"Synthesis, structures and thermal decomposition of ammine MxB12H12 complexes (M = Li, Na, Ca)"

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ABSTRACT

A series of ammine metal-dodecahydro-closo-dodecaboranes, MxB12H12·nNH3 (M = Li, Na, Ca) were synthesized and their structural and thermal properties studied with in situ time-resolved synchrotron radiation powder X-ray diffraction, thermal analysis, Fourier transformed infrared spectroscopy, and temperature-programmed photographic analysis. The synthesized compounds, Li2B12H12·7NH3, Na2B12H12·4NH3 and CaB12H12·6NH3, contain high amounts of NH3, 43.3, 26.6 and 35.9 wt % NH3, respectively, which can be released and absorbed reversibly at moderate conditions without decomposition, thereby making the closo-boranes favorable 'host' materials for ammonia or indirect hydrogen storage in the solid state. In this work, fifteen new ammine metal dodecahydro-closo-dodecaborane compounds are observed by powder X-ray diffraction, of which six are structurally characterized, Li2B12H12·4NH3, Li2B12H12·2NH3, Na2B12H12·4NH3, Na2B12H12·2NH3, CaB12H12·4NH3 and CaB12H12·3NH3. Li2B12H12·4N...

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

Bjarne R. S. Hansen, Nikolay Tumanov, Antonio Santoru, Thomas Klassen, Martin Dornheim, Yaroslav Filinchuk and Torben R. Jensen

A series of ammine metal-dodecahydro-closo-dodecaboranes, $M_xB_{12}H_{12+2}NH_3$ ($M = Li, Na, Ca$) were synthesized and their structural and thermal properties studied with in situ time-resolved synchrotron radiation powder X-ray diffraction, thermal analysis, Fourier transformed infrared spectroscopy, and temperature-programmed photographic analysis. The synthesized compounds, Li$_2$B$_{12}$H$_{12}$·7NH$_3$, Na$_2$B$_{12}$H$_{12}$·4NH$_3$ and CaB$_{12}$H$_{12}$·6NH$_3$, contain high amounts of NH$_3$, 43.3, 26.6 and 35.9 wt% NH$_3$, respectively, which can be released and absorbed reversibly at moderate conditions without decomposition, thereby making the closo-boranes favorable ‘host’ materials for ammonia or indirect hydrogen storage in the solid state. In this work, fifteen new ammine metal dodecahydro-closo-dodecaborane compounds are observed by powder X-ray diffraction, of which six are structurally characterized, Li$_2$B$_{12}$H$_{12}$·4NH$_3$, Li$_2$B$_{12}$H$_{12}$·2NH$_3$, Na$_2$B$_{12}$H$_{12}$·4NH$_3$, Na$_2$B$_{12}$H$_{12}$·2NH$_3$, CaB$_{12}$H$_{12}$·4NH$_3$ and CaB$_{12}$H$_{12}$·3NH$_3$. Li$_2$B$_{12}$H$_{12}$·4NH$_3$ and Na$_2$B$_{12}$H$_{12}$·4NH$_3$ are isostructural and monoclinic ($P2_1/n$) whereas Na$_2$B$_{12}$H$_{12}$·2NH$_3$ and CaB$_{12}$H$_{12}$·3NH$_3$ are both trigonal with space groups $P3m1$ and $R3c$, respectively. Generally, coordination between the metal and the icosahedral closo-borane anion is diverse and includes point sharing, edge sharing, or face sharing, while coordination of ammonia always occurs via the lone pair on nitrogen to the metal. Furthermore, a liquid intermediate is observed during heating of Li$_2$B$_{12}$H$_{12}$·7NH$_3$. This work provides deeper insight into the structural, physical, and chemical properties related to thermal decomposition and possible ammonia and hydrogen storage.

Introduction

Metal borohydrides have received significant scientific attention, owing to their potential use for hydrogen storage. However, light metal borohydrides generally decompose at high temperatures due to unfavorable thermodynamic and kinetic properties. Furthermore, reversible hydrogen storage is challenging to achieve owing to formation of stable metal dodecahydro-closo-dodecaboranes, $M_xB_{12}H_{12+2}$, during decomposition, which hampers hydrogen release and uptake. However, metal dodecahydro-closo-dodecaboranes are a versatile class of compounds, which may have potential use in cancer treatment, as ion conductors in polymer chemistry, hydrogen storage, or ammonia storage materials (indirect hydrogen storage). Recently, attention has been directed towards ammonia, NH$_3$, as a hydrogen carrier. Although the storage of liquid ammonia in a steel vessel is well established, solid-state storage can mitigate the hazards of toxicity and smell, while retaining a high hydrogen density. NH$_3$ contains 17.7 wt% H, and can coordinate to metal cations to form solid ammine complexes, $i.e.$ MgCl$_2·6NH_3$, Mn(BH$_4$)$_2·6NH_3$, Li$_2$B$_{12}$H$_{12}·7NH_3$, or Rb$_2$B$_{12}$H$_{12}·5NH_3$. These compounds can be considered potential candidates for solid-state ammonia storage. In low-temperature polymer electrolyte membrane fuel cell (LT PEM FC) applications, the use of NH$_3$(g) can be detrimental, but NH$_3$ can be split into H$_2$ and N$_2$ using an appropriate catalyst.
(typically Ni or Ru) or using NaNH2-mediated NH3 cracking. Ammonia can also be used directly in a solid oxide fuel cell (SOFC) with a Fe-based catalyst. Additionally, ammonia can be used in reduction of NOx exhaust gases in diesel vehicles, e.g. with NH3 stored in a solid metal halide salt. Previously, formation of Li3B12H12·7NH3 has been demonstrated from Li3B12H12 in contact with gaseous or liquid NH3, and Rb2B12H12·6NH3 and CaB12H12·6NH3 have been structurally investigated, but are only stable at T < -38 °C.

In the following, the NH3 uptake and release properties of a series of ammine metal-dodecahydro-closo-dodecaboranes are described. Li3B12H12·7NH3, Na2B12H12·6NH3 and CaB12H12·6NH3 are synthesized and studied with in situ time-resolved synchrotron radiation powder X-ray diffraction (in situ SR-PXD), thermal analysis (TGA-DSC-MS), Fourier transformed infrared spectroscopy (FTIR) and temperature-programmed photographic analysis (TPPA), revealing up to fifteen new compounds, where six are structurally determined.

### Experimental

#### Sample preparation

Metal dodecahydro-closo-dodecaboranes, M3B12H12 (M = Li, Na and Ca) were purchased from Katchem, Prague, Czech Republic. Anhydrous materials were obtained by heating the as-received samples to 230 °C under dynamic vacuum for 10 hours, following an earlier reported procedure. The anhydrous M3B12H12 (M = Li, Na and Ca) compounds were placed in a round bottom flask under Ar atmosphere, which was cooled by a water bath (T ≈ 5–10 °C). A flow of NH3 was passed over the sample for ca. 15 minutes, without air exposure. Shortly after start of NH3 flow (30 to 120 seconds), the volume of the powders increased and the reaction was exothermic (an initial synthesis, without a cooling bath, revealed the flask was hot to the touch). Table 1 presents an overview of the samples. It should be noted that K2B12H12 does not react with NH3 at the applied conditions (see ESI).

Reversible NH3 release and uptake in Na2B12H12·4NH3 and CaB12H12·6NH3 was studied by heating the samples under dynamic vacuum to either 250 or 300 °C (ΔT/Δt = 10 °C min⁻¹), kept isothermally for 30 minutes and then cooled naturally to RT. The samples were then placed in the flask again and exposed to a flow of gaseous NH3 as described above. Diffractograms were obtained at RT after each step (Fig. 13 and 14).

#### Thermal analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was performed on a Netzsch STA 409 C, which was connected via a capillary tube (ca. 2 m) to a Hiden Analytical HAL 201 mass spectrometer (MS). The samples were transferred to Al2O3 crucibles under argon atmosphere in a glove box with circulation purifier (p(O2), H2O < 1 ppm) and heated from RT–585 °C (ΔT/Δt = 5 °C min⁻¹) in the combined system under an Ar-flow of 50 mL min⁻¹.

#### Fourier transformed infrared spectroscopy (FTIR)

Attenuated Total Reflectance Fourier Transformed Infrared spectroscopy was conducted in a Nicolet 380 Avatar spectrometer. The sample was placed over the infrared radiation source and immediately covered by a tight screw. Thus, the total air exposure of the materials is limited to a few seconds. The spectra were collected in the wavenumber range of 4000–400 cm⁻¹ with 32 scans and wavenumber resolution of 4 cm⁻¹ (data spacing 1.929 cm⁻¹).

#### In-house powder X-ray diffraction (PXD)

In-house PXD was carried out using a Bruker D8 Discover X-ray diffractometer with Cu radiation (Cu Kα, 50 kV, 40 mA) and VANTEC-500 2D detector. Air-tight sample holders (Bruker, Germany) were used to prevent contamination of the sample. Otherwise PXD was performed using a Rigaku Smart Lab X-ray diffractometer configured with a Cu X-ray source and a parallel beam multilayer mirror (Cu Kα, λ = 1.5418 Å). Data were collected at RT between 5° and 55° 2θ at 2° min⁻¹. Samples were mounted in 0.5 mm borosilicate glass capillaries and sealed with glue.

#### Synchrotron radiation powder X-ray diffraction (SR-PXD)

In situ time-resolved SR-PXD data were measured at beamline X04SA at the Swiss Light Source (SLS), Villigen, Switzerland, at beamline 1117 at the synchrotron MAX-II, Lund, Sweden, or at beamline P02.1 at Petra III, Deutsches Elektronen Synchrotron (DESY), Hamburg, Germany.

At SLS, the SR-PXD data were collected with a MYTHEN detector at a wavelength of 0.7750 Å. A standard LaB6 sample was used for calibration. All samples were sealed in 0.5 mm glass capillaries (wall thickness 0.01 mm) under helium atmosphere and were measured at variable temperature using a heating rate of ΔT/Δt = 5 °C min⁻¹.

At MAXlab, SR-PXD data were collected with a MAR165 CCD detector system and a wavelength of 0.9938 Å. The used sample cell was specially developed for studies of gas/solid reactions and allows variable pressures and temperatures to be applied. The powdered samples were mounted in a sapphire single-crystal tube (Al2O3, outer diameter 1.09 mm, inner diameter 0.79 mm), inside an argon-filled glove box (p(O2), H2O < 1 ppm). The sample temperature was controlled with a hot air blower temperature-calibrated to an internal NaCl

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**Table 1** Sample overview of M3B12H12 and M2B12H12·nNH3 (M = Li, Na, Ca). The synthesis was performed by passing a flow of gaseous NH3 through the sample at T = 5–10 °C

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li3B12H12·4H2O heated to 230 °C for 10 h, dyn. vac.</td>
<td>Li3B12H12</td>
</tr>
<tr>
<td>Li3B12H12 + NH3 (g)</td>
<td>Li3B12H12·7NH3</td>
</tr>
<tr>
<td>Na2B12H12·4H2O heated to 230 °C for 10 h, dyn. vac.</td>
<td>Na2B12H12</td>
</tr>
<tr>
<td>Na2B12H12 + NH3 (g)</td>
<td>Na2B12H12·4NH3</td>
</tr>
<tr>
<td>CaB12H12·H2O heated to 230 °C for 10 h, dyn. vac.</td>
<td>CaB12H12</td>
</tr>
<tr>
<td>CaB12H12 + NH3 (g)</td>
<td>CaB12H12·6NH3</td>
</tr>
</tbody>
</table>
sample. During desorption measurements the samples were typically heated to 450 °C with a heating rate of $\Delta T/\Delta t = 5 ^\circ C \text{ min}^{-1}$ under \sim 1 bar Ar.

At Petra III, the formation of ammine metal dodecahydro-closo-boranes was studied by loading the anhydrous samples in sapphire single-crystal tube (Al2O3, outer diameter 1.0 mm, inner diameter 0.6 mm) and measured at RT with varying ammonia pressure, $0 < p(\text{NH}_3) < 6.5 \text{ bar}$, at beamline P02.1 (DESY), which is equipped with an amorphous silicon area detector (PerkinElmer XRD1621) and a wavelength of $\lambda = 0.2077 \text{ Å}$. The experiments were performed according to a previous report.39

The FIT2D program was used to remove diffraction spots originating from the single-crystal sapphire tubes and subsequently to transform raw data to powder patterns.40

**Crystal structure determination**

Data collected at the Materials Science Beamline at SLS (PSI) were used for structure solution and refinement. Powder patterns were indexed using the FOX software.41 Structures were solved by direct-space Monte Carlo methods using FOX41 and were refined using Rietveld method by Fullprof Suite software.42 Details of structure determination for each compound are given in ESL.† Final Rietveld refinements plots and refinement indicators are shown in Fig. S5–S8,† and experimental structural parameters and atomic coordinates are listed in Tables S2–S9.

**Temperature-programmed photographic analysis (TPPA)**

Temperature-programmed photographic analysis was performed by collecting photographs using a digital camera while heating the samples from RT to 350 or 400 °C ($\Delta T/\Delta t = 5 \text{ °C min}^{-1}$) using a setup previously described.43 Samples (~15 mg) were pressed into pellets (5 mm diameter) and sealed under argon in a glass vial connected to an argon-filled balloon to maintain an inert atmosphere and constant pressure. A thermocouple was in contact with the sample within the glass vial to monitor the temperature during thermolysis. The glass vial was encased within an aluminum block with open viewing windows for photography, to provide near-uniform heating by cartridge heaters, interfaced to a temperature controller.

**Results**

**Initial sample characterization**

All metal dodecahydro-closo-dodecaborane samples were characterized with FTIR and PXD before and after ammonia-treatment, as shown in Fig. 1 and 2. Vibrational signals for the $[\text{B}_{12}\text{H}_{12}]^{-}$ anion are observed in all samples at ca. 2480, 1070 and 720 cm$^{-1}$ in accord with previous work44 or predicted by DFT calculations.45,46 This shows that the B$_{12}$H$_{12}$-icosahedra are still present after the ammonia treatment, underlining the chemical stability of the metal dodecahydro-closo-dodecaboranes. Note, however, that the B–H stretching peaks (~2480 cm$^{-1}$) merge into one peak after NH$_3$ treatment. This has previously been observed and is attributed to a gain in symmetry of the boron icosahedra.20,47 Vibrational signals from NH$_3$ are observed at 3380 cm$^{-1}$ (N–H stretch) and 1140 cm$^{-1}$ (N–H wagging) in the ammine metal dodecahydro-closo-dodecaborane samples. Minor O–H stretching and bending modes from H$_2$O are also observed in the samples despite being in a dehydrated state, likely because the samples were briefly exposed to air, and metal dodecahydro-closo-dodecaboranes are known to be deliquescent.19

Diffractograms of the reactant M$_x$B$_{12}$H$_{12}$ (M = Li, Na, Ca) are consistent with the known structures of anhydrous Li$_x$B$_{12}$H$_{12}$, Na$_x$B$_{12}$H$_{12}$ and CaB$_{12}$H$_{12}$, whereas diffractograms of the ammoniated samples reveal unknown diffraction patterns.
(Fig. 2). The ammine lithium dodecahydro-closo-dodecaborane sample is identical to the previously reported Li$_2$B$_{12}$H$_{12}$·7NH$_3$, which was synthesized in a similar way,$^{20}$ and from structure solutions using the in situ SR-PXD at SLS, Na$_2$B$_{12}$H$_{12}$·4NH$_3$ was determined (discussed later). Rietveld refinement of the RT diffractogram from the in situ SR-PXD confirms the presence of Li$_2$B$_{12}$H$_{12}$·7NH$_3$ using the reported structural model of Li$_2$B$_{12}$H$_{12}$·7NH$_3$ extracted from single-crystal diffraction (Fig. S4†). However, the powdered sample of Li$_2$B$_{12}$H$_{12}$·7NH$_3$ reveals diffraction peaks at 2θ = 8.90° (1 1 2) and 9.02° (0 1 3) not observed in the previously reported experimental data and a broad Bragg peak at 2θ = 7.78° (−1 1 2) not included in the calculated model.$^{20}$ The broad peak at 2θ = 7.78° may be due to stacking faults generated by the n-glide plane.

The in situ formation of ammine metal dodecahydro-closo-
dodecaboranes was also studied at synchrotron facility Petra III, using a setup described elsewhere.$^{39}$ The data clearly indicate a complete one-step ammonia uptake reaction within ∼30 seconds of exposure to gaseous NH$_3$ (Fig. S1–S3†). The composition of two products obtained after the reaction with ammonia was derived by structural solution to be Li$_2$B$_{12}$H$_{12}$·7NH$_3$ and Na$_2$B$_{12}$H$_{12}$·4NH$_3$ and the composition of the calcium compound is estimated to CaB$_{12}$H$_{12}$·6NH$_3$ based on the thermal analysis; however structure solution was not possible.

**Structural analysis of the series M$_x$B$_{12}$H$_{12}$ (M = Li, Na, Ca)**

Six new ammine metal dodecahydro-closo-borane compounds are identified and structurally investigated using in situ time resolved SR-PXD data and the crystallographic details are listed in Table 2 and atomic coordinates and bond lengths are provided in Tables S2–S9 in the ESI†.

The known compound Li$_2$B$_{12}$H$_{12}$·7NH$_3$, decomposes via two intermediates; Li$_2$B$_{12}$H$_{12}$·4NH$_3$ (observed in the temperature range 60 to 200 °C) and Li$_2$B$_{12}$H$_{12}$·2NH$_3$ (observed in the temperature range 190 to 210 °C). In the latter case, PXD data quality did not allow complete structural solution, but a chemical composition is proposed in a cubic unit cell, a = 20.8754(3) Å and space group I213 (Table 2).

The structure of Li$_2$B$_{12}$H$_{12}$·4NH$_3$ (P2$_1$/n) is shown in Fig. 3, where Li-atoms coordinate to two [B$_{12}$H$_{12}$]$_2^{2-}$ anions via a single H-atom (point sharing, η$^1$) or three H-atoms (face sharing, η$^3$), respectively (Li–H distances vary between 1.87 (η$^1$) to 2.24 Å (η$^3$)). Each Li-atom coordinates to two NH$_3$ molecules via the lone pair on nitrogen and Li–N bond distances are in the range 2.31 to 2.46 Å. In total, Li-atoms coordinate to two NH$_3$ molecules and four H-atoms, generating distorted octahedra around Li.

The directly synthesized ammine sodium dodecahydro-
closo-dodecaborane, Na$_2$B$_{12}$H$_{12}$·4NH$_3$, is isostructural to Li$_2$B$_{12}$H$_{12}$·4NH$_3$ but with a larger unit cell. Rietveld refinement of the structural model is shown in Fig. S7.$^†$

![Fig. 3](image)

**Table 2** Structural data and hydrogen content for the new ammine metal dodecahydro-closo-dodecaboranes, M$_x$B$_{12}$H$_{12}$·nNH$_3$ (M = Li, Na, Ca)

| Chemical Formula | Li$_2$B$_{12}$H$_{12}$·4NH$_3$ | Li$_2$B$_{12}$H$_{12}$·2NH$_3$ | Na$_2$B$_{12}$H$_{12}$·4NH$_3$ | Na$_2$B$_{12}$H$_{12}$·2NH$_3$ | CaB$_{12}$H$_{12}$·4NH$_3$ | CaB$_{12}$H$_{12}$·3NH$_3$
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<td>Monoclinic</td>
<td>Trigonal</td>
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<td>P2$_1$/n (no. 14)</td>
<td>Pn (no. 164)</td>
<td>E3 (no. 167)</td>
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<tr>
<td>$\rho$ [°C]</td>
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<td>200</td>
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<tr>
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<td>c [Å]</td>
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<td>9097.13(20)</td>
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<td>1381.41(1)</td>
<td>1482.24(4)</td>
<td>2049.40(8)</td>
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<tr>
<td>$\mu$ [Å$^3$]</td>
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<td>9097.13(20)</td>
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<td>M [g mol$^{-1}$]</td>
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<td>255.93</td>
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*Temperature for data collection. $^b$Proposed composition.
An intermediate ammine sodium dodecahydro-closo-dodecaborane compound is observed by in situ SR-PXD in the temperature range 65 to 120 °C. The composition was determined as Na₂B₁₂H₁₂·2NH₃, which crystallizes in the trigonal space group P3m1, a = 7.1672(1) Å, c = 7.1574(2) Å, see Fig. 4. The [B₁₂H₁₂]²⁻-anions are located at the corners of the unit cell, and Na-atoms are surrounded by three [B₁₂H₁₂]²⁻-anions (coordinated via edge sharing, η⁴) and one NH₃ molecule (directed along the c-axis) in a tetrahedral manner, even though the coordination number, CN(Na) = 7 (Fig. 4b). The Na–H bond distance is 2.27 Å and the Na–N distance is 2.29 Å, which is slightly shorter than in Na₂B₁₂H₁₂·4NH₃ (Na–N distances in the range 2.40 to 2.43 Å).

The initial structure and chemical composition of the synthesized ammine calcium dodecahydro-closo-dodecaborane cannot be determined from X-ray data, owing to overlapping Bragg peaks and relatively low crystallinity. However, thermal analysis suggests the composition CaB₁₂H₁₂·6NH₃ (discussed later). In the in situ SR-PXD experiment, two intermediate compounds are structurally identified as CaB₁₂H₁₂·2NH₃, observed in the temperature range 90 to 190 °C and CaB₁₂H₁₂·3NH₃ from 190 to 260 °C. The SR-PXD data quality did not allow complete structural solution of CaB₁₂H₁₂·4NH₃ but a monoclinic unit cell was indexed (Table 2).

In the structure of CaB₁₂H₁₂·3NH₃, shown in Fig. 5, Ca-atoms have 9-fold coordination; six H-atoms in total, as each [B₁₂H₁₂]²⁻-anion coordinates to the Ca-atom by tridentate face sharing (η³), and three NH₃ molecules that coordinate equatorially. Thus, the geometry is a tricapped trigonal prism, which is typical for CN = 9. The H-positions are tentative and on NH₃ the hydrogen atoms are disordered by a two-fold axis. Hence, six H positions with occupancy 0.5 are shown, because of temperature disorder. The Ca–N distance is 2.46 Å, which is in line with the Ca–N distance in CaCl₂·8NH₃ (2.52 Å)⁴⁹ and the Ca–H (from B₁₂H₁₂) distance is 2.59 Å. The structure stacks along the c-axis as observed in Fig. 5b, forming one-dimensional chains. CaB₁₂H₁₂·3NH₃ is isostructural to CaB₁₂H₁₂·3H₂O, where the Ca–O distance is 2.33 Å.⁴⁰

In Fig. 6 the unit cell volume per formula unit (V/Z) of the known and new ammine metal dodecahydro-closo-dodecaborane compounds is plotted versus the number of NH₃ molecules in the structure. Linear fits of Li₂B₁₂H₁₂·nNH₃, Na₂B₁₂H₁₂·nNH₃ and CaB₁₂H₁₂·nNH₃ volumes per formula unit (V/Z) show slopes of 37.3 Å³/NH₃ (R² = 0.9964), 34.9 Å³/NH₃ (R² = 0.9953) and 34.8 Å³/NH₃ (R² = 0.9991), which reflects the size of one NH₃ molecule. This agrees well with the volume of NH₃ in the solid state V(NH₃) = 33.9 Å³ at T = −80 °C,⁵⁰ and follows the same trend as observed for other ammine metal borohydrides reported previously, M[B(H₄)₉]·nNH₃ (M = Sr, Ca,⁵¹ Y, Gd, Dy⁵² and Mn⁵³). Notice, not all data are measured at RT, which may give rise to increased volumes, owing to thermal expansion, and thus larger slopes on Fig. 6.

The ability of a metal dodecahydro-closo-dodecaborane to coordinate NH₃ is related to the charge density of the cation, but also the size of the anion. Hence, Li₂B₁₂H₁₂ can coordinate seven NH₃, Na₂B₁₂H₁₂ coordinates four NH₃, whereas K₂B₁₂H₁₂ does not coordinate any NH₃ in structures stable at RT. Furthermore, Na₂B₁₂H₁₂ coordinates four NH₃, whereas NaBH₄ does not react with NH₃.¹ Thus it seems that higher cation charge density and large, weakly coordinating anions may provide higher amounts of ammonia in the solid state. In addition, more NH₃ can be stored in these compounds by lowering temperature during synthesis, i.e. [Li(NH₃)₄]Li₂B₁₂H₁₂·2NH₃ was formed at −78 °C, but transforms into Li₂B₁₂H₁₂·7NH₃ at RT.²⁵

**Thermal decomposition of ammine metal dodecahydro-closo-dodecaboranes**

Thermal decomposition of Li₂B₁₂H₁₂·7NH₃. To elucidate the decomposition mechanism of Li₂B₁₂H₁₂·7NH₃, in situ SR-PXD (Fig. 7), TGA-DSC-MS (Fig. 8), and TPPA (Fig. S9†) was per-
formed. From RT–75 °C diffraction from Li$_2$B$_{12}$H$_{12}$·7NH$_3$ is observed by in situ SR-PXD but decreases in intensity from $T = 60$ °C, while Bragg peaks from Li$_2$B$_{12}$H$_{12}$·4NH$_3$ appear and increase in intensity (Fig. 7b2). This is in agreement with TGA-DSC-MS data (Fig. 8) where a mass loss of 16.8 wt% NH$_3$ between $T = 60–110$ °C is observed (calculated mass loss for three NH$_3$ molecules is 18.6 wt%). The lower mass loss is discussed later. By in situ SR-PXD, thermal expansion of Li$_2$B$_{12}$H$_{12}$·4NH$_3$ is observed from $T \approx 150$ °C, where several peaks shift ca. 0.1° towards lower 2$\theta$ values (higher $d$-spacing), indicated with dashed lines in Fig. 7b3. At $T = 190$ °C Bragg peaks from Li$_2$B$_{12}$H$_{12}$·2NH$_3$ are observed by in situ SR-PXD, which correlates well with TGA-DSC-MS data, showing two endothermic events and a mass loss of 11.7 wt% from two NH$_3$ molecules (calc. mass loss 12.4 wt%) in the temperature range 160–225 °C.

The Li$_2$B$_{12}$H$_{12}$·7NH$_3$ sample was also studied using TPPA, providing visual inspection of the thermal events (Fig. S9†). The pellet visibly shrinks in two steps from 55–115 °C and from 145–185 °C (Fig. S9a–c†), which correlates well with the first two NH$_3$ releases observed with in situ SR-PXD and TGA-DSC-MS. The sample melts at $T \approx 190$ °C and transforms to a transparent liquid containing a white, cloudy suspension.
The melting is also observed by DSC at $T \approx 190 \, ^\circ C$ and at 210 °C by in situ SR-PXD, where only a broad hump at $2\theta = 6.5^\circ$ is observed. Upon further heating, TPPA data reveal drying of the droplet, and slowly it increases in size. This 'drying-process' is supported by in situ SR-PXD, where diffraction reappears at $T = 240 \, ^\circ C$. Here, there are two unknown compounds (denoted u1 and u2), where u1 shifts gradually towards higher $2\theta$, indicating a decreasing unit cell volume, which may support the continuous NH$_3$ release as observed in TGA-DSC-MS in this temperature range (250–305 °C). It was not possible to obtain a unit cell from indexing of either u1 or u2.

Another set of diffraction peaks from an unknown compound (denoted u3) is observed at 275 °C that continue until 300 °C, when the in situ SR-PXD experiment was stopped. By TGA-DSC-MS, a mass loss of 9.2 wt% NH$_3$ is detected in the temperature range 260–325 °C, indicating the loss of 1–2 NH$_3$ molecules (calc. mass loss 6.2–12.4 wt%). Furthermore, the order–disorder transition and decomposition of Li$_2$B$_{12}$H$_{12}$ is observed in TGA-DSC at $T = 350$ and 410 °C which coincides with anhydrous Li$_2$B$_{12}$H$_{12}$ as shown with the dashed line in the DSC data. The melting of the sample may explain the irregular DSC signal observed from 200–325 °C since the TPPA data indicate that NH$_3$ is released in a drying process where pure or partly ammoniated Li$_2$B$_{12}$H$_{12}$ is left as a brittle, powdery crust.

The observation of a liquid intermediate has been reported for LiBH$_4$ with NH$_3$. LiBH$_4$ can form three ammoniates under varying NH$_3$ partial pressures at RT, i.e. LiBH$_4$·xNH$_3$ ($x = 1, 2, 3$). LiBH$_4$·2NH$_3$ is liquid, whereas LiBH$_4$·NH$_3$ and LiBH$_4$·3NH$_3$ are solid. The TGA-DSC-MS data of Li$_2$B$_{12}$H$_{12}$·7NH$_3$ suggest that the liquid compound may have a composition near Li$_2$B$_{12}$H$_{12}$·nNH$_3$ ($1 < n < 2$).

Although the initial PXD data only show diffraction from Li$_2$B$_{12}$H$_{12}$·7NH$_3$, the total observed mass loss by TGA, 37.8 wt%, is less than the calculated mass loss for the release of 7 NH$_3$ molecules, 43.3 wt%. Surprisingly, the NH$_3$-release between 260 and 325 °C is not observed in a previous report of Li$_2$B$_{12}$H$_{12}$·7NH$_3$, where release of 43.3 wt% NH$_3$ below 200 °C was realized. However, the present DSC events observed below 200 °C occur at temperatures similar to the previous report. Even though the starting material is similar, the samples clearly behave differently, perhaps owing to differences in the experimental setup or synthesis. The low mass loss may be a result of the sample not being fully ammoniated, even though Li$_2$B$_{12}$H$_{12}$·7NH$_3$ was the only observed compound, or the sample contains an amorphous impurity, although no indication hereof is currently identified.

Thermal decomposition of Na$_2$B$_{12}$H$_{12}$·4NH$_3$. The in situ SR-PXD data in Fig. 9 present the thermal decomposition of Na$_2$B$_{12}$H$_{12}$·4NH$_3$. A diffractogram obtained at RT before the
experiment, shows a mixture of both Na$_2$B$_{12}$H$_{12}$·4NH$_3$ and Na$_2$B$_{12}$H$_{12}$·2NH$_3$, indicating some ammonia had been released prior to the experiment (Fig. 9b1). Diffracted intensity of Na$_2$B$_{12}$H$_{12}$·4NH$_3$ disappears at $\sim 70 \, ^\circ$C and diffracted intensity from Na$_2$B$_{12}$H$_{12}$·2NH$_3$ begins to disappear at $T = 100 \, ^\circ$C, but is observed until 125 °C (Fig. 9b2). At this temperature a third compound (denoted u4) appears which is observed until $\sim 135 \, ^\circ$C (Fig. 9b3). Following this, diffraction from Na$_2$B$_{12}$H$_{12}$ is observed together with a few peaks from another unknown compound (denoted u5) that gradually shifts towards higher 2θ values in the temperature range 135–190 °C (Fig. 9b4). This indicates a decrease in unit cell volume, likely as a consequence of NH$_3$ release. The suggested composition of u4 may be Na$_2$B$_{12}$H$_{12}$·NH$_3$ and u5 may be Na$_2$B$_{12}$H$_{12}$·0.5NH$_3$ or Na$_2$B$_{12}$H$_{12}$ with 1–2 interstitial NH$_3$ molecules, however the composition could not be structurally determined. At $T > 200 \, ^\circ$C, Na$_2$B$_{12}$H$_{12}$ is the only observed compound and the high-temperature order–disorder phase transition of Na$_2$B$_{12}$H$_{12}$ is observed at 260 °C (Fig. 9b5). This indicates all NH$_3$ is released below 200 °C.

The thermal analysis of Na$_2$B$_{12}$H$_{12}$·4NH$_3$ (Fig. 10) correlates well with the in situ SR-PXD data as three endothermic events are observed at $T = 80$, 125 and 140 °C. The phase transition of Na$_2$B$_{12}$H$_{12}$ occurs at 268 °C and the sample starts to decompose at an onset temperature of $T \approx 400 \, ^\circ$C, in agreement with the behavior of pure Na$_2$B$_{12}$H$_{12}$ (shown as dashed lines in Fig. 10). The total observed mass loss is 19.0 wt%, but the calculated ammonia content of Na$_2$B$_{12}$H$_{12}$·4NH$_3$ is 26.6 wt% NH$_3$. As shown in Fig. 9a both Na$_2$B$_{12}$H$_{12}$·4NH$_3$ and Na$_2$B$_{12}$H$_{12}$·2NH$_3$ are observed, indicating that some Na$_2$B$_{12}$H$_{12}$·4NH$_3$ converts to Na$_2$B$_{12}$H$_{12}$·2NH$_3$ at room temperature after synthesis. Hence, Na$_2$B$_{12}$H$_{12}$·4NH$_3$ may have limited stability at RT.

In the TPPA measurement of Na$_2$B$_{12}$H$_{12}$·4NH$_3$, shrinkage of the pellet was observed from 60–100 °C and 112–130 °C (Fig. S10f) agreeing well with the observations from thermal analysis and the in situ SR-PXD data. Another visual change occurs above the phase transition of Na$_2$B$_{12}$H$_{12}$ at 270 °C, where the pellet slowly increases in volume until the measurement is stopped at 350 °C, possibly underlining the higher volume of the disordered high-temperature polymorph of Na$_2$B$_{12}$H$_{12}$.

**Thermal decomposition of CaB$_{12}$H$_{12}$·6NH$_3$.** Thermal analysis of sample CaB$_{12}$H$_{12}$·6NH$_3$, presented in Fig. 11, shows four thermal events where NH$_3$ is released, followed by decomposition of CaB$_{12}$H$_{12}$ starting at $T = 350 \, ^\circ$C with H$_2$ release. The TGA-DSC-MS data indicate that the four NH$_3$ release events occur as follows: two NH$_3$ molecules are...
released at $T = 120 \, ^\circ\mathrm{C}$, one $\text{NH}_3$ molecule is released at $T = 200 \, ^\circ\mathrm{C}$, two $\text{NH}_3$ molecules are released at $T = 250 \, ^\circ\mathrm{C}$, and one $\text{NH}_3$ molecule is released at $T = 310 \, ^\circ\mathrm{C}$. The TGA data reveal a total mass loss of 31.2 wt%, which is lower than the calculated 36.0 wt% $\text{NH}_3$ of $\text{CaB}_{12}\text{H}_{12}\cdot6\text{NH}_3$. TPPA shows that the pellet decreases in volume in multiple steps corresponding to the $\text{NH}_3$ release, observed at temperatures equal to the TGA-DSC-MS data (Fig. S11†).

The in situ SR-PXD data are presented in Fig. 12, where the decomposition of $\text{CaB}_{12}\text{H}_{12}\cdot6\text{NH}_3$ reveals five different unknown structures. The observed structural changes fit well with the thermal analysis. It was not possible to index or solve most of the structures owing to peak overlap and low crystallinity, however the structural solutions and composition of $\text{CaB}_{12}\text{H}_{12}\cdot4\text{NH}_3$ (observed between 90–190 °C) and $\text{CaB}_{12}\text{H}_{12}\cdot3\text{NH}_3$ (190–260 °C) agree well with the thermal analysis where the DSC signal and TGA mass loss indicate the release of $\sim3$ $\text{NH}_3$ molecules from RT–200 °C. By combining TGA and in situ SR-PXD data, the unknown structures may be assigned as: $\text{CaB}_{12}\text{H}_{12}\cdot6\text{NH}_3$' (RT–70 °C), $\text{CaB}_{12}\text{H}_{12}\cdot5\text{NH}_3$' (70–90 °C), $\text{CaB}_{12}\text{H}_{12}\cdot4\text{NH}_3$ (90–190 °C), $\text{CaB}_{12}\text{H}_{12}\cdot3\text{NH}_3$ (190–260 °C), and $\text{CaB}_{12}\text{H}_{12}\cdot2\text{NH}_3$' (260–275 °C). Another in situ SR-PXD experiment was conducted at Maxlab (beamline I711), where the sample was heated to 450 °C. Here the formation of $\text{CaB}_{12}\text{H}_{12}$ and subsequent decomposition was observed at 300 and 350 °C, in agreement with the thermal analysis (Fig. S12†). Thus, the sample does not decompose until all $\text{NH}_3$ has been released, similar to what was observed in ammoniated $\text{LiB}_{12}\text{H}_{12}$ and $\text{NaB}_{12}\text{H}_{12}$.

Ammonia release and uptake

The reversible $\text{NH}_3$ release and uptake for $\text{LiB}_{12}\text{H}_{12}\cdot7\text{NH}_3$ has been reported previously, where a sample of $\text{LiB}_{12}\text{H}_{12}$ remains unchanged after 10 cycles, indicating excellent reversibility of $\text{NH}_3$ release and uptake.20 Here the high thermal stability of metal dodecahydro-closo-dodecaborane is an advantage, as it allows the release and uptake of $\text{NH}_3$ at moderate temperatures without altering or decomposing the metal dodecahydro-closo-dodecaborane. For $\text{NaB}_{12}\text{H}_{12}$ and $\text{CaB}_{12}\text{H}_{12}$, the reversible release and uptake of $\text{NH}_3$ was demonstrated by powder X-ray diffraction as presented in Fig. 13 and 14. In both cases, $\text{NH}_3$ is absorbed at RT and released at 250 and 300 °C under dynamic vacuum for $\text{NaB}_{12}\text{H}_{12}$ and $\text{CaB}_{12}\text{H}_{12}$, respectively. Both $\text{NaB}_{12}\text{H}_{12}$ and $\text{CaB}_{12}\text{H}_{12}$ show good reversibility over two $\text{NH}_3$ release and uptake cycles.

Discussion

The thermal decomposition of ammine $\text{M}_{x}\text{B}_{12}\text{H}_{12}$ ($\text{M} = \text{Li, Na, Ca}$) shows that $\text{NH}_3$ was released from all samples in multiple
steps, giving rise to interesting structural changes observed by in situ synchrotron radiation X-ray diffraction. The thermal decomposition of Li$_2$B$_{12}$H$_{12}$-7NH$_3$ is complex with several intermediate ammine metal dodecahydro-closo-dodecaboranes, and two are structurally identified. At ca. 190 to 240 °C, the sample is molten and after recrystallization several unknown compounds are observed. For Na$_2$B$_{12}$H$_{12}$-4NH$_3$, the release of ammonia occurs in three steps and the intermediate compound Na$_2$B$_{12}$H$_{12}$-2NH$_3$ was solved. CaB$_{12}$H$_{12}$ releases ca. six ammonia molecules in four steps and two intermediate compounds are determined as CaB$_{12}$H$_{12}$-4NH$_3$ and CaB$_{12}$H$_{12}$-3NH$_3$.

The samples only release NH$_3$ and the decomposition temperature of the metal dodecahydro-closo-dodecaborane is unaltered compared to pristine metal dodecahydro-closo-dodecaborane. It should be noted that minor release of H$_2$ is detected simultaneously with NH$_3$ in the MS of all three samples. A fragmentation overlap in the MS between NH$_3$ and H$_2$ is typically not expected and it is believed to be an artifact from the experimental setup. A part of the coupling line between TGA-DSC and MS is made of plastic and contain a filter to prevent powder from entering the MS capillary. It is possible this filter was dirty and, when exposed to ammonia, hydrogen from a side reaction could be carried trough. Nevertheless, the observation of the pure M$_x$B$_{12}$H$_{12}$ compounds by in situ SR-PXD, and that NH$_3$ is reversible cycled, allows us to conclude that no decomposition occurs when NH$_3$ is released. Furthermore, no formation of stable B–N compounds is observed in this investigation, otherwise reported for some ammine metal borohydrides, e.g. Mn(BH$_4$)$_2$-6NH$_3$ in an exothermic reaction possibly via dihydrogen bonds between BH$_4^-$ and NH$_3$ (H$^\delta^-$⋯H$^\delta^+$). Other more stable metal borohydrides release ammonia without reaction, and may store ammonia reversibly, e.g. M(BH$_4$)$_2$, M = Ca or Sr.$^{15,66}$ The high thermal stability of the metal dodecahydro-closo-dodecaboranes makes them suitable for NH$_3$ storage at low to moderate temperatures, and the reversibility is demonstrated for ammine Na$_2$B$_{12}$H$_{12}$ and CaB$_{12}$H$_{12}$, and reported previously for ammine Li$_2$B$_{12}$H$_{12}$. The reported temperatures for NH$_3$ release in Li$_2$B$_{12}$H$_{12}$-7NH$_3$ (release of 43.3 wt% NH$_3$ at 200 °C) differ significantly from the ammonia release observed by in situ SR-PXD, TGA-DSC-MS and TPPA in the present study (release of 37.4 wt% NH$_3$ below 350 °C) and these results are reproducible for multiple samples. It remains unclear why such large differences to the previous report are observed, since deviations of this magnitude are not typically ascribed to only experimental differences or synthesis conditions.

The gravimetric NH$_3$ density may limit the potential NH$_3$ storage in the light metal dodecahydro-closo-dodecaboranes studied here, since the [B$_{12}$H$_{12}$]$^{2-}$ anion is heavy compared to chloride. For instance, MgCl$_2$-6NH$_3$ absorbs ammonia at RT and releases a total of 51.77 wt% ammonia in three steps at temperatures comparable to the metal dodecahydro-closo-dodecaboranes (150 to 325 °C). Nevertheless, the total hydrogen content of the ammine metal dodecahydro-closo-dodecaboranes is high (Tables 2 and 3), but only hydrogen indirectly stored as NH$_3$ is reversibly accessible. For comparison, the hydrogen content of selected ammine metal chlorides is listed together with the studied ammine metal dodecahydro-closo-dodecaboranes in Table 3.
Table 3  The ammonia and hydrogen content of selected ammine metal chlorides and dodecahydro-closo-dodecaboranes30

<table>
<thead>
<tr>
<th>Compound</th>
<th>$M$ (g mol$^{-1}$)</th>
<th>NH$_3$ content (wt%)</th>
<th>H content from NH$_3$ (wt%)</th>
<th>Total H content (wt%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl$_2$·8NH$_3$</td>
<td>247.23</td>
<td>41.33</td>
<td>9.78</td>
<td>9.78</td>
<td>30</td>
</tr>
<tr>
<td>MgCl$_2$·6NH$_3$</td>
<td>197.40</td>
<td>51.77</td>
<td>9.19</td>
<td>9.19</td>
<td>30</td>
</tr>
<tr>
<td>Li$<em>3$B$</em>{12}$H$_{12}$·7NH$_3$</td>
<td>274.93</td>
<td>43.36</td>
<td>7.70</td>
<td>12.10</td>
<td>20+This work</td>
</tr>
<tr>
<td>Na$<em>2$B$</em>{12}$H$_{12}$·4NH$_3$</td>
<td>255.93</td>
<td>26.62</td>
<td>4.73</td>
<td>9.45</td>
<td>This work</td>
</tr>
<tr>
<td>CaB$<em>{12}$H$</em>{12}$·6NH$_3$</td>
<td>284.09</td>
<td>35.97</td>
<td>6.39</td>
<td>10.64</td>
<td>This work</td>
</tr>
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</table>

* Only hydrogen originating from NH$_3$ is considered.

Conclusions

This investigation reveals the synthesis and complex ammonia release reactions from Li$_3$B$_{12}$H$_{12}$·7NH$_3$, Na$_2$B$_{12}$H$_{12}$·4NH$_3$, and CaB$_{12}$H$_{12}$·6NH$_3$. The thermal decomposition is investigated using a range of complementary techniques, in situ time-resolved synchrotron radiation powder X-ray diffraction (in situ SR-PXD), thermal analysis (TGA-DSC-MS), Fourier transformed infrared spectroscopy (FTIR), and temperature programmed photographic analysis (TPPA). The ammonia release reactions reveal fifteen new compounds, where six of those are structurally characterized. This work shows that ammine metal dodecahydro-closo-dodecaboranes have ammonia storage density and properties comparable to similar metal halides, mainly assigned to the high thermal stability of large dodecahydro-closo-dodecaborane anions. Furthermore, ammonia is stored reversibly and may be considered as indirect hydrogen storage. This work provides deeper insight into the structural, physical, and chemical properties related to thermal decomposition and possible ammonia and hydrogen storage of metal dodecahydro-closo-dodecaborane-based materials.

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