## Supplementary Information

# Synthesis, Structure and Dehydrogenation of Magnesium Amidoborane Monoammoniate

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#### **Experimental Procedures:**

Synthesis of  $Mg(NH_2BH_3)_2 \cdot NH_3$ : MgNH was prepared as described in Ref. 8 A mixture of homemade MgNH (~95 % in purity) and NH\_3BH\_3 (97%, Sigma Aldrich) in the molar ratio of 1 to 2 was milled on a Retsch PM400 at 200 rpm for 10 hours. All the materials handlings were performed inside a Mbraun glovebox that was filled with purified argon.

*Thermal desorption behavior*: Temperature dependences of hydrogen desorption from the post milled sample was conducted on a homemade temperature-programmed desorption coupled with a mass spectrometer (TPD-MS). Differential scanning calorimetry (DSC) measurements were performed on a Netsch 449C TG/DSC unit. A dynamic flow mode was employed with purified argon as a carrier gas and the heating rate was set at 2 °C/min. The quantitative measurements of gas evolution from samples (i. e., volumetric release) were performed on a home-made Sievert type reactor.

 $NH_3$  detection: NH<sub>3</sub> concentration was determined by using a conductivity meter (Thermo Scientific) with the accuracy of 0.1 µS/cm. 100 ml of (0.0006 M) diluted sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solution was prepared. At the end of quantitative measurement (i. e., volumetric dehydrogenation conducted in the Sievert type reactor), gaseous product accumulated in the reactor was bubbled in the diluted H<sub>2</sub>SO<sub>4</sub> solution. The change in conductivity of the solution reflects to the amount of NH<sub>3</sub> trapped by the solution and correlates to NH<sub>3</sub> co-produced in the dehydrogenation.

*Characterization*: Structure identifications were carried out on a PANalytical X'pert diffractometer with Cu K $\alpha$  radiation (40 kV, 40 mA) and the synchrotron X-ray powder diffractometer at Shanghai Synchrotron Radiation Facility. The obtained data were indexed using TREOR or DICVOL programs. Candidate structures were obtained by performing simulated annealing with four formula units of Mg(NH<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>·NH<sub>3</sub> in the unit cell. Rietveld structural refinement analyses were performed using the Rietica programs.<sup>S1</sup> FTIR measurements were conducted on a Varian 3100 unit in DRIFT mode. <sup>11</sup>B NMR experiments were carried out on the Varian Inova 800-MHz (18.8 T) nuclear magnetic resonance (NMR) spectrometer at PNNL and the <sup>11</sup>B NMR signals were referenced to BF<sub>3</sub>Et<sub>2</sub>O at 0 ppm.

*Crystal data of MgAB·NH*<sub>3</sub>: measurement at room temperature, formula MgN<sub>3</sub>B<sub>2</sub>H<sub>13</sub>, monoclinic, space group *P21/A*, a = 8.8815(6) Å, b = 8.9466(6) Å, c = 8.0701(5) Å,  $\beta = 94.0744(48)$  °, V = 639.62(7) Å<sup>3</sup>, Z = 4,  $\rho_{cal} = 1.049$  gcm<sup>-3</sup>. CSD-421368 contains the supplementary crystallographic data for this paper.

#### **Theoretical Calculation:**

For the first-principle calculations based on the density function theory (DFT) and the pseudo-potential plane wave method, we adopted the projector augmented wave (PAW) pseudo-potentials<sup>S2</sup> as implemented in the Vienna ab initio simulation package (VASP).<sup>S3,S4</sup> The generalized gradient approximation (GGA-PW91) was used to treat the electronic exchange-correlation energy. Full ionic relaxation and volumetric relaxation were conducted on the geometry optimized candidate structure until self-consistency was achieved within a tolerance of a total energy of 0.01 meV and atomic forces of 0.01 eV/Å.

### **Figures and Tables**



Figure S1. Reactions of NH<sub>3</sub>BH<sub>3</sub> (AB) and hydrides in THF.

ca. 1 equiv. of H<sub>2</sub> (per AB) can be released from LiH-AB and CaH<sub>2</sub>-2AB to form LiAB and CaAB. However, in the case of MgH<sub>2</sub>-2AB, a kind of interaction does occur but H<sub>2</sub> evolution did not stop at 1 equiv. H<sub>2</sub>, indicating that "MgAB" is rather unstable and it will further decompose in THF solution.



**Figure S2.** Simulated structure of Mg(NH<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>. Magnesium is represented by green sphere, nitrogen by blue sphere, boron by orange sphere, and hydrogen by white sphere.

In comparison to MgAB·NH<sub>3</sub>, MgAB has less ligand coordinated to its Mg center and does not have complete bonding network (either dihydrogen bond or coordination) as there is no close contact between slabs.



*Figure S3.* XRD patterns of post milled MgNH-2AB and post deammoniated  $Mg(NH_2)_2$ -2AB samples.



Figure S4. Rietveld fit of the XRD pattern of MgAB·NH<sub>3</sub>.

The crystal structure of MgAB·NH<sub>3</sub> was determined by combined direct space simulated annealing method and first principle calculations. Since samples were prepared by high energy ball milling, the quality of the XRD data was not good enough to allow the independent determination of all atoms. Therefore, NH<sub>2</sub>BH<sub>3</sub> and NH<sub>3</sub> were treated as rigid bodies with common bond lengths and bond angles during direct space simulated annealing and refinement, which lead to large final agreement factors of Rp = 11.98 % and Rwp = 17.55 %. To identify the crystal structure of MgAB·NH<sub>3</sub>, first-principles calculations were used. The fully relaxed structure of MgAB·NH<sub>3</sub> from first-principles calculations has lattice constants of a = 8.8174 Å, b= 9.0794 Å, c = 8.1299 Å, and  $\beta = 95.2014$  °, which is consistent with the observed pattern. The discussion on the structural information in this paper was based on the calculated crystal structure of MgAB·NH<sub>3</sub>.



*Figure S5.* DSC measurement on MgAB·NH<sub>3</sub> at the heating rate of 2 °C/min.

Table S1. Calculated structural parame	ter of Mg(NH <sub>2</sub> BH <sub>3</sub> ) <sub>2</sub> (s	space group C2, $a =$
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	Mg(NH <sub>2</sub> BH <sub>3</sub> ) <sub>2</sub>				
Atoms	Х	у	Z		
Mg1	0.00000	0.76966	0.00000		
B1	0.82339	0.05324	0.81951		
N1	0.64574	0.04540	0.77936		
H1	0.89542	0.88442	0.71438		
H2	0.11683	0.23641	0.25764		
Н3	0.84195	0.04189	0.03678		
H4	0.63216	0.08505	0.60438		
H5	0.39762	0.87576	0.19833		

8.5722 Å, b = 5.6048 Å, c = 5.6216 Å and  $\beta = 85.8476$  °).

**Table S2.** Interatomic distances (Å) and bond angles (°) in crystal structure of Mg(NH<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>.

Ato	oms	Bond distance (Å)	Atoms		Bond distance (Å)
Mg1	N1	2.111	N1	H4	1.023
B1	N1	1.556	N1	Н5	1.025
B1	H1	1.254	H2…H5		2.084
B1	H2	1.213	Н3…Н5		2.149
B1	H3	1.245	∠B1–N1–Mg1		116.22 °

**Table S3.** Calculated structural parameter of  $Mg(NH_2BH_3) \cdot NH_3$  (space group P21/A,

$Mg(NH_2BH_3)_2 \cdot NH_3$							
Atoms	Х	у	Z	Atoms	Х	у	Z
Mg1	0.23180	0.42535	0.28130	Н5	0.79427	0.17823	0.75396
B1	0.54172	0.27410	0.20300	Н6	0.70739	0.16250	0.51990
B2	0.73086	0.24825	0.63841	H7	0.81683	0.40806	0.47338
N1	0.47063	0.38665	0.31862	H8	0.94460	0.35540	0.61731
N2	0.83181	0.38311	0.59648	Н9	0.68387	0.28259	0.21758
N3	0.72493	0.99484	0.03085	H10	0.50173	0.29549	0.05691
H1	0.81817	0.92962	0.01757	H11	0.50289	0.14749	0.23799
H2	0.72868	0.07529	0.94230	H12	0.51911	0.48818	0.30497
Н3	0.63411	0.92884	0.99276	H13	0.50151	0.35794	0.43907
H4	0.60503	0.28932	0.67553				

a = 8.8174 Å, b = 9.0794 Å, c = 8.1299 Å and  $\beta = 95.2014$  °).

Table	S4.	Interatomic	distances	(Å)	and	bond	angles	(°)	in	crystal	structure	of
Mg(NH	I2BH	3)·NH3.										

Ato	oms	Bond distance (Å)	Ato	oms	Bond distance (Å)
Mg1	N1	2.129	N3	Н3	1.025
Mg1	N2	2.104	Mg1	Н6	2.126
Mg1	N3	2.157	Mg1	Н9	1.993
B1	N1	1.558	Mg1	H11	2.123
B1	Н9	1.251	H1.	··H9	2.330
B1	H10	1.223	H1	·H10	2.132
B1	H11	1.240	H2·	··H5	1.927
N1	H12	1.026	H3…H10		2.379
N1	H13	1.026	H3…H11		2.247
B2	N2	1.569	H4…H8		1.957
B2	H4	1.234	H4…H12		2.310
B2	Н5	1.226	H4…H13		2.144
B2	Н6	1.241	H6…H7		2.321
N2	H7	1.023	Mg1…B1		2.510
N2	H8	1.025			
N3	H1	1.027	∠B1–N1–Mg1		117.97 °
N3	H2	1.028	∠B2–N2–Mg1		111.20 °

Table S5. Amount of NH<sub>3</sub> coproduced in the dehydrogenation process of MgAB·NH<sub>3</sub>.

Post dehydrogenated	No of equiv. $H_2$	NH <sub>3</sub> in the
$MgAB \cdot NH_3$	released	gaseous product
100 °C	2.7	454 ppm
150 °C	4.2	285 ppm
200 °C	4.9	89 ppm
300 °C	5.7	Not detected

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