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Abstract

A new ammine complex, Li₂B₁₂H₁₂·7NH₃, that can reversibly release all the NH₃ at below 200°C and reabsorb NH₃ at room temperature and 0.5 bar was synthesized and investigated for reversible ammonia storage or indirect hydrogen storage.

Keywords

complex, ammine, 7nh₃, li₂b₁₂h₁₂, hydrogen, indirect, storage, ammonia

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Li₂B₁₂H₁₂·7NH₃: a new ammine complex for ammonia storage or indirect hydrogen storage†

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A new ammine complex, Li₂B₁₂H₁₂·7NH₃, that can reversibly release all the NH₃ at below 200 °C and reabsorb NH₃ at room temperature and 0.5 bar was synthesized and investigated for reversible ammonia storage or indirect hydrogen storage.

All direct hydrogen storage materials under investigation today fall short of the US DOE targets.¹ None of the high-capacity (high weight percent) hydrogen storage materials works at mild operating conditions and has good reversibility.² Therefore, ammonia has been proposed as an alternative hydrogen carrier.³ Molecular ammonia contains 17.8 wt% H and can be catalytically converted to hydrogen and nitrogen at temperatures below 380 °C in high yields.⁴ The most recent research on reversible NH₃ storage illustrates how a practical, reversible storage capacity of up to 10 wt% H can be achieved by metal ammines such as Mg(NH₃)₆Cl₂ and Ca(NH₃)₈Cl₂.³ Mg(NH₃)₆Cl₂, for example, releases 4 of the 6 ammonia molecules at around 170 °C and the remaining 2 ammonia below 425 °C, totaling 9.19 wt% H indirectly, and fully absorbs ammonia at room temperature under about 4 bar ammonia overnight. Furthermore, a highly developed ammonia infrastructure including manufacturing, handling, and transporting is already well established around the world.⁵ This gives an advantage for using ammonia as an energy carrier over hydrogen, at least for the short term.

Although there exist many ammine complexes,⁶ so far, only a handful of them such as Ca(NH₃)₈Cl₂, Mg(NH₃)₆Cl₂, and Ni(NH₃)₆Cl₂ have been investigated for indirect hydrogen storage applications, due to the requirements of storage capacity and operating conditions. Therefore, a proper combination of cation and anion which leads to a suitable structure that favors the ammonia pickup and release is key to the search for reversible ammonia storage. The resistance to hydrolysis and oxidation and the high thermal stability of dodecahydro-closo-dodecaborate⁷ make [B₁₂H₁₂]^{2−} an interesting anion for the ammine complex. In order to improve the gravimetric capacity for the ammonia storage, the lightest metal cation, Li, was chosen to balance the electric charge. In this paper, a new ammine complex, Li₂B₁₂H₁₂·7NH₃, is discussed in terms of its structure, indirect hydrogen storage capacity, reversibility,

and thermal stability. Based on this compound, a series of dodecahydro-closo-dodecaborate ammine complexes with different cations can be synthesized and more information can be obtained for indirect hydrogen storage.

All synthesis procedures were performed in a standard high-vacuum line and a glove box unless otherwise stated. Solvents and ammonia are dried prior to use. Li₂B₁₂H₁₂ was prepared according to the published method.⁸ Li₂B₁₂H₁₂·7NH₃ was obtained by charging anhydrous Li₂B₁₂H₁₂ with either dry gaseous ammonia at room temperature or dry liquid ammonia at −78 °C. Thin plate-shaped colorless single Li₂B₁₂H₁₂·7NH₃ crystals were produced in tetrahydrofuran solution. X-Ray single crystal diffraction data were collected on a Nonius Kappa CCD diffractometer and analyzed using SHELXTL-97 structure solution package to resolve the structure.⁹ X-Ray powder diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and infrared (IR) absorption techniques were also applied for characterization.

The crystallographic data are listed in Table 1. Selected bond lengths and bond angles are given in Table 2. The structure is depicted in Fig. 1. The new compound is ionic and consists of [Li(NH₃)₃]⁺, [Li(NH₃)₄]⁺, and anion [B₁₂H₁₂]^{2−}. This structure is quite different from heptahydrate Li₂B₁₂H₁₂·7H₂O⁸ where water molecules form two [Li(4H₂O)]⁺ tetrahedra with eclipsed conformation, and the tetrahedra links to a dimer *via* a common corner.

The ammonia bound to the central Li cation in the [Li(NH₃)₄]⁺ occupy the corners of a distorted tetrahedron. The angle of 96.4(2)° between N₁–Li₁–N₂ is almost the same as 97.8(2)° of N₃–Li₁–N₄, but much smaller than 120.7(2)° of N₁–Li₁–N₃ and 121.7(2)° of N₂–Li₁–N₄. The Li–N distances are about the same, within 3 esd's, from

Table 1 Crystallographic information for Li₂B₁₂H₁₂·7NH₃

Empirical formula	H ₃₃ B ₁₂ Li ₂ N ₇
Formula weight	274.93
Lattice	Monoclinic
Space group	P2 ₁ /n
Z	4
D _{calc} /g cm ^{−3}	0.961
a/Å	8.3050(17)
b/Å	14.729(3)
c/Å	15.728(3)
β/°	98.90(3)
V/Å ³	1900.7(7)
T/°C	−123
μ/mm ^{−1}	0.051
R1 [I > 2σ(I)] ^a	0.0584
wR2 (all data) ^b	0.1849

^a R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^b wR2 = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.00827P)^2 + 0.05P]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

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† Electronic supplementary information (ESI) available: Experimental details on synthesis and characterization of both Li₂B₁₂H₁₂ and Li₂B₁₂H₁₂·7NH₃. CCDC reference number 761426. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b923829h

Table 2 Selected bond lengths and angles

Distance/Å	Li ₁ –N ₁	2.096(4)
	Li ₁ –N ₂	2.095(4)
	Li ₁ –N ₃	2.082(4)
	Li ₁ –N ₄	2.095(4)
	Li ₂ –N ₅	2.045(4)
	Li ₂ –N ₆	2.048(5)
	Li ₂ –N ₇	2.038(5)
Angles/°	N ₁ –Li ₁ –N ₂	96.4(2)
	N ₁ –Li ₁ –N ₃	120.7(2)
	N ₁ –Li ₁ –N ₄	100.7(1)
	N ₂ –Li ₁ –N ₃	119.7(1)
	N ₂ –Li ₁ –N ₄	121.7(2)
	N ₃ –Li ₁ –N ₄	97.8(2)
	N ₅ –Li ₂ –N ₆	111.7(2)
	N ₅ –Li ₂ –N ₇	111.2(2)
	N ₆ –Li ₂ –N ₇	110.0(2)

Fig. 1 Asymmetric unit of $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot 7\text{NH}_3$, showing 25% probability thermal ellipsoids. Hydrogen atoms are drawn with an arbitrary radius.

2.096(4) Å of Li₁–N₁ to 2.082(4) Å of Li₁–N₃. With respect to $[\text{Li}(\text{NH}_3)_3]^+$, the 3 Li–N angles have a much smaller range of values (111.0 to 111.7°) than that in the tetrahedral $[\text{Li}(\text{NH}_3)_4]^+$, and Li–N distance is similar, *i.e.* about 2.045 Å. The Li–N distance in $[\text{Li}(\text{NH}_3)_3]^+$ is shorter than that in the tetrahedral $[\text{Li}(\text{NH}_3)_4]^+$, where the extra N atom increases the steric hindrance and electric repulsion. The Li cation is situated above the center of the trigonal plane formed by the three N atoms, and is coordinated to three B–H vertices. On the contrary, the $[\text{Li}(\text{NH}_3)_4]^+$ is attracted to the $[\text{B}_{12}\text{H}_{12}]^{2-}$ through Coulomb attraction, since the shortest H–H distance ($\text{H}_{2\text{B}}\text{–H}_3$) is 2.280(7) Å, much longer than the common dihydrogen bond lengths, 1.7–2.2 Å.¹⁰

The reversibility of ammonia storage can be demonstrated through powder XRD pattern (Fig. 2). The starting anhydrous $\text{Li}_2\text{B}_{12}\text{H}_{12}$ was charged with ammonia by two means: under 0.5 bar ammonia and liquid ammonia. Both ways produce the same ammine complex as indicated by the XRD pattern (Fig. 2, b and c). The desorption was carried out at 200 °C under dynamic vacuum. The temperature was chosen based on the DSC and TGA results which are discussed later in the paper. It is clear that after the 1st and 3rd desorption, the host material maintains the same structure as the starting anhydrous $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (Fig. 2, a, d, and f). The ammine complex after the 1st and 3rd charge also shares the same structure as indicated by the powder

Fig. 2 Powder XRD patterns. Samples were loaded into capillaries and sealed in a glove box.

XRD pattern, which is identical to the calculated pattern based on single crystal diffraction of $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot 7\text{NH}_3$ (Fig. 2, b, e and g).

The infrared absorption of the anhydrous $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and ammine complex is shown in Fig. 3. The integrity of the boron cage after desorption was verified again since the spectrum from the anhydrous $\text{Li}_2\text{B}_{12}\text{H}_{12}$ shows the same absorption peaks as after the 3rd desorption (Fig. 3, a and c). Note that the characteristic stretching absorption peak from B–H at 2470 cm^{-1} splits into 2458 cm^{-1} and 2515 cm^{-1} for the anhydrous $\text{Li}_2\text{B}_{12}\text{H}_{12}$. The split was also found for

Fig. 3 IR spectra. Samples were suspended in IR grade mineral oil.

Fig. 4 DSC traces of $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot 7\text{NH}_3$ with ramp rate of 1, 5 and 10 $^\circ\text{C min}^{-1}$. Inset is the TGA curves with a ramp rate of 5 $^\circ\text{C min}^{-1}$.

$\text{Rb}_3\text{Br}[\text{B}_{12}\text{H}_{12}]^{11}$ and was attributed to the loss of the symmetry of the icosahedral dianion $[\text{B}_{12}\text{H}_{12}]^{2-}$. For the ammine complex, however, the symmetry of the boron cage remains, as indicated by the single characteristic stretching absorption peak at 2470 cm^{-1} . As for the IR spectrum of the ammine complex, the peak at 3360 cm^{-1} and 1150 cm^{-1} is associated with the characteristic NH_3 absorption.¹² The ammine complex is extremely sensitive to moisture since the strong absorption peak at 3600 cm^{-1} associated with water was found after the material was exposed to air for 15 min, and the NH_3 absorption at 1150 cm^{-1} disappeared as well.

The thermal stability of the compound can be derived from DSC (Fig. 4) and TGA curves (Fig. 4 inset). There are four endothermic peaks during heating, with the first three peak positions shifting to higher temperature when the ramp rate is increased from 1 $^\circ\text{C min}^{-1}$ to 10 $^\circ\text{C min}^{-1}$. Combined with the TGA curve (the inset), it is found that these three peaks are associated with ammonia desorption. The last endothermic peak at 350 $^\circ\text{C}$ is due to a phase change, since there is no weight loss beyond 250 $^\circ\text{C}$ and XRD study of the material heat treated at 370 $^\circ\text{C}$ for 30 min showed a different pattern than that of the initial complex (see ESI†). Both TGA and DSC curves indicate that the ammine complex decomposes in steps. As can be found from the TGA curve, after the first step, *i.e.* around 100 $^\circ\text{C}$, 3 out of the 7 ammonia were discharged, and then the remaining 4 ammonia were released during the second step at about 200 $^\circ\text{C}$. Thus, the ammine complex can give off 43.36 wt% NH_3 at below 200 $^\circ\text{C}$. $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ releases six ammonia through three steps: $6 \rightarrow 2$, $2 \rightarrow 1$, $1 \rightarrow 0$, at about 170 $^\circ\text{C}$, 300 $^\circ\text{C}$ and 400 $^\circ\text{C}$ respectively.³ Although these data

were obtained using a different technique (temperature programmed desorption) with a different setup, it still shows that $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot 7\text{NH}_3$ has better desorption behavior, *i.e.* higher capacity at lower temperatures, which is crucial for real applications.

Our preliminary investigation has shown that no degradation in capacity has been found after 10 cycles, which indicates that $\text{Li}_2\text{B}_{12}\text{H}_{12}$ can reversibly charge and discharge 43.36 wt% NH_3 under such moderate conditions. The noticeable reversibility of this new ammine complex at mild working conditions indicates that it may be a promising candidate for indirect hydrogen storage. Other cations such as calcium, potassium and aluminum can be explored. Our preliminary results have ruled out the ammine complexes of $\text{MgB}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ due to their low storage capacities.

In summary, anhydrous $\text{Li}_2\text{B}_{12}\text{H}_{12}$ picks up seven ammonia at room temperature under 0.5 bar and it releases all the ammonia under 200 $^\circ\text{C}$; thus, this compound can store 43.36 wt% NH_3 under very mild operating conditions. The remarkable reversibility makes it suitable for ammonia storage or indirect hydrogen storage.

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