Supplementary Information

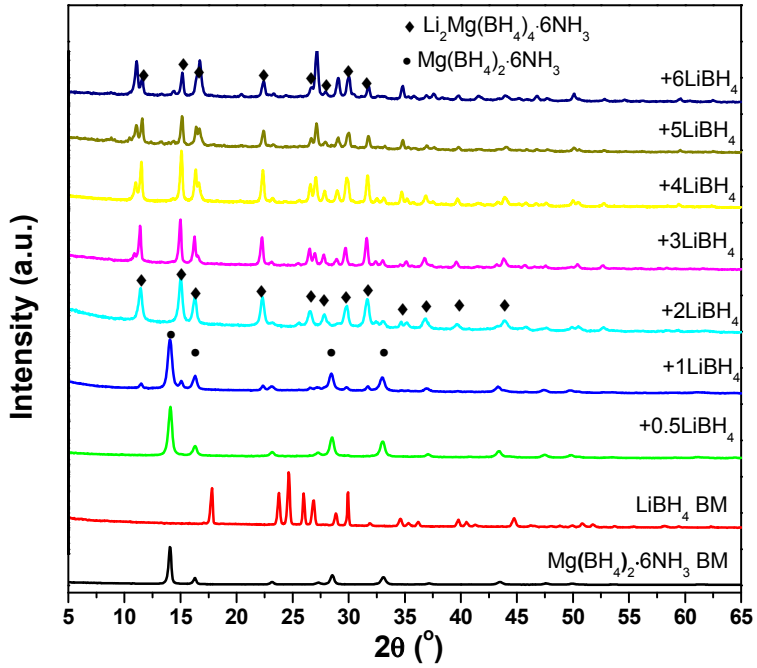

Fig. S1 XRD patterns of $Mg(BH_4)_2·6NH_3$-$x$$LiBH_4$ (x=0.5-6) systems prepared by mechanochemical method.

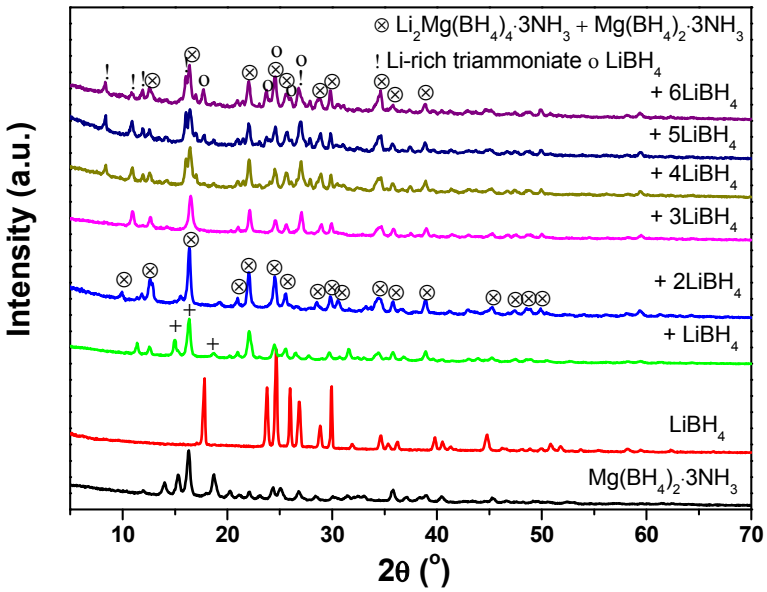

Fig. S2 XRD patterns of $Mg(BH_4)_2·3NH_3$-$x$$LiBH_4$ (x=1-6) systems prepared by mechanochemical method. A single phase (Li,Mg) mixed-cation borohydride triammoniate was detected with the composition of $Li_2Mg(BH_4)_4·3NH_3$.

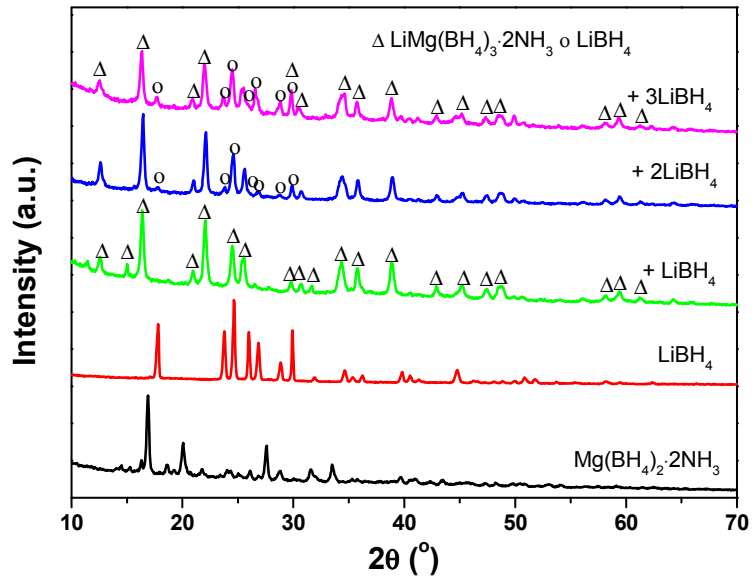

Fig. S3 XRD patterns of $Mg(BH_4)_2{\cdot}2NH_3$-$x$$LiBH_4$ (x=1-3) systems prepared by mechanochemical method. A single phase (Li,Mg) mixed-cation borohydride diammoniate was obtained with the composition of $LiMg(BH_4)_3{\cdot}2NH_3$.

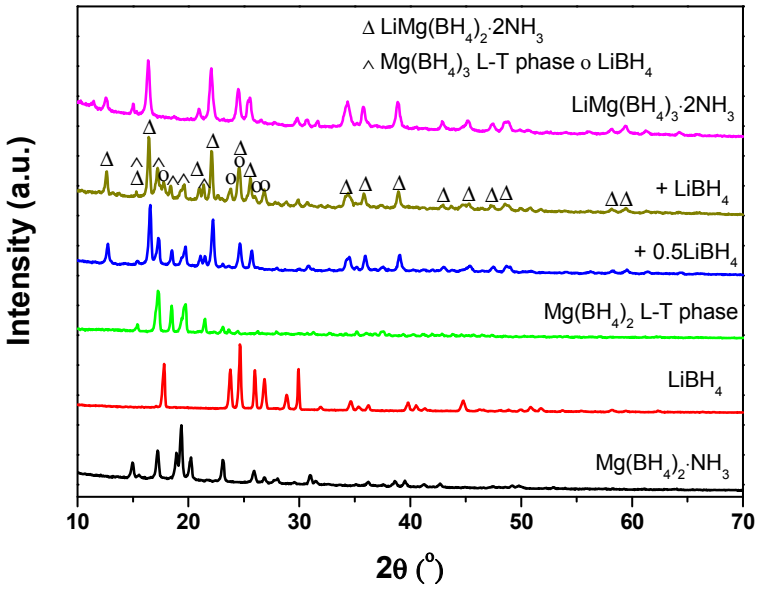

Fig. S4 XRD patterns of $Mg(BH_4)_2{\cdot}NH_3$-$x$$LiBH_4$ (x=0.5, 1) systems prepared by mechanochemical method. No new diffraction peaks were observed in the XRD profiles of the post-milled $Mg(BH_4)_2{\cdot}NH_3$-$x$$LiBH_4$ (x=0.5, 1) samples, and $LiMg(BH_4)_3{\cdot}2NH_3$ and $Mg(BH_4)_2$ were detected as the resultant products.

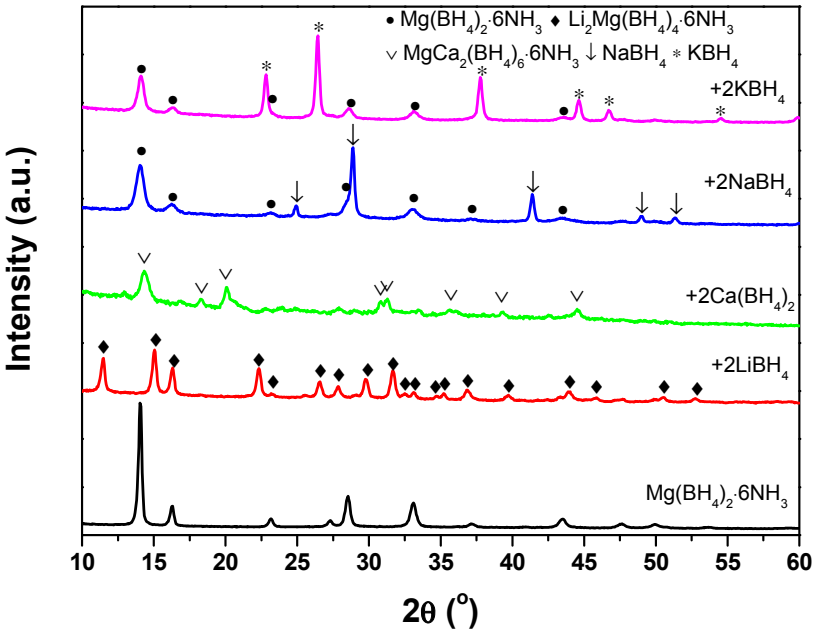

Fig. S5 XRD patterns of the $Mg(BH_4)_2 \cdot 6NH_3$-$2M(BH_4)_n$ (M=Li, Ca, Na, K; n is the valence of M) systems prepared by mechanochemical method. $MgCa_2(BH_4)_6 \cdot 6NH_3$ was identified to be a new single-phase compound while no new reflection was detected for $Mg(BH_4)_2 \cdot 6NH_3$-$2NaBH_4$ and $Mg(BH_4)_2 \cdot 6NH_3$-$2KBH_4$ systems.

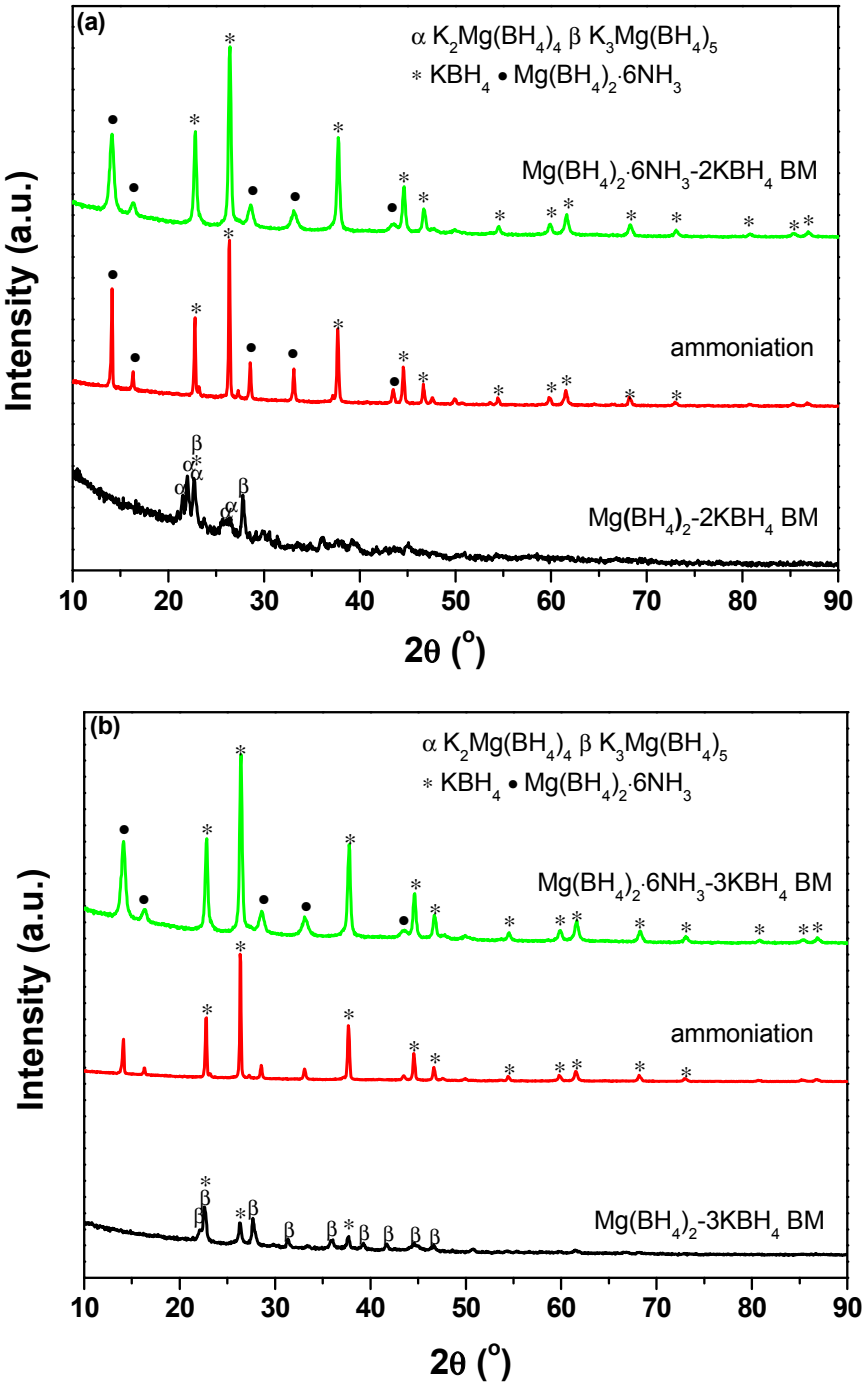

Fig. S6 XRD patterns of (a) $Mg(BH_4)_2$-$2KBH_4$ and (b) $Mg(BH_4)_2$-$3KBH_4$ systems after ball milling and subsequently ammoniation.

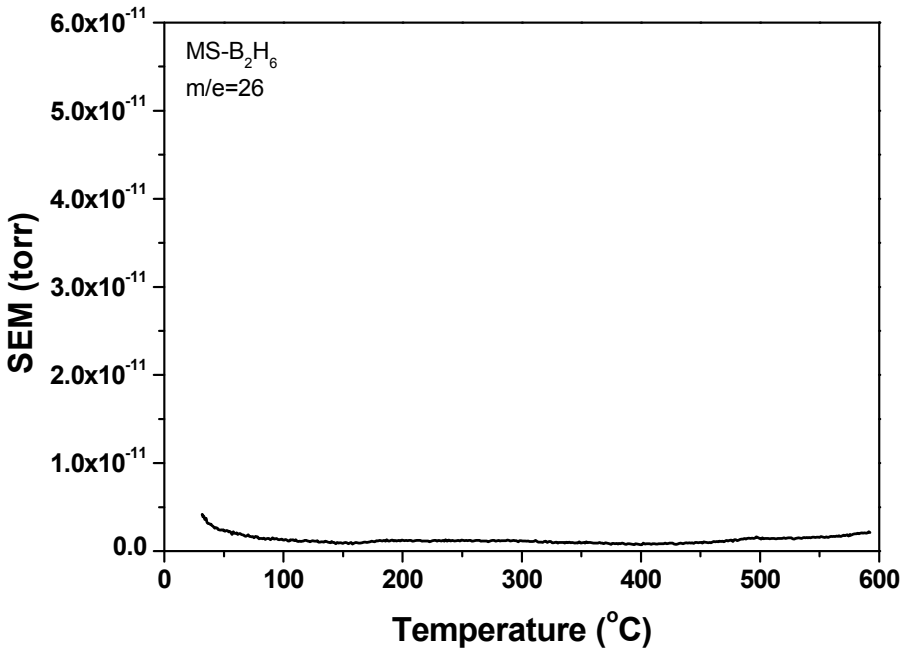

Fig.S7 MS curve of B_2H_6 during the thermal decomposition of $Li_2Mg(BH_4)_4{\cdot}6NH_3$.

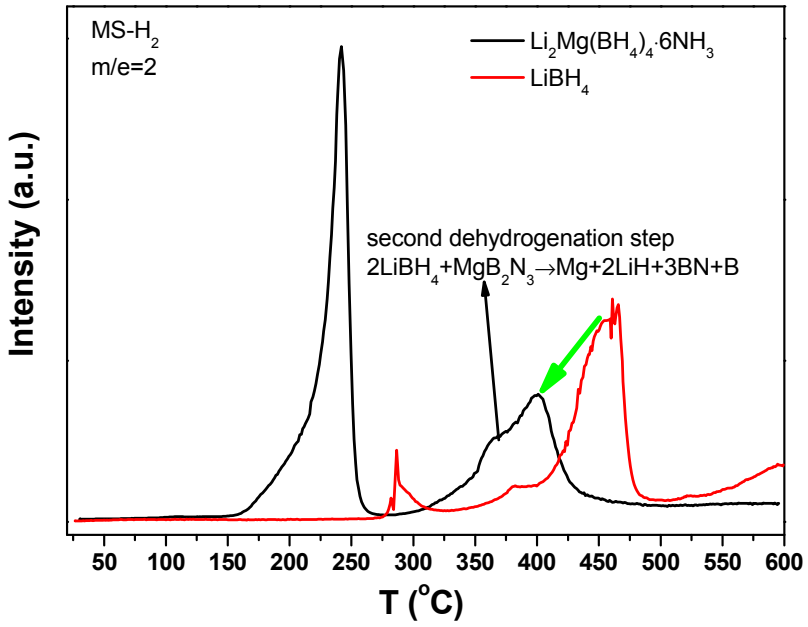

Fig. S8 MS spectra of $Li_2Mg(BH_4)_4{\cdot}6NH_3$ and $LiBH_4$.

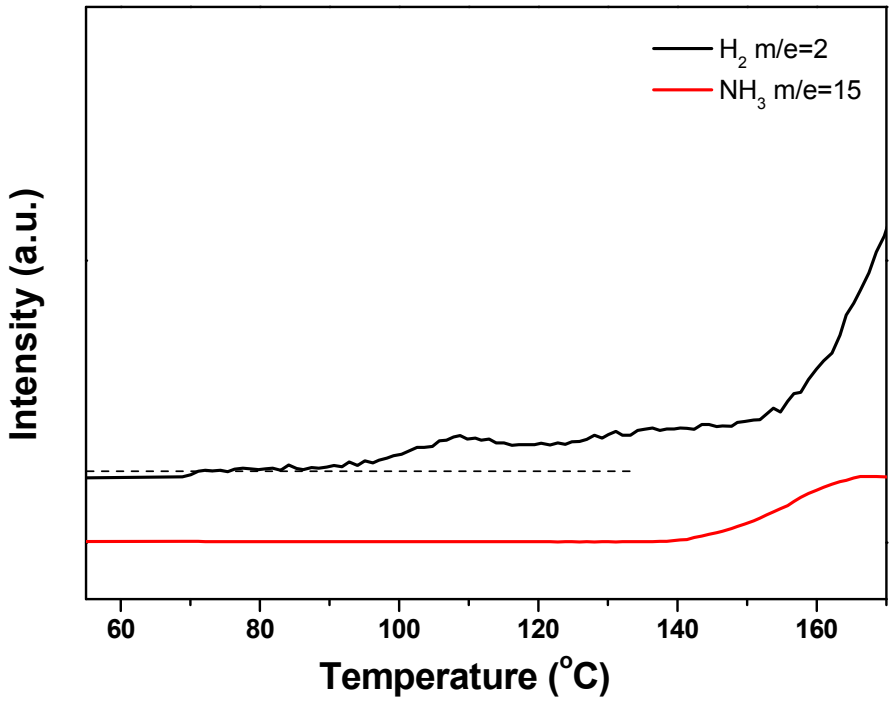

Fig. S9 An enlarge view of the MS spectrum of $Li_2Mg(BH_4)_4 \cdot 6NH_3$ at low temperatures.

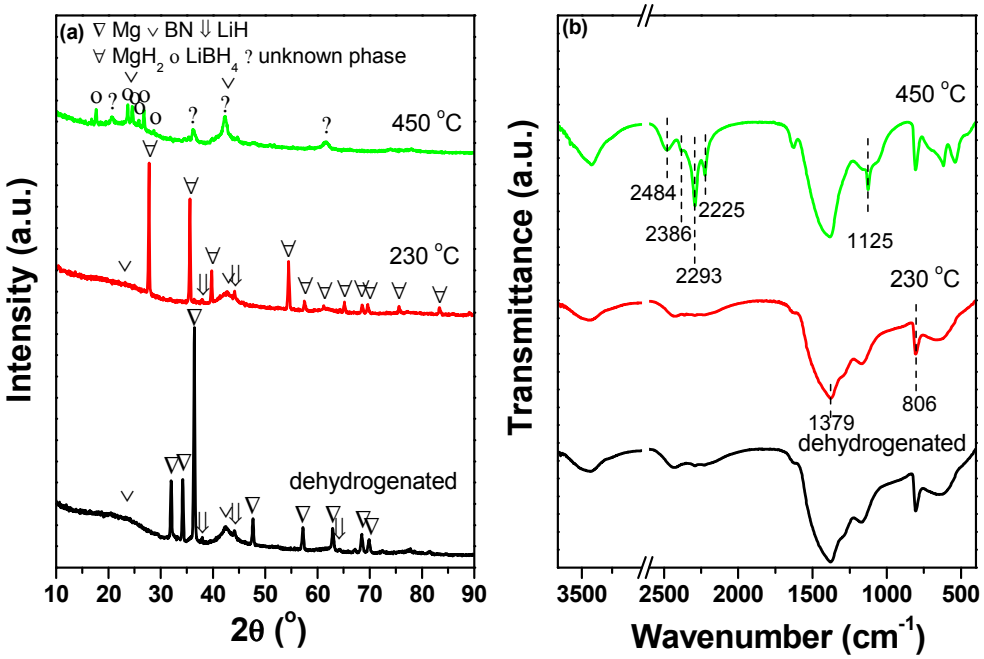

Fig. S10 (a) XRD patterns and (b) FTIR spectra of the re-hydrogenated $Li_2Mg(BH_4)_4 \cdot 6NH_3$ samples at different stages.

Table S1. Absorption bands (in cm^{-1}) obtained for $Li_2Mg(BH_4)_4 \cdot 6NH_3$, $Mg(BH_4)_2 \cdot 6NH_3$ and $LiBH_4$

Sample	$Li_2Mg(BH_4)_4 \cdot 6NH_3$	$Mg(BH_4)_2 \cdot 6NH_3$	$LiBH_4$
N-H bands	3349	3360	
	3270	3268	
	3216	3202	
	2389 (shoulder)		2390
	2290	2292	2292
	2225	2248	2224
B-H bands	1406	1406	
	1263		1242
	1220	1203	
	1184		
	1124	1085	1126

Table S2. Experimental and crystallographic details for $Li_2Mg(BH_4)_4 \cdot 6NH_3$.

Chemical formula	$Li_2Mg(BH_4)_4 \cdot 6NH_3$
Formula weight	199.7414
Crystal system	tetragonal
Space group	$P4_32_12$ (no. 96)
Unit cell dimensions	a=10.7656(8) Å b=10.7658(8) Å c=13.843(1) Å
Z	4
Density (calculated)	0.826877 g cm^{-3}
Volume	401 $Å^3$
2θ [°]	$2\theta_{min}$=3°, $2\theta_{max}$=90°
Diffractometer	Phillips X'Pert Pro X-ray
Wavelength	1.5418 Å
Measurement temperature	25 °C
Fitting factors	R_{wp}=0.0545 R_p=0.0409 χ^2=2.316

Table S3. Experimental and calculated structural parameters of $Li_2Mg(BH_4)_4{\cdot}6NH_3$ (Space group $P4_32_12$, No. 96, a=10.7656(8) Å, c= 13.843(1) Å and V=1604.4(3) Å^3.)

Atom	Site	x	y	z
Mg1	*4a*	0.002(1)	0.998(1)	0.75
Li1	*8b*	-0.005(4)	0.498(6)	0.880(9)
B1	*8b*	0.939(1)	0.6659(8)	0.999(4)
H1	*8b*	0.887	0.6402	1.075
H2	*8b*	0.876	0.6274	0.931
H3	*8b*	0.044	0.6195	0.996
H4	*8b*	0.948	0.7789	0.993
B2	*8b*	0.1564(8)	0.558(1)	0.751(3)
H5	*8b*	0.1286	0.604	0.673
H6	*8b*	0.1221	0.449	0.755
H7	*8b*	0.1088	0.621	0.815
H8	*8b*	0.2693	0.565	0.759
N1	*8b*	0.118(2)	0.891(2)	0.8618(4)
H9	*8b*	0.189	0.840	0.8327
H10	*8b*	0.162	0.951	0.9087
H11	*8b*	0.068	0.830	0.9040
N2	*8b*	0.919(1)	0.102(1)	0.8637(4)
H12	*8b*	0.860	0.051	0.9065
H13	*8b*	0.865	0.173	0.8363
H14	*8b*	-0.019	0.146	0.9100
N3	*8b*	0.865(1)	0.837(1)	0.764(1)
H15	*8b*	0.776	0.868	0.754
H16	*8b*	0.876	0.764	0.717
H17	*8b*	0.866	0.798	0.832

Note: The uncertainties of the atomic coordinates for hydrogen atoms are not reported here because they were not freely refined. The isotropic thermal parameters (U_{iso}) were constrained to be identical for the same atom type or same rigid bodies: U_{Mg}=2.0(1), U_{Li}=1.8(1), U_{NH3}=2.5(1), U_{BH4}=2.2(2) (x100 Å^2). All atomic and rigid body positions are fully occupied.

Table S4. Interaction distances (Å) and angles (°) for dihydrogen bonds.

Distance		Angles		Angels	
$H_{11}\cdots H_4$	1.8680	N_1-$H_{11}\cdots H_4$	157.317	B_1-$H_4\cdots H_{11}$	113.107
$H_{12}\cdots H_4$	1.9818	N_2-$H_{12}\cdots H_4$	167.435	B_1-$H_4\cdots H_{12}$	115.773
$H_{17}\cdots H_4$	2.4060	N_3-$H_{17}\cdots H_4$	152.200	B_1-$H_4\cdots H_{17}$	96.825
$H_{10}\cdots H_8$	1.8306	N_1-$H_{10}\cdots H_8$	175.926	B_2-$H_8\cdots H_{10}$	114.662
$H_{14}\cdots H_8$	1.8781	N_2-$H_{14}\cdots H_8$	168.597	B_2-$H_8\cdots H_{14}$	112.757