Sample **Li-B**), comparing it with that of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$. Interestingly, the IR spectra of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ exhibited a striking similarity to that of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$. This observation, combined with the findings from ramping PXRD measurements and the analysis of released gases during synthesis, strongly suggests that $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ was successfully synthesized under the milling conditions employed for Sample **Li-B**.

2.1.2. Synthesis of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$

In our quest to obtain Al-based amidoboranes with Na^+ as a counterion, we explored the wet chemical synthesis approach by reacting NaAlH_4 and EDAB. Previous reports indicated that $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ could be obtained in THF at room temperature within 3 h [41]. Following this, we conducted the synthesis of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ in anhydrous THF with varying stirring times. Specifically, we combined one eq. of NaAlH_4 and two eq. of EDAB in anhydrous THF at room temperature and allowed the reaction to proceed for 24, 48, and 72 h, yielding, respectively, Samples **Na-A**, **Na-B**, and **Na-C** (details are provided about the synthesis method in Section 3.3).

Our results demonstrate that $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ could indeed be formed in THF at room temperature, albeit with a longer reaction time compared to its analog $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$. We monitored the progress of the reaction using PXRD patterns (Figure 3). After 24 h of reaction (Sample **Na-A**), new peaks appeared on the PXRD, indicating the formation of new compounds. Extending the reaction time to 48 and 72 h (Samples **Na-B** and **Na-C**), the peaks attributed to EDAB completely disappeared, while the new peaks matched those observed in Sample **Na-A** (Figure 3). This confirms that the reaction between NaAlH_4 and EDAB was completed within 48 h.

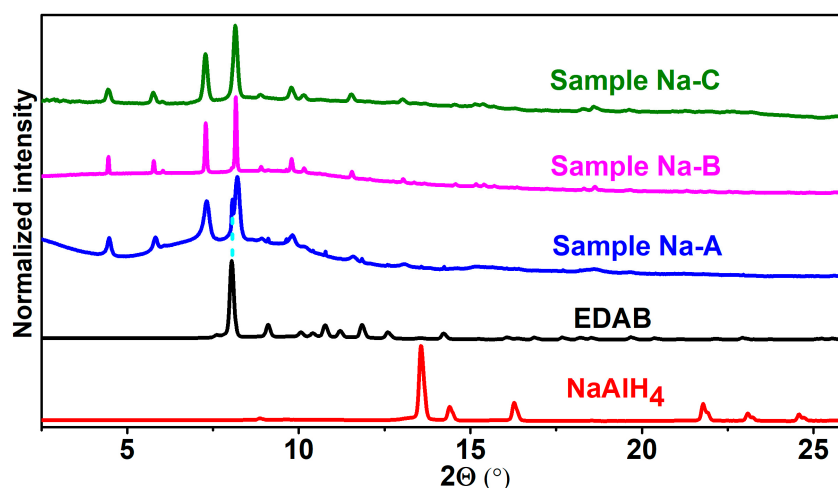


Figure 3. PXRD patterns of NaAlH_4 , EDAB, and Samples **Na-A**, **B**, and **C** (the residual EDAB in Sample **Na-A** is represented by a light blue dashed line, $\lambda = 0.71073 \text{ \AA}$).

To verify the purity of the newly synthesized compound, we performed temperature ramping synchrotron PXRD from room temperature to 225°C (Figure 4). The results demonstrated that all the peaks observed for Sample **Na-B** gradually decreased simultaneously from approximately 121°C and eventually vanished at 165°C . This observation suggests that Sample **Na-B** consists of a single phase, confirming its purity.

We also attempted to synthesize $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ via mechanochemistry. Unfortunately, all the attempts were unsuccessful, despite employing the harshest milling conditions in our ball mill. Considering the significantly longer stirring time of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ required for synthesis (over 24 h) compared to the synthesis of $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ and the unsuccessful mechanochemical synthesis, both indicate that EDAB exhibits higher inertness than AB when reacting with NaAlH_4 . It was reported that MeAB has a higher reactivity than AB with respect to NaAlH_4 [37]. Consequently, MeAB exhibits the highest activity, and EDAB exhibits the highest inertness among AB, MeAB, and EDAB in the reaction with NaAlH_4 .

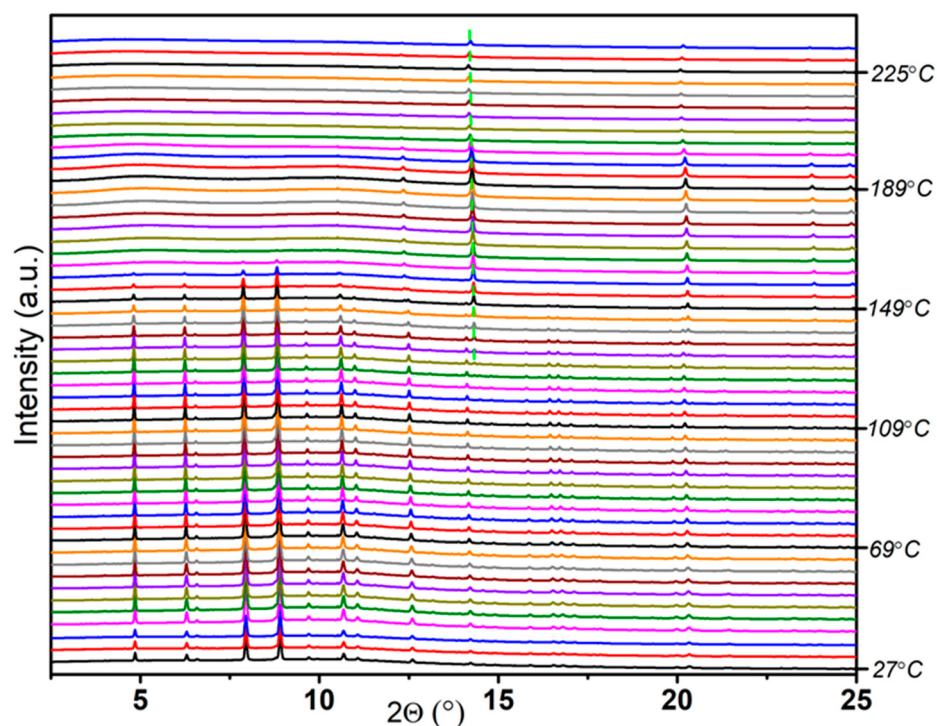


Figure 4. Temperature ramping PXRD pattern of $\text{Na(THF)[Al(BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ (the green dotted line represents the peaks of NaBH_4 , $\lambda = 0.77509 \text{ \AA}$).

2.2. Characterization of $\text{M[Al(BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ ($\text{M} = \text{Li, Na}$)

For structural characterization, we employed synchrotron PXRD data and conducted modeling to determine the structure of this novel Al-based amidoborane complex, $\text{Na(THF)[Al(BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$. Additionally, we analyzed the IR spectra to provide additional support for our structural conclusions.

2.2.1. The Structure of $\text{Na(THF)[Al(BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$

The crystal structure of $\text{Li[Al(BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ could not be determined due to the limited number of diffraction peaks and their significant broadening. Therefore, the structure of $\text{Li[Al(BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ was characterized through IR spectra, which will be discussed later.

Fortunately, the crystal structure of $\text{Na(THF)[Al(BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ with THF was successfully determined using synchrotron powder X-ray diffraction (SR-PXRD, ESRF, Grenoble, France). Although the disorder of the coordinated THF remains poorly resolved, the structural framework has been well determined. Based on the SR-PXRD data, the crystal structure of $\text{Na(THF)[Al(BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ with THF was modeled in a tetragonal unit cell with space group $\text{P4}/n$. In this anionic complex, each $[\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3]^{2-}$ anion provides two pairs of electrons from two nitrogen atoms, forming a chelate coordinated with the central Al^{3+} ions. This arrangement contributes to the enhanced stability of the compound $\text{Na(THF)[Al(BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ compared to its analogs, $\text{Na[Al(NH}_2\text{BH}_3)_4]$ and $\text{Na[Al(CH}_3\text{NHBH}_3)_4]$.

The central Al^{3+} ion is tetrahedrally coordinated by four nitrogen atoms (Figure 5A), exhibiting a geometry similar to previously reported compounds such as $\text{Na[Al(NH}_2\text{BH}_3)_4]$ [34], $\text{K[Al(NH}_2\text{BH}_3)_4]$ [36], and $\text{Na[Al(CH}_3\text{NHBH}_3)_4]$ [37]. The Al-N distances were fixed at $1.95 \text{ \AA}$, slightly longer than those observed in $\text{Na[Al(NH}_2\text{BH}_3)_4]$ ($1.840(9)$ – $1.929(8) \text{ \AA}$) and $\text{K[Al(NH}_2\text{BH}_3)_4]$ ($1.838(9)$ – $1.909(9) \text{ \AA}$) but similar to those in $\text{Na[Al(CH}_3\text{NHBH}_3)_4]$ ($1.922(1)$ – $1.990(1) \text{ \AA}$).

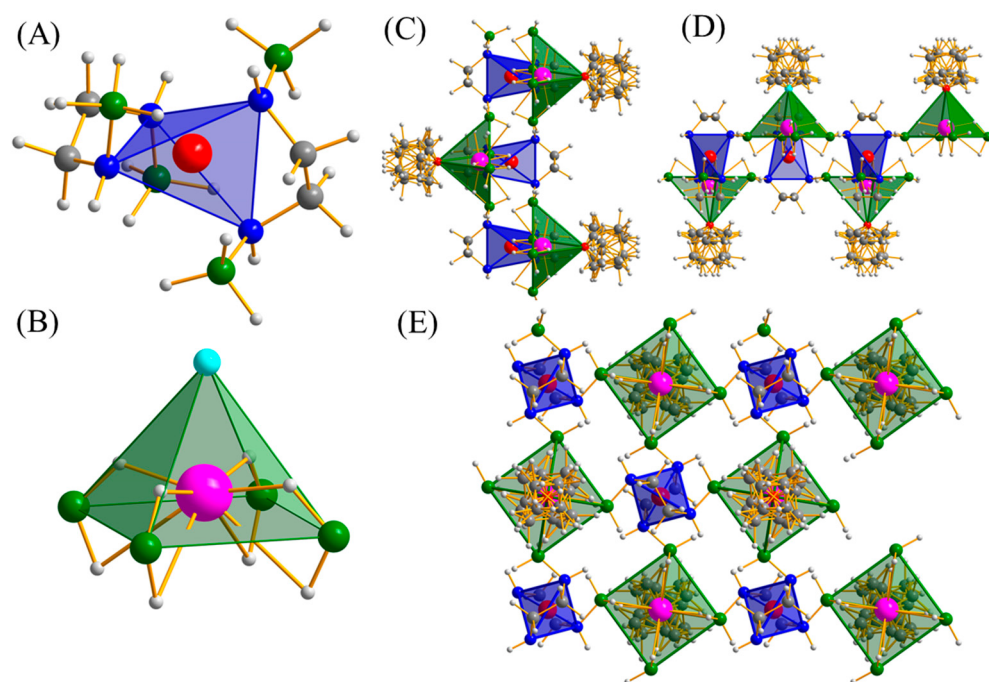


Figure 5. The coordinated geometry of Al^{3+} (A) and Na^+ (B) crystal packing along with a (C), b (D), and c (E) axes (color code: N = blue, B = green, C = grey, H = light grey, O = sky blue, Al = red, and Na = pink).

The Na atoms exhibit a square pyramidal coordination geometry (Figure 5B), with each atom surrounded by four BH_3 groups from four different $[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]^-$ anions, as well as one oxygen atom from the THF solvent molecule. This arrangement differs from the usual octahedral environments observed in compounds like $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ [34], $\text{Na}_2[\text{Mg}(\text{NH}_2\text{BH}_3)_4]$ [28], and $\text{Na}_2[\text{Ca}(\text{NH}_2\text{BH}_3)_4]$ [31], as well as the triangular bipyramidal environment in $\text{Na}[\text{Al}(\text{CH}_3\text{NHBH}_3)_4]$ [37].

The THF exhibits disorder around the four-fold symmetry axis, which could be better resolved by studying a single crystal. Similar to the reported $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ and $\text{Na}[\text{Al}(\text{CH}_3\text{NHBH}_3)_4]$, the $[\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3]^{2-}$ units display a bridging coordination mode, connecting Al^{3+} and Na^+ ions, resulting in the formation of a three-dimensional polymeric structure (Figure 5C–E).

2.2.2. The IR Spectra of $\text{M}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ ($\text{M} = \text{Li}$ and Na)

To characterize the structure of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ and compare it with $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, we conducted ATR-IR spectra measurements on LiAlH_4 , NaAlH_4 , EDAB, $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, and $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$. The IR spectra of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ and $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ exhibit characteristic peaks in comparison to the reactant EDAB, indicating structural differences between these compounds (Figure 6).

The IR spectra show the presence of stretching modes for N–H ($3114\text{--}3346\text{ cm}^{-1}$), C–H ($2838\text{--}3010\text{ cm}^{-1}$), and B–H ($2033\text{--}2499\text{ cm}^{-1}$) in both $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ and $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$. There is no significant difference compared to the precursor EDAB. Additionally, new peaks appear in these two new complexes within the Al–N bond region (highlighted by the red rectangle) between 400 and 800 cm^{-1} , similar to other compounds such as $\text{Li}[\text{Al}(\text{NH}_2)_4]$ [42], $\text{Na}[\text{Al}(\text{NH}_2)_4]$ [43,44], $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ [34], and $\text{Na}[\text{Al}(\text{CH}_3\text{NHBH}_3)_4]$ [37]. All of the above suggest that $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ has a similar tetrahedrally coordinated Al–N-chelated geometry.

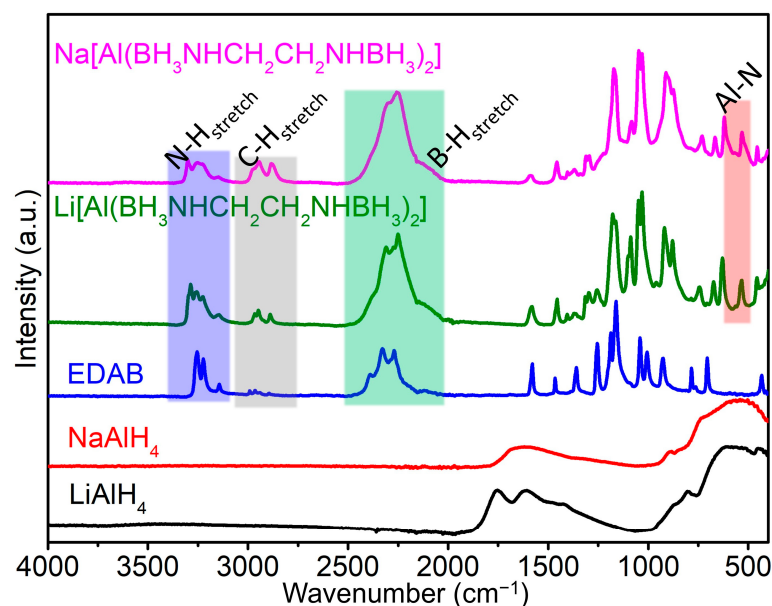


Figure 6. The IR spectra of LiAlH_4 , NaAlH_4 , EDAB, $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, and $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ (the stretch bond areas of N-H, C-H, and B-H are represented by blue, gray, and green rectangles; the Al-N bond is represented by a red rectangle).

Furthermore, the intensity of C-H stretching in $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ is higher than that in $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ and EDAB (as indicated by the gray area in Figure 6). This observation can be attributed to the presence of the C-H bonds of the THF molecules coordinating with Na^+ in $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$. This finding is consistent with the structural analysis and the results of thermal decomposition. The latter will be discussed in the following section.

2.3. Thermal Dehydrogenation of $M[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ ($M = \text{Li}$ and Na)

2.3.1. Thermal Dehydrogenation of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$

Before studying the thermal decomposition of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, we conducted a PXRD analysis to assess its stability in the air. The results revealed that $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ is highly sensitive to air. After being exposed to air for just a minute, the peaks attributed to the free EDAB noticeably increased. Furthermore, after 15 min, the signals corresponding to $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ completely disappeared (Figure 7). Only the peaks of EDAB were observed in the PXRD pattern, indicating that the Al-N bond was broken upon the contact of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ with air.

Due to the extreme instability of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ in air, its thermal stability was examined using thermogravimetric analysis (TGA) under an inert argon atmosphere, covering a temperature range from room temperature to 280°C . The TGA results showed that the thermal decomposition of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ started at approximately 104°C . In contrast to the starting compound EDAB [40], the thermal decomposition of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ did not exhibit weight oscillation (jet effect), as can be seen in Figure 8A, which is considered a drawback of the thermal dehydrogenation of NH_3BH_3 and its derivatives.

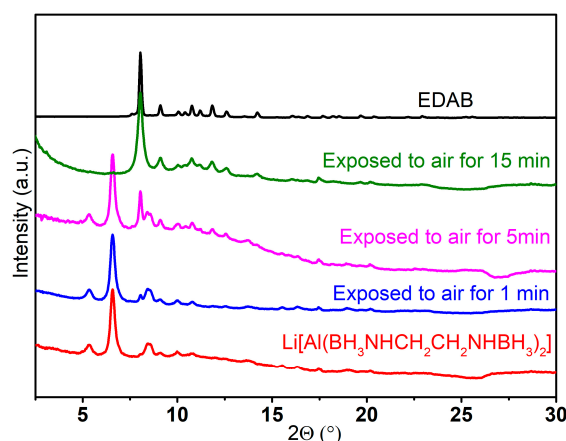


Figure 7. PXRD pattern of EDAB, $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, and $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ exposed to air for 1, 5, and 15 min ($\lambda = 0.71073 \text{ \AA}$).

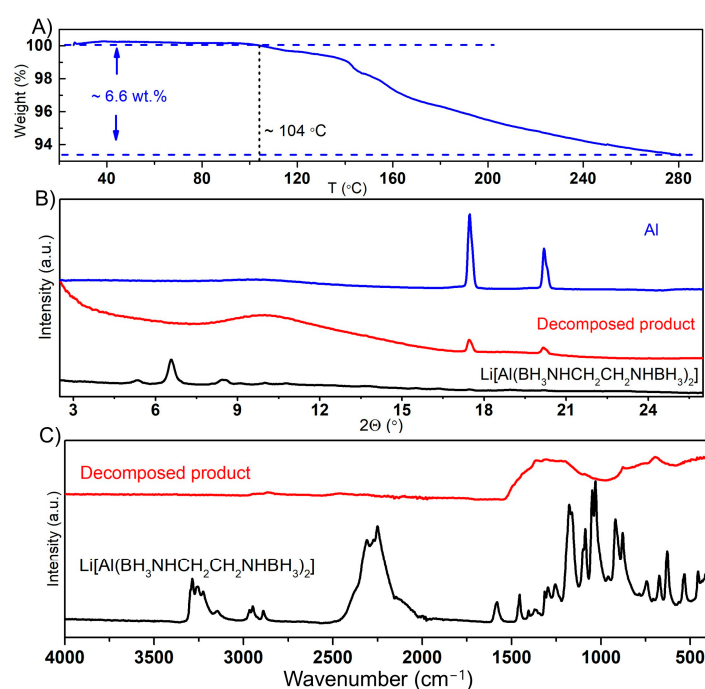


Figure 8. Thermogravimetric analysis (TGA) of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ (A); PXRD pattern of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, the thermally decomposed product, and aluminum (B); ATR-IR spectra of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ and of the thermally decomposed product (C) ($\lambda = 0.71073 \text{ \AA}$).

Based on PXRD and IR analyses, the solid decomposition products obtained after heating at 280°C were identified as amorphous phase(s) lacking N-H and B-H bonds but containing metallic aluminum (Figure 8B,C). The mass loss during the thermal decomposition of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ was approximately 6.6 wt.%, which is within the expected value for the release of pure H_2 (7.8% for theoretical hydrogen content of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, excluding hydrogen on carbon).

The purity of the gas released during the thermal dehydrogenation of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ was analyzed using temperature-programmed mass spectrometry (TPMS) in the temperature range from room temperature to 280°C . The TPMS analysis was performed within a glovebox under an argon atmosphere to prevent contamination by moisture, as $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ is highly sensitive to it. Due to the small size of the crucible, the signals' intensities for the released gases in the mass spectrometry results

were not as high as that of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$. Nevertheless, the hydrogen signals were visible, despite the challenges associated with detecting hydrogen due to its light weight. No signals corresponding to other gases were observed, confirming that ammonia (NH_3), diborane (B_2H_6), ethylenediamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), and THF were not released during the decomposition process. Only hydrogen was detected (Figure 9).

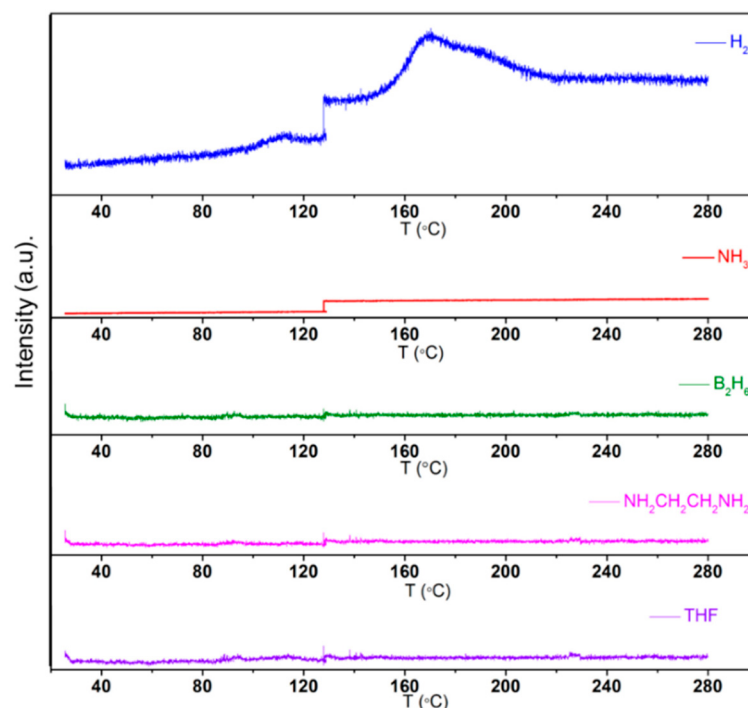


Figure 9. Mass spectrometry data for $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ decomposition.

These findings indicate that $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ releases approximately 6.6 wt.% of pure hydrogen when heated to 280 °C. The successful formation of this novel Al-based amidoborane compound suggests that it effectively suppresses the release of unwanted by-products during thermal hydrogen desorption. These by-products are particularly prominent in NH_3BH_3 and are also observed, though to a lesser extent, in other metallic amidoboranes [12], such as NaNH_2BH_3 , $\text{NaLi}(\text{NH}_2\text{BH}_3)_2$, $\text{NaMg}(\text{NH}_2\text{BH}_3)_3$, etc.

2.3.2. Thermal Dehydrogenation of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$

First, the stability of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ in the air was investigated based on PXRD and compared to $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$. The Na-based compound demonstrated higher stability in ambient air (Figure 10). No changes were observed in the PXRD pattern of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ during the initial 30 min of exposure to air. However, after 1 h, the peaks corresponding to EDAB appeared due to hydrolysis, and after 2.5 h of exposure, the PXRD pattern of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ completely changed into that of EDAB.

The coordination of THF to Na^+ in $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ may contribute to the better binding of $[\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3]^{2-}$ to Al^{3+} . This may hinder the interaction of water molecules with both Al and Na, leading to the increased stability of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ over a longer period of time in ambient air.

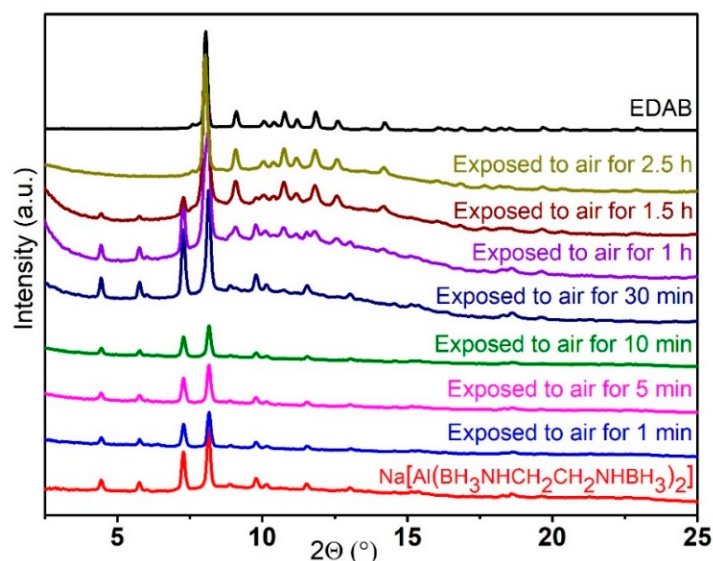


Figure 10. The PXRD patterns of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, exposed to air for different periods of time, and the pattern of EDAB ($\lambda = 0.71073 \text{ \AA}$).

Due to the good stability of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ in the air, we studied its thermal decomposition under an inert nitrogen atmosphere using an instrument installed outside of a glovebox. The thermal decomposition of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ occurs in a single step, initiated at approximately 55°C and exhibiting a continuous weight loss without oscillation (jet effect), in contrast to the behavior observed in the case of EDAB [40] (Figure 11A). Compared to $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, decomposing at 104°C , the sodium salt started to decompose at a lower temperature (55°C). After heating to 240°C , the solid decomposition products were identified as the known crystalline NaBH_4 , along with some unknown crystalline and amorphous phases containing C-H bonds (Figure 11B,C). The formation of BH_4^- during the thermal decomposition is similar to $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ [34] and $\text{Na}[\text{Al}(\text{CH}_3\text{NHBH}_3)_4]$ [37]. The mass loss during the thermal decomposition of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ from room temperature to 240°C was $\sim 13.3 \text{ wt.}\%$. This value exceeds the hydrogen content of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, which is $5.4 \text{ wt.}\%$ (excluding H on carbon). This should be caused by the release of THF coordinated to Na^+ evolving along with hydrogen during the thermal decomposition.

To better understand the dehydrogenation of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, we performed mass spectrometry analysis in the temperature range from 40°C to 240°C . The results revealed that hydrogen and THF were released. Notably, we did not find the signals of ammonia (NH_3), diborane (B_2H_6), or ethylenediamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), which are usually released along with H_2 during the thermal dehydrogenation of NH_3BH_3 and its derivatives (Figure 12).

To avoid the influence of the THF on the hydrogen released from $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, we attempted to remove THF from $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ via pumping at elevated temperatures or via washing with other lower boiling point solvents (such as diethyl ether and dichloromethane). We also tried to synthesize $\text{Na}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ in other solvents such as toluene, 1,4-dioxane and dichloromethane, hexane, etc. However, all attempts were unsuccessful in removing THF from its adduct with $\text{Na}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ without the decomposition of the latter. From the mass spectrometry (Figure 12), we found that H_2 is released from about 60°C , and THF release started at about 90°C . This is why we cannot remove THF via vacuum at elevated temperatures. Overall, the formation of

$\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ suppressed the liberation of common byproducts such as NH_3 and B_2H_6 .

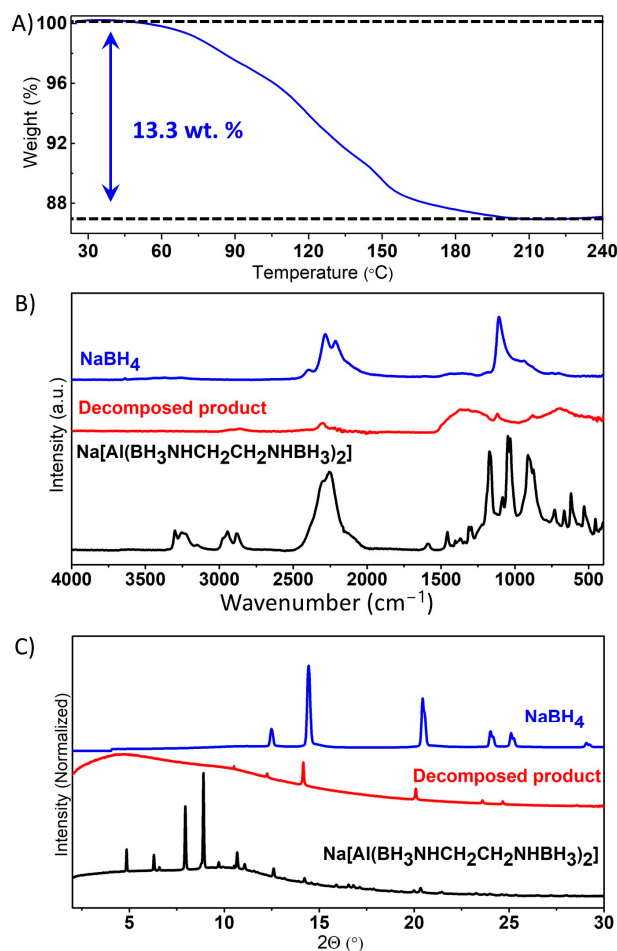


Figure 11. Thermogravimetric analysis (TGA) of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ (A); ATR-IR spectra of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, the thermally decomposed product containing NaBH_4 (B); PXRD patterns of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, the thermally decomposed product and of NaBH_4 (C) ($\lambda = 0.77509 \text{ \AA}$).

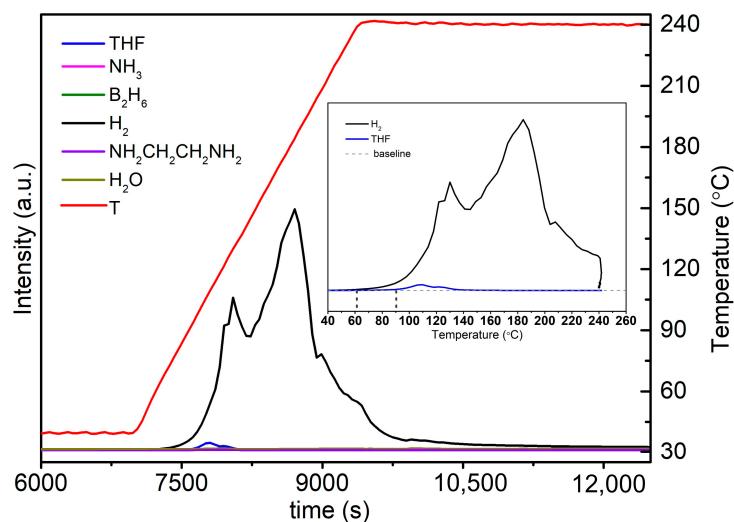


Figure 12. Mass spectrometry data for $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ decomposition.

3. Materials and Methods

All samples were obtained from commercially available NaAlH_4 (93%), LiAlH_4 (>98%), NaBH_4 (97%), $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \cdot 2\text{HCl}$ (98%), and anhydrous THF ($\geq 99.9\%$), toluene (99.85%), hexane ($\geq 99.9\%$), diethyl ether ($\geq 99.5\%$), 1,4-dioxane ($\geq 99.5\%$), and CH_2Cl_2 (99.5%), which were purchased from Sigma-Aldrich Co., Ltd., (Saint Louis, MO, USA). All operations were performed in a glovebox with a high-purity argon atmosphere.

3.1. Synthesis of $\text{BH}_3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{BH}_3$ (EDAB)

EDAB was obtained through a procedure adapted from the literature [38]. In brief, the synthesis was performed as follows. Powdered NaBH_4 (1.40 g, 37 mmol), $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \cdot 2\text{HCl}$ (2.40 g, 18 mmol), and THF (250 mL) were added to a 500 mL, three-neck, round-bottom flask. The obtained suspension was then vigorously stirred at room temperature under an argon atmosphere for 48 h. Then, the solid co-product (NaCl) was removed from the reaction mixture by filtration, and the solvent of the collected filtrate was removed through evaporation under reduced pressure (using a rotary evaporator) to obtain EDAB. The white solid was washed with diethyl ether three times and then dried under a vacuum for 4 h to eliminate residual solvents. The product was characterized by means of ^1H (Figure 13A), ^{11}B (Figure 13B), and ^{13}C (Figure 13C) NMR and PXRD (Figure 13D). Notably, the ^{11}B NMR spectrum exhibits a broad peak instead of the expected multiplet. This phenomenon is likely attributed to the structural characteristics of EDAB. Due to its relatively long molecular framework, EDAB may undergo bending or folding, creating a more complex chemical environment for the terminal boron atoms. As a result, these boron nuclei are not only influenced by their directly bonded hydrogen atoms but also by additional intramolecular hydrogen interactions, which may disrupt the expected coupling patterns and lead to the observed broad peak.

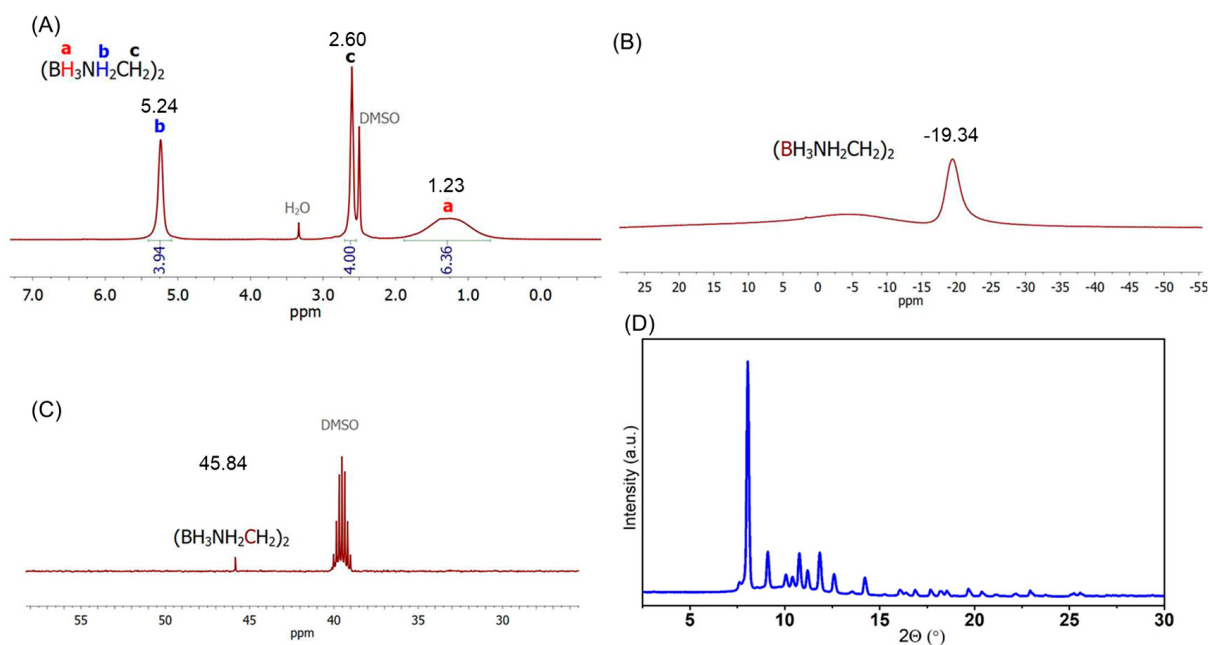


Figure 13. ^1H (A), ^{11}B (B), ^{13}C NMR (C) spectra and PXRD (D) pattern of EDAB ($\lambda = 0.71073\text{ \AA}$).

3.2. Synthesis Method of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$

Sample Li-A: 1 eq. of LiAlH_4 (26.9 mg, 0.7 mmol) and 2 eq. of EDAB (124.63 mg, 1.4 mmol) were placed into an 80 mL stainless steel vial with three 10 mm diameter stainless steel balls and milled in a planetary ball mill (Fritsch Pulverisette 7 Premium line, Fritsch, Markt Einersheim, Germany). The evolution of the gas pressure and temperature during

the reaction was observed using the Easy GTM detection system accessory (Fritsch). The rotation speed was set to 600 rpm, and the ball-to-powder mass ratio was 30:1. The synthesis was performed using 240 milling cycles of 3 min milling interrupted by 5 min cooling breaks to yield dark gray powder. The product was characterized by means of PXRD (Figure 14).

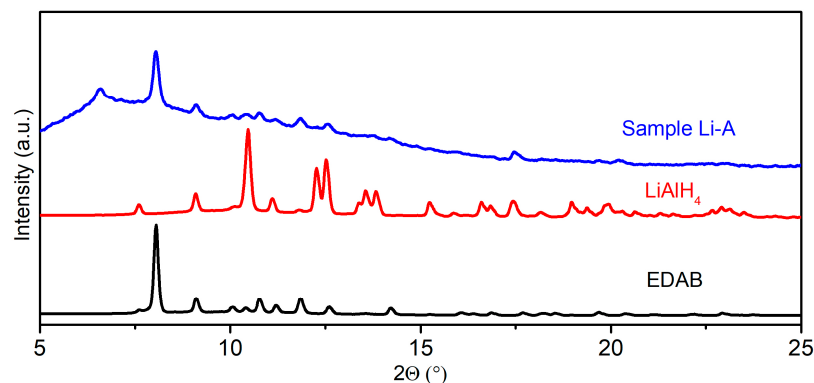


Figure 14. PXRD patterns of EDAB, LiAlH_4 , and Sample **Li-A** ($\lambda = 0.71073 \text{ \AA}$).

Sample Li-B: The samples were produced using the same quantities of the reactants as for Sample **Li-A**. The rotation speed was set to 500 rpm, and the ball-to-powder mass ratio was 80:1. The synthesis was performed using 50 milling cycles of 30 min milling interrupted by 15 min cooling breaks to yield dark gray powder. The product was characterized by means of PXRD (Figure 1).

3.3. Synthesis Method of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$

Powdered NaAlH_4 (81 mg, 1.5 mmol), EDAB (263.3 mg, 3.0 mmol), and anhydrous THF (30 mL) were added to a 100 mL, one-neck, round-bottom Schlenk flask. The obtained suspension was then vigorously stirred at room temperature under an argon atmosphere for 24 (Sample **Na-A**), 48 (Sample **Na-B**), and 72 h (Sample **Na-C**), respectively. Then, the solvent was removed using a vacuum, and the resulting white solid was dried under a vacuum for another 5 h to eliminate residual solvents. The product was characterized by means of PXRD (Figure 3).

Attempts for the Synthesis of $\text{Na}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ without THF solvents

The procedure was similar to that of Sample **Na-B**. Powdered NaAlH_4 (81 mg, 1.5 mmol), EDAB (263.3 mg, 3.0 mmol), and anhydrous toluene, hexane, diethyl ether, 1,4-dioxane, or CH_2Cl_2 (30 mL) were added to a 100 mL, one-neck, round-bottom Schlenk flask. The obtained suspension was then vigorously stirred at room temperature under an argon atmosphere for 48 h. Then, the solvent was removed using a vacuum, and the resulting white solid was dried under a vacuum for another 5 h to eliminate residual solvents.

Attempts to remove THF solvents in Sample Na-B

A sample of **Na-B** powder (~100 mg) was placed into a glass tube and dried under a vacuum at 30 °C, 50 °C, and 70 °C for 48 h, using a tubular oven to remove THF solvents.

3.4. NMR Experiments

^1H , ^{13}C , and ^{11}B nuclear magnetic resonance spectra were recorded on a Bruker Avance 500 MHz spectrometer (Bruker, Billerica, MA, USA). ^1H , ^{13}C , and ^{11}B NMR chemical shifts are reported in ppm and calibrated against the residual signals of the deuterated DMSO.

3.5. Powder X-Ray Diffraction

Samples were carefully filled into 0.7 mm thin-walled glass capillaries (Hilgenberg GmbH, Malsfeld, Germany) within an argon-filled glovebox. To prevent contact with air, the capillaries were sealed with grease before being taken out of the glovebox. The sealed capillaries were then cut and promptly placed into wax on a goniometer head, ensuring that no air entered the capillary. Diffraction data were immediately collected using a MAR345 image-plate detector equipped with an Incoatec Mo ($\lambda = 0.71073 \text{ \AA}$) Microfocus (1 μS 2.0) X-ray source operating at 50 kV and 1000 μA . The resulting two-dimensional images were azimuthally integrated using the Fit2D software (V17.006), with LaB₆ serving as a calibrant.

Synchrotron PXRD patterns were collected with a PILATUS@SNBL diffractometer (SNBL, ESRF, Grenoble, France) equipped with a Dectris PILATUS 2M single-photon counting pixel area detector ($\lambda = 0.77509 \text{ \AA}$). Powder patterns were obtained by using raw data processed using the SNBL Toolbox software (<https://soft.snbl.eu/snbltb/snbltb.html>, version 2018.2.27, accessed on 20 February 2025), using the data for LaB₆ as a standard.

3.6. Crystal Structure Determination

The synchrotron PXRD data for Na(THF)[Al(BH₃NHCH₂CH₂NHBH₃)₂] were indexed in the tetragonal unit cell, and their structure was solved using global optimization using FOX software (version 1.9.7.0) [45]. The anions were modelled by conformationally free Z-matrices restraining bond distances and angles. Rietveld refinements were carried out in Fullprof [46], treating amidoboranes as separate rigid bodies within the complex anion and refining Na and Al as free atoms. The symmetry was confirmed using the ADDSYM routine in the program PLATON [47].

3.7. Fourier Transform Infrared Spectroscopy (FTIR)

Attenuated total reflectance (ATR)-IR spectra were recorded using a Bruker Alpha spectrometer. The spectrometer was equipped with a Platinum ATR sample holder, which featured a diamond crystal for single-bounce measurements. The entire experimental setup was located within an argon-filled glovebox to maintain an inert atmosphere during the measurements.

3.8. Thermogravimetric Analysis (TGA)

TGA measurements for the Li[Al(BH₃NHCH₂CH₂NHBH₃)₂] sample were conducted using a Netzsch STA 449 F3 TGA/DSC (Netzsch, Selb, Germany). The TGA/DSC was equipped with a stainless-steel oven and located within an argon-filled glovebox to ensure an inert atmosphere during the measurements. The sample was loaded into Al₂O₃ crucibles and subjected to a heating rate of 5 °C/min under an argon flow of 100 mL/min.

TGA measurements for the Na(THF)[Al(BH₃NHCH₂CH₂NHBH₃)₂] sample was conducted using a Mettler Toledo (New York, NY, USA) TGA/SDTA 851e instrument. The sample was placed in Al₂O₃ crucibles and subjected to a heating rate of 5 °C/min under a nitrogen flow of 100 mL/min.

3.9. Mass Spectrometry

Mass spectrometry analysis of Li[Al(BH₃NHCH₂CH₂NHBH₃)₂] was carried out with the use of a Hiden Analytical HPR-20 QMS (Hiden Analytical Ltd., Warrington, UK) sampling system, which was installed in a glovebox. The samples were loaded into an Al₂O₃ crucible and heated from room temperature to 300 °C (5 °C/min) in an argon flow of 100 mL/min. Gas evolution was monitored by recording the highest intensity peak for each gas, i.e., m/z of 2, 17, 26, 30, and 42 for H₂, NH₃, B₂H₆, NH₂CH₂CH₂NH₂, and THF respectively.

Mass spectrometry measurements for $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ were performed using a Hidden Catlab reactor combined with a quantitative gas analyzer (QGA) hidden quadrupole mass spectrometer (Hidden Analytical Ltd., Warrington, UK), which is installed outside of the glovebox. Before the experiment, samples were loaded into a quartz tube in between two layers of glass cotton under the protective atmosphere of an argon-filled glovebox. The two extremities of the quartz tube were sealed with Parafilm before being removed from the glovebox. The quartz tube was then installed in the sample holder outside the glovebox after quickly removing the Parafilm, and the argon flow (40 mL/min) was switched on immediately to prevent the contact of the sample with air. Samples were heated to 40 °C and kept isothermally for ~ 2 h to stabilize the temperature. Heating was then performed at a rate of 5 °C/min up to 240 °C corresponding to $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, followed by a 1 h isotherm. Gas evolution was monitored by recording the highest intensity peak for each gas, i.e., m/z of 2, 17, 18, 26, 28, 30, and 42 for H_2 , NH_3 , H_2O , B_2H_6 , N_2 , $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, and THF, respectively. H_2O and N_2 were monitored to check if the sample had come into contact with air or not.

4. Conclusions

We successfully synthesized $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ and $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ using mechanochemical synthesis and a wet chemical approach in THF from one equivalent of MAlH_4 ($\text{M} = \text{Li}$ and Na) and two equivalents of $\text{BH}_3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{BH}_3$, respectively. In comparison to NH_3BH_3 and $\text{CH}_3\text{NH}_2\text{BH}_3$, $\text{BH}_3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{BH}_3$ exhibited higher inertness and required more energy input to form an Al-N bond when reacting with NaAlH_4 . This favors the reaction conditions between otherwise extremely reactive LiAlH_4 and $\text{BH}_3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{BH}_3$ through mechanochemical synthesis and thus avoids the explosive reaction that occurs between LiAlH_4 and NH_3BH_3 .

In the structure of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$, the Al^{3+} ion is tetrahedrally coordinated to two $[\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3]^{2-}$ anions through nitrogen atoms and forms chelates. The formation of the Al-N bond in $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ and $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ was confirmed through IR spectroscopy.

Thermogravimetric analysis (TGA) and mass spectrometry revealed that $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ releases 6.6 wt.% of pure hydrogen from room temperature to 280 °C. The TGA and mass spectrometry analysis of $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ indicated that the released hydrogen was contaminated with THF. Nevertheless, the formation of $\text{Li}[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ and $\text{Na}(\text{THF})[\text{Al}(\text{BH}_3\text{NHCH}_2\text{CH}_2\text{NHBH}_3)_2]$ effectively suppressed the release of by-products that typically contaminate hydrogen during the thermal dehydrogenation of NH_3BH_3 and its derivatives, such as NH_3 and B_2H_6 .

In this work, it has been confirmed that the substitution on the N-side of NH_3BH_3 allows the formation of stable chelate complexes that exhibit an effective suppression of the release of the common gaseous impurities. Furthermore, these compounds are the first examples of chelated aluminum amidoborane complexes.

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