# **Supporting Information**

Li(NH<sub>3</sub>)B<sub>3</sub>H<sub>8</sub>: A new ionic liquid octahydrotriborate

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## **Experimental Procedures**

### **Reagents and general procedures**

The source materials, NaBH<sub>4</sub> 95%, diethyl ether 99.5%, tetrahydrofuran 99.5%, Na  $\geq$ 99.7%, K  $\geq$ 99.7%, BH<sub>3</sub>·THF solution 1 M, NH<sub>4</sub>Cl 99%, LiH 95%, AlCl<sub>3</sub> 99.9%, ZnCl<sub>2</sub> 99.9%, ZrCl<sub>4</sub> 99% were obtained commercially from SCRC China. All the organic solvents were dried by refluxing over sodium wire, distilled and stored over potassium mirror. NH<sub>3</sub> (Alfa Aesar, China) was purified by soda lime when used. All manipulations were carried out using standard Schlenk line or in a glove box filled with high purity nitrogen.

#### Instruments and characterization

The composition of the sample was analyzed by means of inductively coupled plasma optical emission spectrometry (ICP, Perkin-Elmer Optima 5300). Simultaneous thermo-gravimetric analysis and mass spectrometry (TGA-MS) was conducted under 1 atm argon in the temperature range of room temperature to 400 °C at a heating rate of 5 °C min<sup>-1</sup> using a netzsch STA 409 C analyzer equipped with a quadrupole mass spectrometer for the analysis of the evolved gas. The targeted gaseous products monitored by MS were H<sub>2</sub> (2), NH<sub>3</sub> (17), B<sub>2</sub>H<sub>6</sub> (26), and B<sub>5</sub>H<sub>9</sub> (60). Meanwhile, desorption properties for the sample were also evaluated using Sievert's volumetric methods with heating rate of 5 °C/min under 1 atm argon. Differential scanning calorimetry (DSC) was performed simultaneously on a Netzsch STA 409 PC with pure argon as the purge gas.

FT-IR (Magna-IR 550 II, Nicolet) analyses were conducted to determine the chemical bond. Liquid NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. <sup>11</sup>B spectra were measured on Bruker AVII-

400 spectrometers. Chemical shifts are reported in ppm units, referenced to  $BF_3 \cdot Et_2O$  for <sup>11</sup>B chemical shift.

Synchrotron X-ray powder diffraction (XRPD) data was collected at wavelength of 0.8271 Å by a Mythen-II detector at PD beamline, Australian Synchrotron. The liquid sample was loaded into a 0.7 mm glass capillary then sealed with wax inside an argon atmosphere glovebox. Liquid sample was cooled down from room temperature to 200 K which is below sample freezing temperature at the ramp rate of 6 K min<sup>-1</sup> with an Oxford Cryostream. XRPD data from the solidified samples showed sharp diffraction peaks proving well crystallized structure from the sample. The broad amorphous peak around 11.2 degrees is from glass capillary background. All Bragg peaks can be indexed into a monoclinic unit cell suggesting a pure phase has been obtained. The structure was solved by global optimization in the direct space in the space group of Cc (No. 9) with relaxed rigid bodies of NH<sub>3</sub>, B<sub>3</sub>H<sub>8</sub> and Li atoms of nominal bonding distances as starting numbers. Rietveld refinement results show the lattice parameters are a = 8.8131 (1) Å, b = 8.8626 (1) Å, c = 8.2076 (1) Å,  $\beta$  = 110.1046 (5)°, and V = 602.001(1) Å<sup>3</sup> using TOPAS 5 (Bruker). The refined profile fit is shown in Fig. 2 with the good structure agreement of  $R_{wp}$  = 4.45 %,  $R_B$  = 3.65 %, and GoF = 1.73. The experiment details and crystallographic information are summarized in Table 1, 2. Due to weak scattering of H atoms in X-ray diffraction, first-principles calculations were conducted to validate and find the lowest energy structure.

#### **Computational method**

Density functional theory (DFT) calculations were performed using the VASP 5.4.4 code on Australian Synchrotron Compute Infrastructure (ASCI). The generalized gradient approximation (GGA) with a Perdew-Burke-Ernzerhof (PBE) exchange correlation function<sup>11[1][1]</sup>1 was used. Zero damping DFT-D3 dispersion correction method of Grimme was used to account for significance of Van der Waals (VdW) interactions in the system. The interactions between the ionic cores and the valence electrons were treated by ultrasoft pseudo potentials with atomic pseudo potentials corresponding to Li 2s<sup>1</sup>, N 2s<sup>2</sup>2p<sup>4</sup>, H 1s<sup>1</sup>, and B 2s<sup>2</sup>2p<sup>1</sup>. In all calculations, the cut-off energy of the plane wave was set at 400 eV and Monkhorst Pack *k*-point 3×3×3 was used to ensure the total energy value convergence within 1 meV/atom.

In order to understand the interaction of Li(NH<sub>3</sub>)B<sub>3</sub>H<sub>8</sub> with added ZnCl<sub>2</sub> for hydrogen release performance, we performed *ab-initio* molecular dynamics simulation on 2 ZnCl<sub>2</sub> with 4 Li(NH<sub>3</sub>)B<sub>3</sub>H<sub>8</sub> complexes in a 13×13×13 Å<sup>3</sup> box for 1.5 ps (1500 steps with 1fs per step) within the canonical ensemble (NVT) at 400 K allowing all atoms to move. Then the geometry of the whole system was optimized to calculate the total energy accurately. During the optimization process, the tolerance convergence accuracy was set when the total energy was less than 1.0×10<sup>-5</sup> eV/atom, the maximum force on per atom was less than 0.01 eV/nm, the maximum stress was less than 0.01 GPa, and the maximum displacement between cycles was less than 1×10<sup>-4</sup> eV. The electronic structure was further analyzed by examining the valence electron localization function (VELF). VELF was used as an indicator for

understanding the chemical bonding 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.

## Synthesis of KB<sub>3</sub>H<sub>8</sub>

 $KB_3H_8$  was synthesized using the method described in the literature.<sup>2</sup> 500ml 1 M  $BH_3$ ·THF solution was transferred to the Na/K alloy prepared above under N<sub>2</sub> atmosphere and stirred overnight at room temperature. After the solid residue was filtered off, the solvent was distilled off under reduced pressure. Then, the resulting solid product was washed by 15ml×3 Et<sub>2</sub>O and dried under vacuum to get 4.16g unsolvated KB<sub>3</sub>H<sub>8</sub>.

### Synthesis of NH<sub>4</sub>B<sub>3</sub>H<sub>8</sub>

 $KB_3H_8$  (1.5g) was placed in a 250 ml flask and reacted with  $NH_4CI$  (1.1g, 10% excess) in liquid ammonia at -78 °C. With magnetic stirring, the reaction can be completed within one hour. Ammonia was then removed at a low temperature and the flask was warmed to room temperature.  $NH_4B_3H_8$  was extracted using anhydrous THF followed by pumping off THF, leaving a white powder,  $NH_4B_3H_8$  (1.05g, yield 95.2%).

### Synthesis of Li(NH<sub>3</sub>)B<sub>3</sub>H<sub>8</sub>

The LiH-NH<sub>4</sub>B<sub>3</sub>H<sub>8</sub> mixture with a molar ration of 1.1:1 was grinded at room temperature and turned into liquid very soon with continous H<sub>2</sub> emission. After the evolution of gas diminished, colorless viscous liquid can be obtained by further centrifugal process.

# Results

Sample	Weight (g)	Boron (mg/L)	Li (mg/L)	B/Li	Calculated $NH_3$ Number
Li(NH <sub>3</sub> )B <sub>3</sub> H <sub>8</sub>	0.0271	53.18	11.43	2.99	1.08

**Table S1.** ICP results of  $LiB_3H_8 \cdot NH_3$ .

Formula sum	Li <sub>4</sub> N <sub>4</sub> H <sub>44</sub> B <sub>12</sub>			
Formula weight	257.87 g/mol			
Crystal system	monoclinic			
Space-group	<i>Cc</i> (9)			
	<i>a</i> = 8.812993(45) Å			
Coll parameters	b = 8.862578(48) Å			
Cell parameters	<i>c</i> = 8.207642(42) Å			
	β = 110.10456(52)°			
Cell volume	602.0028(58) Å <sup>3</sup>			
Z	4			
Calc. density	0.7112 g/cm <sup>3</sup>			
R <sub>B</sub>	2.89 %			
R <sub>wp</sub>	4.45 %,			
GoF	1.73			
2Theta	$2\theta_{min} = 3^{\circ}; 2\theta_{max} = 83^{\circ}$			
Measured temperature	200 K			
Diffractometer	RPI diffractometer			

**Table S2.** Experimental and crystallographic details for Li(NH<sub>3</sub>)B<sub>3</sub>H<sub>8</sub>.

 $\label{eq:constraint} \mbox{Table S3}. \quad \mbox{Atomic positions of } Li(NH_3)B_3H_8.$ 

Atom	Wyck.	Occ.	х	у	Z	B(iso)
Li1	4a	1	0.5283(1)	0.6057(1)	0.7710(1)	1.66(3)
N1	4a	1	-0.4854(1)	0.1776(2)	-0.6779(2)	1.57(2)
H1	4a	1	-0.40350	0.15010	-0.57210	1.58(3)
H2	4a	1	-0.58140	0.15250	-0.65520	1.58(3)
H3	4a	1	-0.47910	0.09780	-0.75330	1.58(3)
B1	4a	1	0.5775(1)	-0.7325(2)	0.8898(1)	0.95(2)
B2	4a	1	0.4423(1)	-0.5976(2)	0.9252(2)	0.95(2)
B3	4a	1	0.6616(1)	-0.5734(1)	0.0228(1)	0.95(2)
H11	4a	1	0.58670	-0.71850	0.74530	1.58(3)
H12	4a	1	0.58940	-0.85190	0.93590	1.58(3)
H13	4a	1	0.42650	-0.69940	0.85770	1.58(3)
H14	4a	1	0.71100	-0.66810	0.98430	1.58(3)
H15	4a	1	0.40070	-0.63330	0.05290	1.58(3)
H16	4a	1	0.39620	-0.49740	0.85240	1.58(3)
H17	4a	1	0.68950	-0.60150	0.18130	1.58(3)
H18	4a	1	0.68920	-0.46510	0.98270	1.58(3)

Samples <sup>a</sup>	Major H <sub>2</sub> peak (°C)	H <sub>2</sub> capacity <sup>b</sup> (wt. %)	Weight loss (wt. %)	H₂ purity⁵ (%)
Li(NH <sub>3</sub> )B <sub>3</sub> H <sub>8</sub>	132.9, 261.6	10.8	28.6	94.6
3Li(NH <sub>3</sub> )B <sub>3</sub> H <sub>8</sub> /AICl <sub>3</sub>	118.7	6.8	11.6	97.7
$2Li(NH_3)B_3H_8/ZnCl_2$	111.2, 263.5	6.9	10.8	98.3
$4Li(NH_3)B_3H_8/ZrCl_4$	108.8, 268.4	6.2	14.7	95.9

Table S4. Calculated capacity and purity of H<sub>2</sub> released from Li(NH<sub>3</sub>)B<sub>3</sub>H<sub>8</sub> and its composites.

<sup>a</sup> Non-isothermal heat treatment of the samples corresponding to Figure

3a, S5. <sup>b</sup> The capacity and purity of  $H_2$  were determined using gravimetric and volumetric results, with the assumption that the impurity was only  $B_5H_9$  to facilitate calculation. The wt. % is on a material basis.



**Fig. S1** (a) <sup>11</sup>B NMR result of Li(NH<sub>3</sub>)B<sub>3</sub>H<sub>8</sub> in THF (δ -31.2 ppm). (b) DSC result of Li(NH<sub>3</sub>)B<sub>3</sub>H<sub>8</sub> with a ramping rate of 5 °C min<sup>-1</sup> in Ar, the inset is the image of  $Li(NH_3)B_3H_8$ .



Fig. S2 Rietveld refinement profile for XRPD result of  $Li(NH_3)B_3H_8$  at temperature of 200K.



Fig. S3 Calculated density of the states (DOS) of  $Li(NH_3)B_3H_8$ .



Fig. S4 MS result of  $Li(NH_3)B_3H_8$ , with a heating rate of 5 °C min<sup>-1</sup> in argon.



Fig. S5 TPD and DSC results of  $Li(NH_3)B_3H_8$ , with a heating rate of 5 °C min<sup>-1</sup> in argon.



**Fig. S6** (a) *In situ* FTIR results for the decomposition of Li(NH<sub>3</sub>)B<sub>3</sub>H<sub>8</sub> in temperature range of 30-400 °C, with a heating rate 5 °C min<sup>-1</sup> in argon. (b) The evolution of predominant absorption bands of Li(NH<sub>3</sub>)B<sub>3</sub>H<sub>8</sub>.



Fig. S7 XRD results of  $Li(NH_3)B_3H_8$  with  $AlCl_3$  (a),  $ZnCl_2$  (b) and  $ZrCl_4$  (c) composites at room temperature and 400°C, and FTIR (d) spectra of  $Li(NH_3)B_3H_8$  and its mixtures with  $AlCl_3$ ,  $ZnCl_2$ , and  $ZrCl_4$ .



Fig. S8 TG (a) and MS results of  $Li(NH_3)B_3H_8$  with  $AICl_3(b)$ ,  $ZnCl_2$  (c) and  $ZrCl_4(d)$  composites.

### References

- 1. J. P. Perdew and A. Zunger, *Physical Review B*, 1981, 23, 5048-5079.
- 2. X. Zheng, Y. Yang, F. Zhao, F. Fang and Y. Guo, *Chem. Commun.*, 2017, 53, 11083-11086.