Supporting information for

Synthesis, structures and thermal decomposition of ammine $M_xB_{12}H_{12}$ complexes (M = Li, Na, Ca)

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Sample preparation

$K_2B_{12}H_{12}$ was purchased at Katchem, however no volume or temperature increase was observed during synthesis. PXD and FTIR confirm that no reaction between $K_2B_{12}H_{12}$ and NH_3 occurred at the used physical conditions (not shown).

In situ SR-PXD formation of M-$B_{12}H_{12}$·$x$$NH_3$

$Li_2B_{12}H_{12}$ + NH_3 (g)

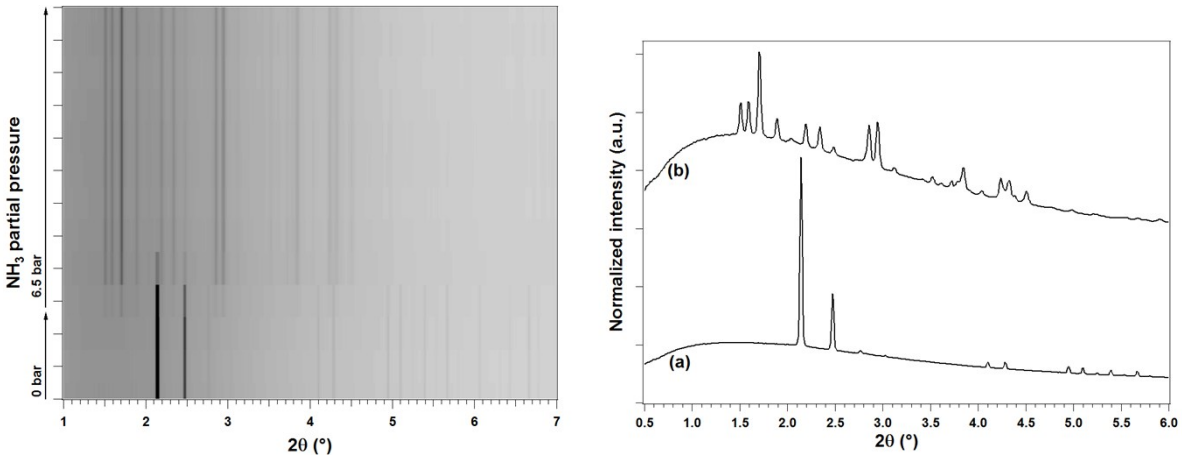


Figure S1. Left: *In situ* SR-PXD data of $Li_2B_{12}H_{12}$ in a sapphire capillary with increasing NH_3 partial pressure. Right: Diffractograms before and after NH_3 reaction, (a) $Li_2B_{12}H_{12}$, (b) $Li_2B_{12}H_{12}$·$7NH_3$.

$Li_2B_{12}H_{12}$ reacts rapidly with NH_3. $Li_2B_{12}H_{12}$·$7NH_3$ is observed within two scans after 6.5 bar NH_3 partial pressure is applied, *i.e.* ~30 seconds, as exposure time was 15 seconds. Diffractograms show the starting and resulting compounds, *i.e.* $Li_2B_{12}H_{12}$ and $Li_2B_{12}H_{12}$·$7NH_3$.

$Na_2B_{12}H_{12}$ + NH_3(g)

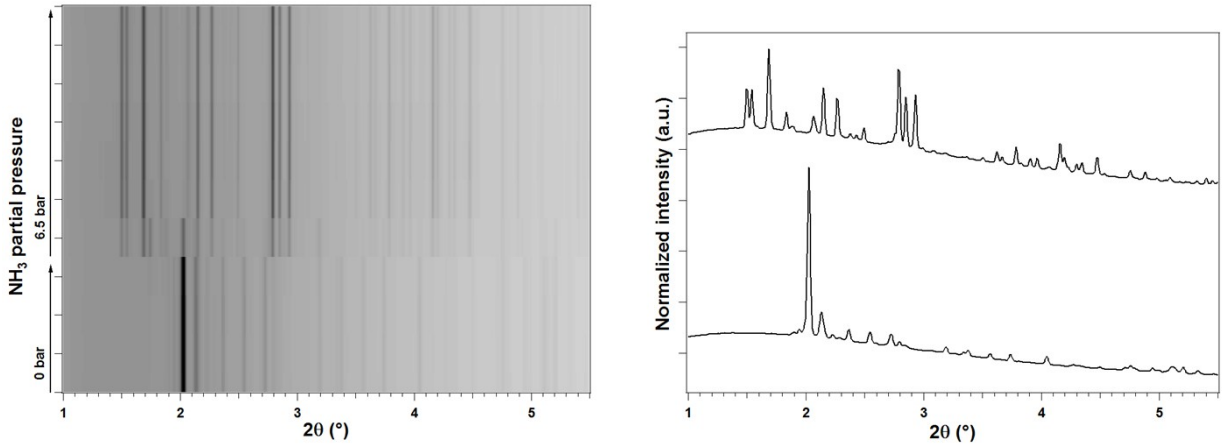


Figure S2 Left: *In situ* SR-PXD data of $Na_2B_{12}H_{12}$ in a sapphire capillary with increasing NH_3 partial pressure. Right: Diffractograms before and after NH_3 reaction showing $Na_2B_{12}H_{12}·H_2O$ and $Na_2B_{12}H_{12}·xNH_3·yH_2O$

$Na_2B_{12}H_{12}$ reacts rapidly with NH_3. An ammoniated compound is observed within two patterns after 6.5 bar NH_3 partial pressure is applied, *i.e.* ~30 seconds, as exposure time was 15 seconds. However that resulting compound is different from as synthesized $Na_2B_{12}H_{12}·4NH_3$. The starting material has a few peaks corresponding to hydrated $Na_2B_{12}H_{12}$, perhaps from contamination in the glovebox or during transport. Thus the resulting compounds may be $Na_2B_{12}H_{12}$ with both H_2O and NH_3. Nevertheless, the fast reaction with NH_3 is demonstrated.

$CaB_{12}H_{12}$ + NH_3(g)

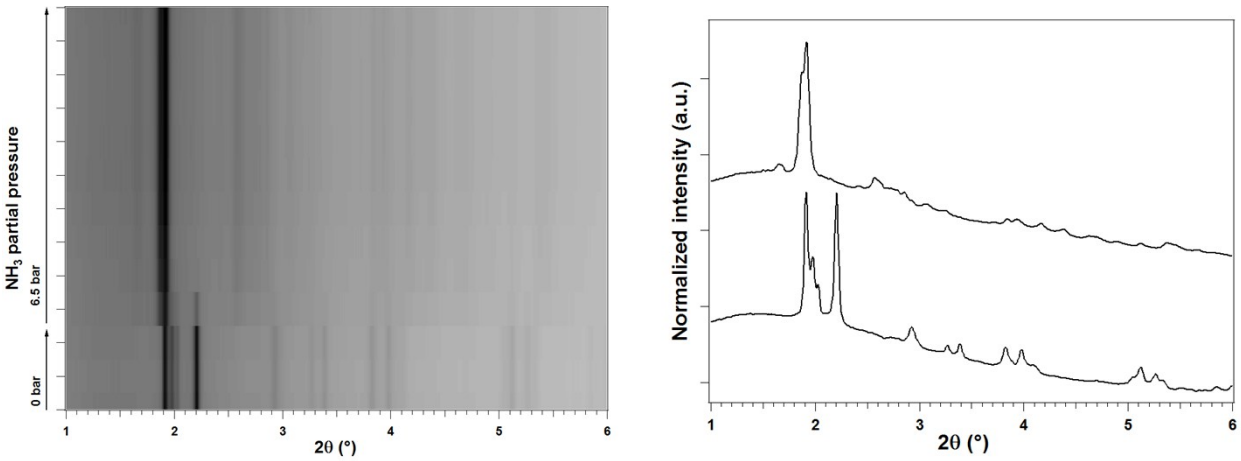


Figure S3 Left: *In situ* SR-PXD data of $CaB_{12}H_{12}$ in a sapphire capillary with increasing NH_3 partial pressure. Right: Diffractograms before and after NH_3 reaction, showing $CaB_{12}H_{12}$ and $CaB_{12}H_{12}$·*n*NH_3.

$CaB_{12}H_{12}$ reacts rapidly with NH_3. $CaB_{12}H_{12}$·*n*NH_3 is observed within two scans after 6.5 bar NH_3 partial pressure is applied, *i.e.* ~30 seconds, as exposure time was 15 seconds. Diffractograms show the starting and resulting compounds.

Rietveld refinement of the *RT* diffractogram from the *in situ* SR-PXD of $Li_2B_{12}H_{12}·7NH_3$, shows good agreement with the reported structure of $Li_2B_{12}H_{12}·7NH_3$ (Figure S4). However, the (-1 1 2) Bragg peak at 2θ = 7.78° is broad compared to the rest of the diffraction peaks, which may contribute negatively to the quality of the refinement. Furthermore, less intense (1 1 2) and (0 1 3) Bragg peaks (at 2θ = 8.90° and 9.02°, respectively) are not observed in the experimental data. Nevertheless refined unit cell parameters correlate well with those reported for $Li_2B_{12}H_{12}·7NH_3$ (at *T* = -123 °C), see Table S1.

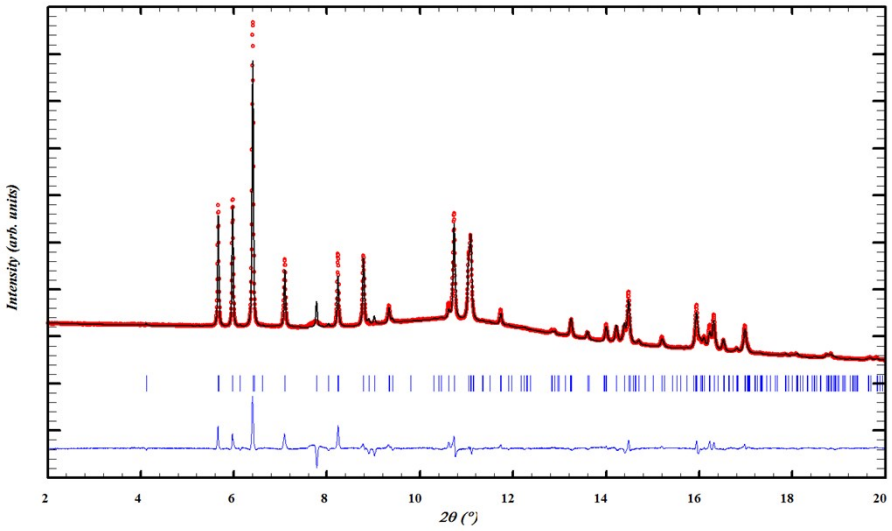


Figure S4. Rietveld refinement of $Li_2B_{12}H_{12}·7NH_3$ at *RT*, λ = 0.7750 Å. The entire in situ SR-PXD plot is presented in Figure 7. Red line: experimental data; black line: calculated diffractogram, blue line: difference pattern. Blue markers: reported structure of $Li_2B_{12}H_{12}·7NH_3$ (R_{Bragg} = 9.31, global χ^2 = 17.9).

Table S1. Unit cell parameters from Rietveld refinement of $Li_2B_{12}H_{12}·7NH_3$ (obtained at 25 °C) as compared to the reported values (obtained at -123 °C).[1]

Temperature (°C)	*a* (Å)	*b* (Å)	*c* (Å)	β (°)
-123	8.3050(2)	14.729(3)	15.728(3)	98.90(3)
25	8.3817(1)	14.865(1)	15.863(7)	98.80(1)

The (1 1 2) and (0 1 3) diffraction peaks (at 2θ = 8.90 and 9.02°) are also not observed in the previously reported experimental data and the broad peak (-1 1 2) is not included in the calculated model, even though the reflection is clearly part of the structure and observed in the experimental data.[1] The broad peak at 2θ = 7.78° can only be modelled with a space group containing a glide plane (e.g. $P2_1/c$) and is otherwise absent (e.g. in $P2_1$) from the model. The broadness of the (-1 1 2) diffraction peak may be due to stacking faults generated by the glide plane. Although the reported structural solution of $Li_2B_{12}H_{12}·7NH_3$ is most likely valid, there are numerous discrepancies when comparing the reported calculated data (ref [1] Figure 2.g) with the reported experimental data (ref [1] Figure 2.b) and CIF file found in structural databases. Similar discrepancies are observed in the present data, making refinement of $Li_2B_{12}H_{12}·7NH_3$ using the reported structural model challenging.

General structure determination details

The FOX software was used for indexing of all powder patterns and for structure solution by global optimization in direct space. Rietveld refinement was done in the Fullprof suite software. In all cases the hydrogen positions are tentative.

Structure determination details for $Li_2B_{12}H_{12}·4NH_3$

The powder pattern measured at 100 °C was used for structure solution. The $Li_2B_{12}H_{12}·4NH_3$ phase is isostructural to the $Na_2B_{12}H_{12}·4NH_3$, so its model was used as initial and refinement was done in the same way, expect for Li^+ parameters. Since Li is a weak scatterer, we could not refine its position from X-ray powder data, so we kept it at same position as Na^+ in the initial model. Thermal displacement factors for anion and ammonia molecule are refined independently, making thermal displacement factors for hydrogen atoms set 1.25 times higher than those of the heavy atoms to which they are attached, while thermal displacement factors for cation was fixed.

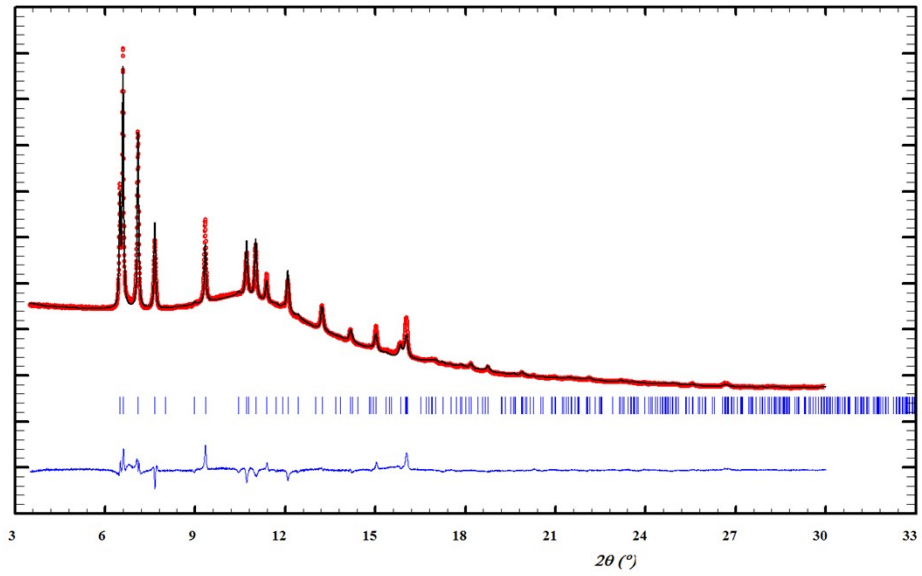


Figure S5. Rietveld refinement of $Li_2B_{12}H_{12}·4NH_3$, obtained at 100 °C, λ = 0.7750 Å, red dots represent the experimental data, the black line is the refined fit and the blue line shows the difference. Tick marks: $Li_2B_{12}H_{12}·4NH_3$. R_{wp} (corrected for background) = 24.59%, χ^2 = 18.25.

Structure determination details for $Na_2B_{12}H_{12}·2NH_3$

The powder pattern measured at 120 °C was used for structure solution. The structural model for $Na_2B_{12}H_{12}·2NH_3$ was found in *P*-3*m*1 space group. The center of the $B_{12}H_{12}^{2-}$ anion is located on 1a position and it is oriented in such way that symmetry elements of the anion and the special position are matched. The Na^+ cation and the N atom of ammonia molecule is located on 2*d* position (1/3, 2/3, z), so only *z* coordinates is refined. The H atom of ammonia is located on 6*i* position. Its coordinates were refined taking into account special position and soft constrain for N-H distance. Thermal displacement factors for cation, anion and ammonia molecule are refined independently, making thermal displacement factors for hydrogen atoms are set 1.2 times higher than those of the heavy atoms to which they are attached.

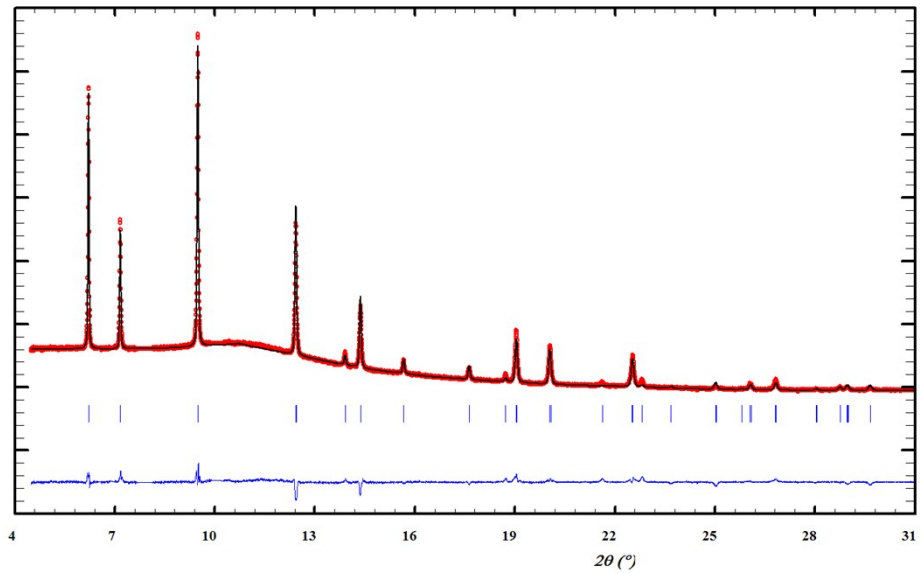


Figure S6. Rietveld refinement of $Na_2B_{12}H_{12}·2NH_3$, obtained at 120 °C, λ = 0.7750 Å, red dots represent the experimental data, the black line is the refined fit and the blue line shows the difference. Tick marks: $Na_2B_{12}H_{12}·2NH_3$. R_{wp} (corrected for background) = 22.1038%, χ^2 = 3.40.

Structure determination details for $Na_2B_{12}H_{12}·4NH_3$

The powder pattern measured at 23 °C was used for structure solution. At this temperature, the sample contains two crystalline phases: $Na_2B_{12}H_{12}·4NH_3$ and $Na_2B_{12}H_{12}·2NH_3$, latter was a modelled using result of previous refinement. The structural model for $Na_2B_{12}H_{12}·2NH_3$ was found in *P*21/*n* space group. The center of the $B_{12}H_{12}^{2-}$ anion is located on 1a position and it is oriented in such way that symmetry elements of the anion and the special position are matched. The Na^+ cation and the N atom of ammonia molecule is located on 2*d* position (1/3, 2/3, *z*), so only *z* coordinates are refined. The H atom of ammonia is located on 6*i* position. Its coordinates was refined taking into account special position and soft constrain for N-H distance. Thermal displacement factors for cation, anion and ammonia molecule are refined independently, making thermal displacement factors for hydrogen atoms set 1.25 times higher than those of the heavy atoms to which they are attached.

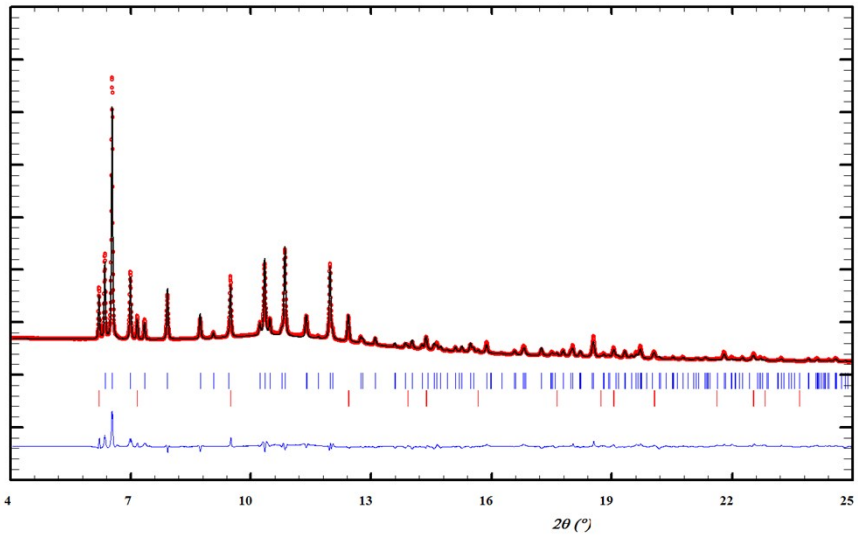


Figure S7. Rietveld refinement of $Na_2B_{12}H_{12}·4NH_3$, obtained at 23 °C, λ = 0.7750 Å, red dots represent the experimental data, the black line is the refined fit and the blue line shows the difference. From refinement the sample contents is determined as 82.3(5) wt% $Na_2B_{12}H_{12}·4NH_3$ and 17.7(2) wt% $Na_2B_{12}H_{12}·2NH_3$. Tick marks: $Na_2B_{12}H_{12}·4NH_3$ (top, blue), $Na_2B_{12}H_{12}·2NH_3$ (bottom, red). R_{wp} (corrected for background) = 25.52%, χ^2 = 182.3.

Structure determination details for $CaB_{12}H_{12}·3NH_3$

The powder pattern measured at 225 °C was used for structure solution. An initial structural model for $CaB_{12}H_{12}·3NH_3$ was found in *I*2/*a* space group with unit cell parameters *a* = 8.8359, *b* = 11.8929, *c* = 14.7748 Å, β = 118.434°, *V* = 1365.30 Å^3. Symmetry analysis in PLATON[2] indicated missing symmetry and suggested *R*-3*c* space group with unit cell parameters *a* = 11.86978(18)**, *c* =** 16.7977(5) Å, *V* = 2049.58(7)Å^3.. The structure was finally solved in this space group. The Ca^{2+} cation is located on 6a position, center of the $B_{12}H_{12}^{2-}$ anion is located on 6b position and it is oriented in such way that symmetry elements of the anion and the special position are matched. The N atom of ammonia molecule is laying on 3-fold axis (18e position), so only *x* coordinate is refined. The H atoms of ammonia are in the general position, but soft distance constrains are applied to keep geometry and orientation of the ammonia molecule. The H atoms of ammonia are disordered by 2-fold axis. Thermal displacement factors for cation, anion and ammonia molecule are refined independently, making thermal displacement factors for hydrogen atoms set 1.2 times higher than those of the heavy atoms to which they are attached.

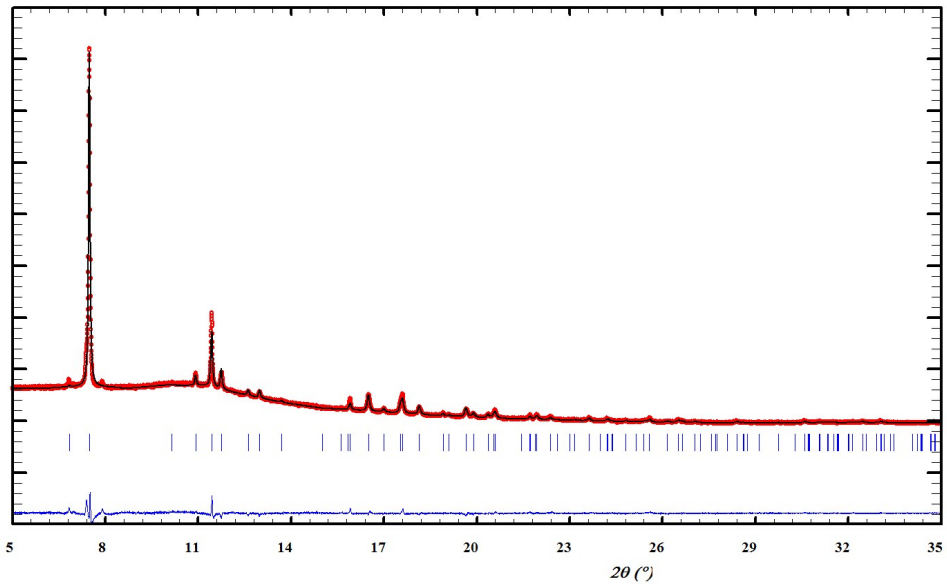
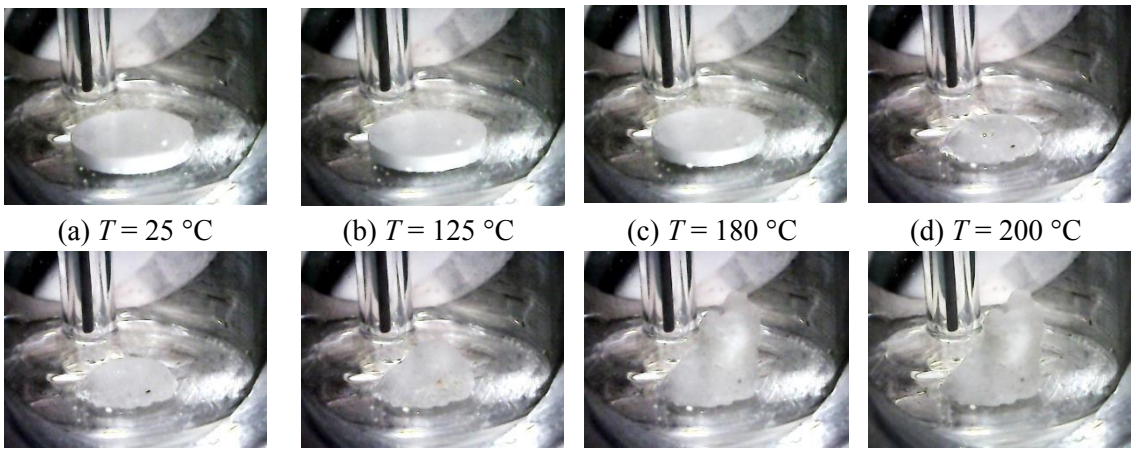


Figure S8. Rietveld refinement of $CaB_{12}H_{12}·3NH_3$, obtained at 225 °C, λ = 0.7750 Å, red dots represent the experimental data, the black line is the refined fit and the blue line shows the difference. Tick marks: $CaB_{12}H_{12}·3NH_3$. R_{wp} (corrected for background) = 22.02%, χ^2 = 3.002.

Temperature programmed photographic analysis (TPPA)

The TPPA measurement of $Li_2B_{12}H_{12}·7NH_3$ is shown below



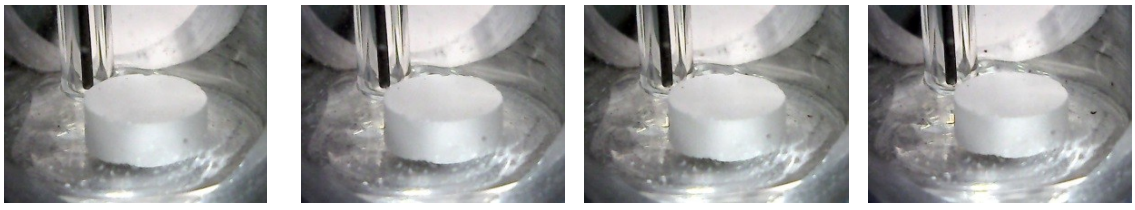
(a) T = 25 °C (b) T = 125 °C (c) T = 180 °C (d) T = 200 °C

(e) T = 215 °C (f) T = 250 °C (g) T = 300 °C (h) T = 350 °C

Figure S9. TPPA measurement of $Li_2B_{12}H_{12}·7NH_3$ in the temperature range *RT* – 350 °C ($\Delta T/\Delta t$ = 5 °C/min).

(a) T = 34 °C (b) T = 110 °C (c) T = 150 °C (d) T = 350 °C

Figure S10. TPPA measurement of $Na_2B_{12}H_{12}·4NH_3$ in the temperature range *RT* – 350 °C ($\Delta T/\Delta t$ = 5 °C/min).



(a) T = 25 °C (b) T = 150 °C (c) T = 250 °C (d) T = 400 °C

Figure S11. TPPA measurement of $Ca_2B_{12}H_{12}·nNH_3$ in the temperature range *RT* – 400 °C ($\Delta T/\Delta t$ = 5 °C/min).

In situ SR-PXD decomposition at Maxlab

$CaB_{12}H_{12}$·*n*NH_3

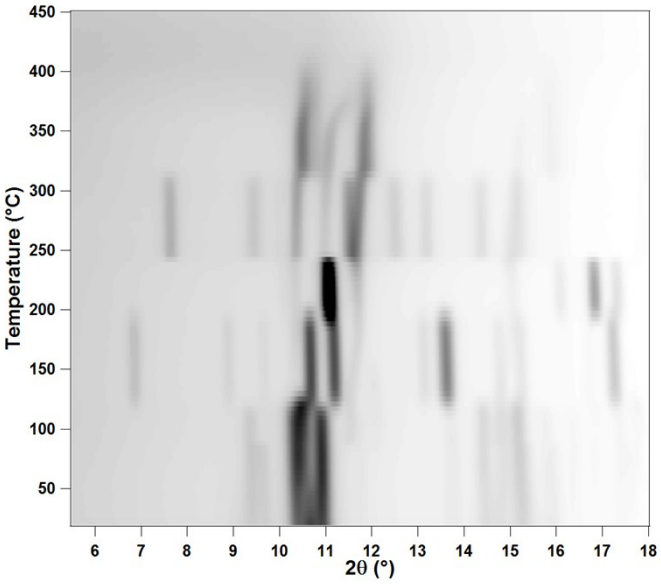


Figure S12. *In situ* SR-PXD of $CaB_{12}H_{12}$·*n*NH_3 in the temperature range *RT* – 450 °C ($\Delta T/\Delta t$ = 5°C/min), λ = 0.9938 Å.

The *in situ* SR-PXD experiment conducted at Maxlab shows the structural changes as observed at SLS at the same temperatures. However, since the sample was heated to higher temperatures the formation of $CaB_{12}H_{12}$ is observed at *T* = 315 °C. $CaB_{12}H_{12}$ decompose and decrease in diffracted intensity from *T* = 350 °C in agreement with the thermal analysis.

Structural Parameters

Table S2. Experimental structural parameters for monoclinic $Li_2B_{12}H_{12}·4NH_3$, space group $P\ 2_1/n$ (No. 14), a = 8.4122(3), b = 9.5193(5), c = 9.6434(5) Å, β = 99.472(4) °, V = 761.70(6) Å^3.

Atom	Wyckoff site	x	y	z	Occupancy	B (Å^2)
N1	4e	-0.0119(6)	0.2002(4)	0.4864(7)	1	11.35(15)
H11	4e	-0.0142(11)	0.1066(8)	0.4665(16)	1	13.62(18)
H12	4e	0.0569(11)	0.2163(12)	0.5682(13)	1	13.62(18)
H13	4e	-0.1120(7)	0.2319(12)	0.4931(15)	1	13.62(18)
N2	4e	0.4229(5)	-0.0072(6)	0.6728(5)	1	11.35(15)
H21	4e	0.3729(12)	-0.0587(14)	0.7322(12)	1	13.62(18)
H22	4e	0.4912(14)	-0.0630(14)	0.6327(11)	1	13.62(18)
H23	4e	0.3487(12)	0.0319(16)	0.6034(10)	1	13.62(18)
Li1	4e	0.58175	0.17913	0.80778	1	8.68
B1	4e	-0.10727	0.0158	-0.16156	1	6.2(3)
B2	4e	0.08469	-0.06287	-0.13483	1	6.2(3)
B3	4e	-0.19902	-0.02451	-0.01191	1	6.2(3)
B4	4e	0.11216	-0.15065	0.03132	1	6.2(3)
B5	4e	-0.07618	-0.15502	-0.07699	1	6.2(3)
B6	4e	-0.06352	-0.12588	0.10615	1	6.2(3)
H1	4e	-0.18475	0.02659	-0.27854	1	7.5(3)
H2	4e	0.14653	-0.10961	-0.23314	1	7.5(3)
H3	4e	-0.34362	-0.04205	-0.02014	1	7.5(3)
H4	4e	0.19633	-0.26241	0.05487	1	7.5(3)
H5	4e	-0.13036	-0.26588	-0.13336	1	7.5(3)
H6	4e	-0.10701	-0.21843	0.18359	1	7.5(3)

Table S3. Bond lengths for monoclinic $Li_2B_{12}H_{12}·4NH_3$, space group $P\ 2_1/n$ (No. 14), a = 8.4122(3), b = 9.5193(5), c = 9.6434(5) Å, β = 99.472(4) °, V = 761.70(6) Å^3.

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
N1	H13	0.9068(91)	B2	H2	1.2368(1)
	H11	0.911(9)		B1	1.7601(1)
	H12	0.9113(122)		B5	1.7777(1)
	Li1	2.3138(62)		B3	1.7808(1)
H11	N1	0.911(9)		B4	1.7880(1)
	H12	1.4890(157)		B6	1.8311(1)
	H13	1.4949(138)	B3	H3	1.2174(1)
	H11	2.1314(120)		B6	1.7605(1)
	H2	2.3409(139)		B2	1.7808(1)
H12	N1	0.9113(122)		B1	1.7867(1)
	H11	1.4890(157)		B5	1.7940(1)
	H13	1.4922(116)		B4	1.8423(1)
	H6	2.3612(123)	B4	H4	1.2774(1)
H13	N1	0.9068(91)		B5	1.7488(1)
	H12	1.4922(116)		B6	1.7639(1)
	H11	1.4949(138)		B2	1.7880(1)
	H3	2.2068(114)		B1	1.8011(1)
N2	H21	0.9081(134)		B3	1.8423(1)
	H22	0.9137(136)	B5	H5	1.2391(1)
	H23	0.9157(112)		B4	1.7488(1)
	Li1	2.4604(50)		B6	1.7735(1)
H21	N2	0.9081(134)		B2	1.7777(1)
	H22	1.4923(168)		B3	1.7940(1)
	H23	1.4983(168)		B1	1.8186(1)
	H2	2.0451(108)	B6	H6	1.2481(1)
	H6	2.1853(133)		B3	1.7605(1)
H22	N2	0.9137(136)		B4	1.7639(1)
	H23	1.4904(172)		B5	1.7735(1)
	H21	1.4923(168)		B1	1.7875(1)
	H6	2.3207(131)		B2	1.8311(1)
H23	N2	0.9157(112)	H1	B1	1.2108(1)
	H22	1.4904(172)	H2	B2	1.2368(1)
	H21	1.4983(168)		H21	2.0451(108)
	H4	2.4732(134)		H11	2.3409(139)
Li1	H5	1.8700(1)	H3	B3	1.2174(1)
	H4	2.2481(1)		H13	2.2068(114)
	N1	2.3138(62)	H4	B4	1.2774(1)
	N2	2.4604(50)		Li1	2.2481(1)
B1	H1	1.2108(1)		H23	2.4732(134)
	B2	1.7601(1)	H5	B5	1.2391(1)
	B3	1.7867(1)		Li1	1.8700(1)
	B6	1.7875(1)	H6	B6	1.2481(1)
	B4	1.8011(1)		H21	2.1853(133)
	B5	1.8186(1)		H22	2.3207(131)
				H12	2.3612(123)

Table S4. Experimental structural parameters for monoclinic $Na_2B_{12}H_{12}·4NH_3$, space group $P\ 2_1/n$ (No. 14), a = 8.6875(2), b = 9.4168(3), c = 9.9096(3) Å, β = 98.3296(18)°, V = 802.14(4) Å^3.

Atom	Wyckoff site	x	y	z	Occupancy	B (Å^2)
N1	4e	-0.0137(4)	0.2082(4)	0.4968(4)	1	7.48(10)
H11	4e	0.0488(10)	0.1316(8)	0.5242(14)	1	8.98(12)
H12	4e	-0.0081(10)	0.2710(11)	0.5678(12)	1	8.98(12)
H13	4e	-0.1125(6)	0.1789(10)	0.4694(15)	1	8.98(12)
N2	4e	0.4114(4)	0.0059(4)	0.6805(4)	1	7.48(10)
H21	4e	0.4090(14)	-0.0725(11)	0.7339(11)	1	8.98(12)
H22	4e	0.4506(14)	-0.0176(14)	0.6029(8)	1	8.98(12)
H23	4e	0.3144(10)	0.0432(14)	0.6583(10)	1	8.98(12)
Na1	4e	0.5818(3)	0.1791(3)	0.8078(3)	1	10.2(9)
B1	4e	-0.10727	0.0158	-0.16156	1	5.2(9)
B2	4e	0.08469	-0.06287	-0.13483	1	5.2(9)
B3	4e	-0.19902	-0.02451	-0.01191	1	5.2(9)
B4	4e	0.11216	-0.15065	0.03132	1	5.2(9)
B5	4e	-0.07618	-0.15502	-0.07699	1	5.2(9)
B6	4e	-0.06352	-0.12588	0.10615	1	5.2(9)
H1	4e	-0.18475	0.02659	-0.27854	1	6.2(12)
H2	4e	0.14653	-0.10961	-0.23314	1	6.2(12)
H3	4e	-0.34362	-0.04205	-0.02014	1	6.2(12)
H4	4e	0.19633	-0.26241	0.05487	1	6.2(12)
H5	4e	-0.13036	-0.26588	-0.13336	1	6.2(12)
H6	4e	-0.10701	-0.21843	0.18359	1	6.2(12)

Table S5. Bond lengths for monoclinic $Na_2B_{12}H_{12}·4NH_3$, space group $P\ 2_1/n$ (No. 14), a = 8.6875(2), b = 9.4168(3), c = 9.9096(3) Å, β = 98.3296(18)°, V = 802.14(4) Å^3.

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)

N1	H13	0.9050(69)	B2	H2	1.2582(1)
	H12	0.9150(119)		B5	1.8074(1)
	H11	0.9199(89)		B1	1.8089(1)
	Na1	2.4026(50)		B6	1.8136(1)
H11	N1	0.9199(89)		B4	1.8268(1)
	H12	1.4887(137)		B3	1.8329(1)
	H13	1.4955(107)	B3	H3	1.2579(1)
H12	N1	0.9150(119)		B5	1.8068(1)
	H11	1.4887(137)		B6	1.8074(1)
	H13	1.5064(143)		B1	1.8224(1)
	H3	2.1921(97)		B2	1.8329(1)
H13	N1	0.9050(69)		B4	1.8355(1)
	H11	1.4955(107)	B4	H4	1.2835(1)
	H12	1.5064(143)		B6	1.8060(1)
	H2	2.4071(144)		B1	1.8155(1)
N2	H23	0.9100(99)		B5	1.8226(1)
	H21	0.9103(113)		B2	1.8268(1)
	H22	0.9122(107)		B3	1.8355(1)
	Na1	2.4294(45)	B5	H5	1.2439(1)
H21	N2	0.9103(113)		B3	1.8068(1)
	H22	1.4896(149)		B2	1.8074(1)
	H23	1.4984(154)		B1	1.8158(1)
	H6	2.0307(104)		B4	1.8226(1)
	H2	2.3757(124)		B6	1.8230(1)
H22	N2	0.9122(107)	B6	H6	1.2551(1)
	H23	1.4891(158)		B4	1.8060(1)
	H21	1.4896(149)		B3	1.8074(1)
	H22	2.3480(136)		B2	1.8136(1)
H23	N2	0.9100(99)		B5	1.8230(1)
	H22	1.4891(158)		B1	1.8280(1)
	H21	1.4984(154)	H1	B1	1.2574(1)
	H2	2.4103(111)	H2	B2	1.2582(1)
Na1	H5	1.9094(30)		H21	2.3757(124)
	H4	2.3287(26)		H13	2.4071(144)
	N1	2.4026(50)		H23	2.4103(111)
	N2	2.4294(45)	H3	B3	1.2579(1)
B1	H1	1.2574(1)		H12	2.1921(97)
	B2	1.8089(1)	H4	B4	1.2835(1)
	B4	1.8155(1)		Na1	2.3287(26)
	B5	1.8158(1)	H5	B5	1.2439(1)
	B3	1.8224(1)		Na1	1.9094(30)
	B6	1.8280(1)	H6	B6	1.2551(1)
				H21	2.0307(104)

Table S6. Experimental structural parameters for trigonal $Na_2B_{12}H_{12}·2NH_3$, space group *P*-3*m* (No. 164), *a* = 7.1672(1), *c* = 7.1574(2) Å, *V* = 318.41(1) Å^3.

Atom	Wyckoff site	x	y	z	Occupancy	B (Å^2)
B1	6i	0.16741	0.08370	0.20340	1	2.1(4)
B2	6i	0.13981	0.27962	0.04485	1	2.1(4)
H1	6i	0.2859	0.14294	0.34736	1	2.5(5)
H2	6i	0.23876	0.47753	0.076596	1	2.5(5)
N1	2d	0.33333	0.66667	0.4852(6)	1	13.53(16)
H11	6i	0.2638(2)	0.7362(2)	0.4435(6)	1	16.2(2)
Na1	2d	0.33333	0.66667	0.8052(3)	1	10.93(10)

Table S7. Bond lengths for trigonal $Na_2B_{12}H_{12}·2NH_3$, space group *P*-3*m* (No. 164), *a* = 7.1672(1), *c* = 7.1574(2) Å, *V* = 318.41(1) Å^3.

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
B1	H1	1.2659(1)	H2	B2	1.2493(1)
	B1	1.7998(1)		H2	2.0334(1)
	B1	1.7998(1)		H2	2.0334(1)
	B2	1.8911(1)		Na1	2.2697(18)
	B2	1.8912(1)	N1	H11	0.9133(26)
	B2	1.9084(1)		H11	0.9133(23)
B2	H2	1.2493(1)		H11	0.9133(23)
	B2	1.8505(1)		Na1	2.2904(48)
	B2	1.8505(1)	H11	N1	0.9133(26)
	B1	1.8911(1)		H11	1.4951(23)
	B1	1.8912(1)		H11	1.4951(23)
	B1	1.9084(1)		H1	2.1193(33)
H1	B1	1.2659(1)	Na1	H2	2.2696(18)
	H11	2.1193(32)		H2	2.2697(18)
				H2	2.2697(18)
				N1	2.2904(48)

Table S8. Experimental structural parameters for trigonal $CaB_{12}H_{12}·3NH_3$, space group *R*-3*c* (No. 167), *a* = 11.86978(18), *c* = 16.7977(5) Å, *V* = 2049.58(7)Å^3.

Atom	Wyckoff site	x	y	z	Occupancy	B (Å^2)
B1	36f	0.00000	-0.08756	0.08099	1	3.92(16)
B2	36f	0.00000	-0.14166	-0.01912	1	3.92(16)
H1	36f	0.00000	-0.14820	0.13710	1	4.7(2)
H2	36f	0.00000	-0.23970	-0.03240	1	4.7(2)
Ca1	6a	0.00000	0.00000	0.25000	1	5.97(10)
N1	18e	0.20716	0.00000	0.25000	0.5	10.5(3)
H11	36f	0.1998(2)	-0.06498(10)	0.21782(7)	0.5	12.6(3)
H12	36f	0.2258(2)	-0.01310(14)	0.30052(5)	0.5	12.6(3)
H13	36f	0.27136(2)	0.07803(8)	0.23169(8)	0.5	12.6(3)

Table S9. Bond lengths for trigonal $CaB_{12}H_{12}·3NH_3$, space group *R*-3*c* (No. 167), *a* = 11.86978(18), *c* = 16.7977(5) Å, *V* = 2049.58(7)Å^3.

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
B1	H1	1.1859(2)	H11	H13	0.8587(18)
	B2	1.8001(1)		H12	0.8597(17)
	B2	1.8001(1)		N1	0.9096(14)
	B2	1.8001(1)		H12	1.4880(15)
	B1	1.8002(1)		H13	1.4884(13)
	B1	1.8002(1)		H11	1.7186(15)
B2	H2	1.1849(2)		H2	2.2665(21)
	B2	1.8002(1)		H1	2.4690(19)
	B2	1.8002(1)	H12	H13	0.8592(16)
	B1	1.8001(1)		H11	0.8597(17)
	B1	1.8001(1)		N1	0.9098(12)
	B1	1.8001(1)		H11	1.4880(15)
H1	B1	1.1859(1)		H13	1.4881(16)
	H11	2.4690(19)		H12	1.7185(12)
H2	B2	1.1849(1)		H2	2.3413(18)
	H11	2.2665(11)	H13	H11	0.8587(18)
	H12	2.3413(14)		H12	0.8592(16)
Ca1	N1	2.4589(1)		N1	0.9096(11)
	N1	2.4589(1)		H12	1.4881(16)
	N1	2.4589(1)		H11	1.4884(13)
N1	H11	0.9096(14)		H13	1.7181(13)
	H13	0.9096(11)			
	H13	0.9096(13)			
	H11	0.9096(12)			
	H12	0.9098(11)			
	H12	0.9098(12)			
	Ca1	2.4589(1)			

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