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Manganese borohydride; synthesis and characterization†

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Solvent-based synthesis and characterization of α-Mn(BH4)2 and a new nanoporous polymorph of manganese borohydride, γ-Mn(BH4)2, via a new solvate precursor, Mn(BH4)2·1/2S(CH3)2, is presented. Manganese chloride is reacted with lithium borohydride in a toluene/dimethylsulfide mixture at room temperature, which yields halide and solvent-free manganese borohydride after extraction with dimethylsulfide (DMS) and subsequent removal of residual solvent. This work constitutes the first example of establishing a successful, reproducible solvent-based synthesis route for a pure, crystalline, stable transition metal borohydride. The new polymorph, γ-Mn(BH4)2, is shown to be the manganese counterpart of the zeolite-like compound, γ-Mg(BH4)2 (cubic, a = 16.209(1) Å, space group Ia3d). It is verified that large pores (diameter > 6.0 Å) exist in this structure. The solvate, Mn(BH4)2·1/2S(CH3)2, is subsequently shown to be the analogue of Mg(BH4)2·1/2S(CH3)2. As the structural analogies between Mg(BH4)2 and Mn(BH4)2 became evident a new polymorph of Mg(BH4)2 was identified and termed ζ-Mg(BH4)2. ζ-Mg(BH4)2 is the structural counterpart of α-Mn(BH4)2. All synthesis products are characterized employing synchrotron radiation-powder X-ray diffraction, infrared spectroscopy and thermogravimetric analysis in combination with mass spectroscopy. Thermal analysis reveals the decomposition of Mn(BH4)2 to occur at 160 °C, accompanied by a mass loss of 14.8 wt%. A small quantity of the desorbed gaseous species is identified as diborane (ρMn(Mn(BH4)2) = 9.5 wt% H2), while the remaining majority is found to be hydrogen.

Introduction

The increasing world-wide energy demand necessitates still new approaches for implementing safe and environmentally benign forms of energy, to replace fossil fuels.1 Current research efforts within hydrogen storage focus on high storage densities, prolific thermodynamic and kinetic properties and reversibility, to allow renewable energy storage for mobile applications.2 The current technology utilizes high pressure hydrogen tanks; e.g. p(H2) ~ 700 bar for the automotive industry.3 As an alternative to pressure tanks, solid state chemical storage of hydrogen is being investigated. For example, utilization of hydride materials to act as solid state storage media for renewable energy is intensely studied. Several classes of materials are investigated, such as metal alloys, magnesium based hydrides and metal borohydrides.3–6 The latter exhibit fascinating characteristics, both structurally and chemically.7–9 Borohydrides hold high hydrogen contents; however release of hydrogen is achieved under less than favorable conditions and in certain cases undesired release of diborane poses a challenge.10,11 and they often suffer from slow kinetics. A well-known example is LiBH4, holding 18.4 wt% hydrogen, unfortunately being considerably hampered by its enthalpy of decomposition (~67 kJ mol⁻¹). Several methods for improving the hydrogen storage properties of such compounds exist,12 formation of reactive hydride composites (RHC’s),13,14 incorporation into nanoporous carbon scaffolds (nano confinement),15,16 anion substitution4,17,18 and formation of bimetallic materials.19,20 However, so far synthesis of the ideal hydrogen storage material based on borohydrides has not been achieved. Rehydrogenation of the storage materials is another challenge. Hydrogen pressure of 950 bar and 400 °C have been shown to hydrogenate MgB2 to Mg(BH4)2 over several days,21 but this is no practical solution. Among transition metal

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†Electronic supplementary information [ESI] available: Rietveld refinement plots, further experimental details, gas desorption quantification estimation methods, ex situ powder X-ray diffraction plots for decomposition reactions and crystal data from refined and calculated models as CIF files. See DOI: 10.1039/c4dt03501a
borohydrides,\textsuperscript{22–26} manganese borohydride is an interesting candidate owing to its reportedly low temperature of decomposition.\textsuperscript{27,28} Unfortunately, thermal decomposition of Mn(BH\textsubscript{4})\textsubscript{2} is accompanied with the liberation of hydrogen, but also some diborane.\textsuperscript{25} Reactive manganese borohydride – metal hydride composites may be designed to suppress the release of diborane.\textsuperscript{29} Bimetallic borohydrides, e.g. LiZn\textsubscript{2}(BH\textsubscript{4})\textsubscript{3}, releases a hydrogen–diborane mixture of approximately 1:1 composition, and has even been used as an indirect source of diborane.\textsuperscript{30} Preceding work on Mn(BH\textsubscript{4})\textsubscript{2}, employing solvent based synthesis routes, provided tetrahydrofuran (THF) adducts. However, pure Mn(BH\textsubscript{4})\textsubscript{2} could not be extracted due to the high temperatures needed to remove THF, causing the borohydride to decompose.\textsuperscript{31} A mechanochemical approach afforded non-crystalline materials, which by spectroscopic methods proved to be a mixed cation manganese borohydride.\textsuperscript{28} The first structural characterization of α-Mn(BH\textsubscript{4})\textsubscript{2} prepared from a mechanochemical metathesis reaction between MnCl\textsubscript{2} and LiBH\textsubscript{4} was presented recently.\textsuperscript{32} However, the synthesis product, α-Mn(BH\textsubscript{4})\textsubscript{2}, contains LiCl and thus calls for new methods. For researchers to tailor materials properties fulfilling the demands of solid state hydrogen storage, high purity chemicals are needed. Furthermore, providing new synthesis routes gives important insight into the reaction pathways and properties of the materials in question. In this work we present the synthesis of a new solvate and two polymorphs of Mn(BH\textsubscript{4})\textsubscript{2}, obtained as halide- and solvent free products.

**Experimental section**

**Synthesis**

2.52 g (20.0 mmol, 1.33 equivalents, 33% excess) finely ground MnCl\textsubscript{2} (Aldrich, ≥99%, anhydrous) was suspended in an 80:20 toluene-dimethylsulfide mix (50 mL) (anh., Sigma-Aldrich) at room temperature. Two equivalents (0.65 g, 30 mmol) of finely ground LiBH\textsubscript{4} (Sigma-Aldrich, ≥98%) was added to the pink MnCl\textsubscript{2} suspension at room temperature, left stirring and shortly after a pale yellow solid formed. The reaction mixture was left stirring at room temperature overnight, turning into a more homogenous and progressively more yellow suspension as stirring proceeded. The mixture was filtered, after which the resulting clear yellow solution was evaporated under pressure, providing firstly a viscous yellow oil, followed by solid Mn(BH\textsubscript{4})\textsubscript{2}:2S(CH\textsubscript{3})\textsubscript{2} as the only product. Following heating under vacuum (110 °C/2 x 10\textsuperscript{-2} mbar) for 16–24 h provided α-Mn(BH\textsubscript{4})\textsubscript{2}. Collecting the viscous oil before it is solidified, and subsequently drying it under vacuum at RT for 3 days provides γ-Mn(BH\textsubscript{4})\textsubscript{2} (with traces of α-Mn(BH\textsubscript{4})\textsubscript{2}). All manipulation of solids were performed in an argon filled glovebox (O\textsubscript{2}/H\textsubscript{2}O < 0.1 ppm) equipped with a circulation purifier. All manipulation of solvents and solutions are performed using argon as protective atmosphere and inert syringe handling techniques in standard Schlenk glass equipment.

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

SR-PXD data were collected at (a) BM01A at the Swiss-Norwegian Beamlines (SNBL) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France and (b) at the synchrotron MAX-II, Lund, Sweden in the research laboratory MAX-lab, beamline 1711.

(a) **SR-PXD at SNBL.** The samples were ground in a mortar and mounted in glass capillaries (o.d. 0.5 mm) sealed with glue inside an argon-filled glovebox with a circulation purifier (p(O\textsubscript{2}, H\textsubscript{2}O) < 0.1 ppm). The 2D powder data were recorded using a MAR345 Imaging Plate detector and a selected wavelength of 0.6967 Å. For all measurements the capillaries were oscillated by 30° during exposure to the X-ray beam for 30 s, followed by a readout time of ~83 s. At RT single PXD patterns were collected at three different sample-to-detector distances 150, 250 and 390 mm in order to obtain both data at high diffraction angle and data with higher resolution at low diffraction angles. Subsequently, the sample was heated from RT to 200 °C at a rate of 2 °C min\textsuperscript{-1}, while SR-PXD data were collected. The temperature was controlled with the Oxford Cryostream 700+. The in situ data were collected using a sample-to-detector distance of 390 mm.

(b) **In situ SR-PXD at MAX-lab.** The powdered sample was mounted in a sapphire (Al\textsubscript{2}O\textsubscript{3}) single crystal tube (o.d. 1.09 mm, i.d. 0.79 mm) in an argon-filled glovebox p(O\textsubscript{2}, H\textsubscript{2}O) < 1 ppm. The tube was attached to a specially developed sample cell designed for studies of gas/solid reactions and allowing for high pressures and temperatures to be applied. During heating the temperature was controlled with a thermocouple placed in the sapphire tube ~1 mm from the sample.\textsuperscript{33} A heating rate of 5 °C min\textsuperscript{-1} was applied up to temperatures of 300 °C, while vacuum, argon atmosphere (p(Ar) = 1 bar) or hydrogen pressure (p(H\textsubscript{2}) = 10 bar) was applied to the samples. SR-PXD data was collected by a MAR165 CCD detector system using X-ray exposure time of 30 s and selected wavelengths of λ = 0.9920, 1.0096 or 1.0080 Å.\textsuperscript{34,35} The FIT2D program\textsuperscript{36} was used for calibrating the wavelengths using a standard (NIST) LaB\textsubscript{6} sample, masking diffraction spots from the single crystal sapphire sample holder and transforming all obtained raw images from both SNBL and MAX-lab to 2D-powder patterns. Uncertainties of the integrated intensities were calculated at each 2θ-point by applying Poisson statistics to the intensity data, considering the geometry of the detector.\textsuperscript{37}

**Structural refinement by the rietveld method**

Rietveld refinement was carried out using the program FullProf.\textsuperscript{38} In general, backgrounds were described by linear interpolation between selected points. For all structures scale-factors, cell parameters, profile parameters and overall displacement factor, B\textsubscript{iso}, were refined as a minimum. Furthermore, zero-shift was refined for all data. Note that the high χ\textsuperscript{2} values reflect mainly the extremely high counting statistics of the powder diffraction data obtained from modern 2D-detectors.
The structure of Mn(BH₄)₂·1/2S(CH₃)₂ was refined by simultaneous Rietveld refinement of two SR-PXD data sets measured on the same sample at SNBL at RT with a sample-to-detector distance of 150 and 390 mm, respectively to take full advantage of both high angle data (150 mm dataset) and high resolution at low angle (390 mm dataset). Two sets of Bragg reflections were identified in the data, one assigned to α-Mn(BH₄)₂ as being similar to the diffraction pattern for Mg(BH₄)₂·1/2S(CH₃)₂. Hence, Mn was substituted for Mg in the monoclinic structural model for Mg(BH₄)₂·1/2S(CH₃)₂ (space group Cc) as presented in ref. 39 and this was used as starting model for the refinement together with the structural data for Mn(BH₄)₂ as given in ref. 32. For Mn(BH₄)₂·1/2S(CH₃)₂ all atomic positions were refined using 40 distance constraints for interatomic distances and 37 for angles. Only positions (not the orientation) of the CH₃ and BH₄ units were refined. As for the displacement factors, those for Mg(BH₄)₂·1/2S(CH₃)₂ were used as starting points and the displacements factors were refined freely for Mn and S while those for the CH₃ and BH₄ groups were refined together. The final discrepancy factors for the 150 and 390 mm datasets are: $\chi^2 = 1360$ and 1450, $R_{wp} = 0.913$ and 1.99% (not corrected for background), $R_p = 2.38$ and 4.28% (corrected for background), $R_B$(Mn(BH₄)₂·1/2S(CH₃)₂) = 1.03 and 1.29% and $R_B$(Mn(BH₄)₂) = 1.64 and 2.55%. The refinement profiles are shown in Fig. S2.1.† Crystal data and atomic coordinates are listed in Table S2.1.† The structure of γ-Mn(BH₄)₂ was refined from SR-PXD data (MAX-lab, $\lambda = 0.9920$ Å) measured at RT. One set of Bragg reflections in the data was assigned to γ-Mn(BH₄)₂ (being similar to the diffraction pattern for γ-Mg(BH₄)₂). Hence, Mn was substituted for Mg in the structural model for γ-Mg(BH₄)₂ (space group Idd3a) and this was used as starting point for the refinement. Reflections from a small amount of α-Mn(BH₄)₂ were refined from the model for Mn(BH₄)₂ as given in ref. 32. Furthermore, the SR-PXD data contains reflections (see ESIT† for d-spacings) from one or more unidentified compounds, which may be a manganese analogue of ε-Mg(BH₄)₂ as described in ref. 40. However, the small amount and the low number of Bragg peaks hamper indexing as well as comparison with published data. For γ-Mn(BH₄)₂, Mn is located on a special position, hence only positions (not the orientation) of the BH₄ units were refined. The final discrepancy factors are: $\chi^2 = 21.51$, $R_{wp} = 5.95%$ (not corrected for background), $R_p = 25.7%$ (corrected for background), $R_B$(γ-Mn(BH₄)₂) = 14.8%. The fact that undescribed reflections remain in the refinement is clearly seen from the relatively high agreement factors. The refinement profiles are shown in Fig. S2.2.† Crystal data and atomic coordinates are listed in Table S2.2.† The structure of ζ-Mg(BH₄)₂ was refined from SR-PXD data (SNBL, ESRF, $\lambda = 0.7035$ Å) measured at 224 °C. Realizing that the diffraction pattern of ζ-Mg(BH₄)₂ is similar to that of α-Mn(BH₄)₂ (space group P3₁2₁2) allowed to develop a structural model for ζ-Mg(BH₄)₂ by substitution of Mg for Mn, which was used as starting point for the refinement. The refinement profiles are shown in Fig. S2.3.† Due to the quality of the data, the BH₄ units were refined as rigid bodies and only positions (not orientations) of the tetrahedra were refined, and individual displacement factors were not refined. The final discrepancy factors are: $\chi^2 = 21.5$, $R_{wp} = 0.420%$ (not corrected for background), $R_p = 25.1%$ (corrected for background), $R_B$(ζ-Mg(BH₄)₂) = 13.6%.

**Thermal analysis, TGA-DSC/TPD-MS.** Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were collected for Mn(BH₄)₂·1/2S(CH₃)₂ and α-Mn(BH₄)₂ using a Perkin-Elmer STA 6000 instrument coupled to a Hiden HPR 20 QIC mass spectrometer (MS) via a heated capillary. The atomic mass ranges probed were set up to detect all fragments of dimethylsulfide, diborane and hydrogen respectively. The measurements were performed in a continuous flow of Ar (65 mL min⁻¹) using Al₂O₃ crucibles fitted with a lid to prevent exposure to air when mounted. Gases produced from the decomposition during heating were led through a small hole in the lid and through the inlet of the MS probe. The heating rate was 5 °C min⁻¹ until reaching 250 °C.

**Infrared spectroscopy.** Infrared spectra were collected by Attenuated Total Reflectance - Fourier Transformed Infrared Spectroscopy (ATR-FTIR), using a Nicolet 380 Avatar spectrometer. The sample powder was placed directly on the infrared radiation source and immediately covered by a tight screw. The total exposure of the materials to air is limited to a few seconds in this manner. The spectra were collected in the wavenumber range of 4000–400 cm⁻¹ with 32 scans.

**Results and discussion**

**Synthesis**

The method utilized for synthesis of Mn(BH₄)₂ is a solvent based metathesis reaction, usually performed mechanochemically.⁴¹,⁴² The present approach requires no ball milling or activation such as heating or high pressures, i.e. finely ground MnCl₂ and LiBH₄ (filtered through 112 μm sieves) suspended in toluene/DMS react according to Scheme 1 below.

In this manner formation of ternary chlorides, e.g. Li- or NaMn-chlorides, or bi-metallic borohydrides, previously reported to form mechanochemically from MnCl₂ and LiBH₄ or NaBH₄, is avoided.⁴³,⁴⁴ Dimethylsulfide (DMS) as co-solvent and extraction solvent has several advantages. Firstly, the reaction is allowed to proceed faster as the products are being

![Scheme 1](image-url)
dissolved in DMS as it forms. Secondly, it eliminates the problem of strong coordination of the metal cation to donor (sulfur in DMS) atoms in certain coordinating solvents, i.e. circumventing the problem of removing e.g. tetrahydrofuran (THF).\textsuperscript{31} Thirdly, the materials are separated from any unreacted starting materials and byproducts (i.e. LiCl) formed during the reaction, since only Mn(BH$_4$)$_2$ is dissolved as shown in Scheme 1. After removing excess DMS, the product obtained is a hard, yellowish powder of Mn(BH$_4$)$_2$·1/2S(CH$_3$)$_2$ (Fig. S1.1\textsuperscript{†}). Manganese in Mn(BH$_4$)$_2$·1/2S(CH$_3$)$_2$ coordinates relatively weakly to sulfur, thus the solvent can be removed under mild conditions. The coordination is broken at temperatures low enough to preserve the Mn(BH$_4$)$_2$ ($T < 110$ °C), in contrast to earlier attempts of desolvating Mn(BH$_4$)$_2$ 3THF, where temperatures required ($T > 140$ °C) were high enough that decomposition occurred.\textsuperscript{31} In contrast, subjecting the diethylether magnesium borohydride complex to a longer drying process,\textsuperscript{45} diethylether can be extracted at $T > 180$ °C providing the high temperature polymorph $\beta$-Mg(BH$_4$)$_2$.\textsuperscript{46} For these reasons neither diethylether nor THF was used as solvent in this work. Furthermore, diethylether has some solubility of LiCl and LiBH$_4$, which may contaminate the reaction product.\textsuperscript{47,48} The weak coordination of DMS to manganese in Mn(BH$_4$)$_2$·1/2S(CH$_3$)$_2$ is specifically demonstrated by the formation of $\gamma$-Mn(BH$_4$)$_2$, which is a new nanoporous compound, arising from the gentle (vac/RT) removal of DMS molecules from the cavities (see the structural discussion below). After desolvation, $\gamma$-Mn(BH$_4$)$_2$ is obtained as a yellowish, sometimes brown powder.

New synthesis methods, which provide halide free metal hydrides for consideration for solid-state hydrogen storage is of significant interest. Recently, yttrium and gadolinium borohydrides were prepared using dimethyl sulfide as a solvent providing new solvates as intermediates, M(BH$_4$)$_3$S(CH$_3$)$_2$ (M = Y or Gd), which transformed to $\alpha$-Y(BH$_4$)$_3$ or Gd(BH$_4$)$_3$ at $\sim$140 °C.\textsuperscript{49} Other halide free rare earth metal borohydrides, Eu(BH$_4$)$_2$ and Sm(BH$_4$)$_2$, are prepared by a metathesis reaction of trivalent metal chlorides and LiBH$_4$ in ethereal solution, combined with solvent extraction using dimethyl sulfide.\textsuperscript{50}

Crystal structures of Mn(BH$_4$)$_2$·1/2S(CH$_3$)$_2$ and $\gamma$-Mn(BH$_4$)$_2$

The solvate, Mn(BH$_4$)$_2$·1/2S(CH$_3$)$_2$ crystallizes in a monoclinic unit cell, $a = 7.6914(4)$, $b = 13.8731(8)$, $c = 12.4278(7)$ Å and $\beta = 103.973(4)$° ($V = 1286.84(13)$ Å$^3$, $Z = 4$), space group $Cc$. The 3D framework of Mn(BH$_4$)$_2$·1/2S(CH$_3$)$_2$ contains two Mn atoms: one (Mn2) is tetrahedrally coordinated to four BH$_4$ groups, while the other (Mn1) coordinates to four BH$_4$ groups and one S(CH$_3$)$_2$ ligand to form a trigonal bipyramid (Fig. 1). Each BH$_4$...
Table 1  Structural parameters for the isostructural Mn(BH₄)₂ and Mg(BH₄)₂ polymorphs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>Cell parameters (Å)</th>
<th>β (°)</th>
<th>V (Å³)</th>
<th>Z</th>
<th>V/Z</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(BH₄)₂·1/2S(CH₃)₂</td>
<td>Cc</td>
<td>a = 7.6914(4)</td>
<td>103.973(4)</td>
<td>1286.84(13)</td>
<td>4</td>
<td>321.71</td>
<td>—a</td>
</tr>
<tr>
<td>Mg(BH₄)₂·1/2S(CH₃)₂</td>
<td>Cc</td>
<td>a = 7.6325(4)</td>
<td>103.833(3)</td>
<td>1274.94(13)</td>
<td>4</td>
<td>318.74</td>
<td>39</td>
</tr>
<tr>
<td>α-Mn(BH₄)₂</td>
<td>P₃₁2</td>
<td>a = 10.435(1)</td>
<td>—</td>
<td>1021.8(3)</td>
<td>9</td>
<td>113.53</td>
<td>32</td>
</tr>
<tr>
<td>ζ-Mg(BH₄)₂</td>
<td>P₃₁2</td>
<td>a = 10.424(3)</td>
<td>—</td>
<td>1009.7(7)</td>
<td>9</td>
<td>112.19</td>
<td>—a</td>
</tr>
<tr>
<td>γ-Mn(BH₄)₂</td>
<td>I₆₃a</td>
<td>a = 16.2099</td>
<td>—</td>
<td>4258.6</td>
<td>24</td>
<td>177.44</td>
<td>—a</td>
</tr>
<tr>
<td>γ-Mg(BH₄)₂</td>
<td>I₆₃a</td>
<td>a = 15.757(16)</td>
<td>—</td>
<td>3912.6(7)</td>
<td>24</td>
<td>163.03</td>
<td>39</td>
</tr>
</tbody>
</table>

α This work.

The unit cell is coordinated by two Mn atoms. The Mn–B distances within the [Mn(BH₄)₄]-tetrahedra range from 2.360(6) to 2.533(7) Å while angles range from 97.51(15) to 128.0(2)°. The Mn–S coordination distance in the [Mn(BH₄)₄(S(CH₃)₂)]₃-trigonal bipyramid is 2.705(9) Å, while Mn–B distances range from 2.451(7) to 2.603(8) Å, which is somewhat longer than those observed within the [Mn(BH₄)₄]-tetrahedra in accordance with the increase in coordination number. B–Mn–B distances range from 90.7(3) to 119.3(2)°. Further information can be found in the ESL. The unit cell volume of Mn(BH₄)₂·1/2S(CH₃)₂ is only slightly larger (~1%) than that of the isostructural magnesium analogue Mg(BH₄)₂·1/2S(CH₃)₂. The desolvated γ-Mn(BH₄)₂ crystallizes in the high symmetry cubic space group la3d with unit cell parameters a = 16.2094(13) Å (V = 4258.93(60) Å³, Z = 24). The structure consists of a 3D framework build from a single Mn atom tetrahedrally coordinated to four BH₄ units and each BH₄ unit bridges two Mn atoms. The framework has large permanent pores and represents the second only example of porous borohydrides (isostructural to γ-Mg(BH₄)₂).

Furthermore, we show that α-Mn(BH₄)₂ is isostructural to another new Mg(BH₄)₂ polymorph, denoted ζ-Mg(BH₄)₂. On the basis of this observation, we have used the Rietveld refinement method to refine X-ray data obtained for the ζ-Mg(BH₄)₂ polymorph. Structural and experimental details for Mg(BH₄)₂ can be found in Table 1 and in the ESI respectively. In Fig. 2 (left) the diffraction patterns for ζ-Mg(BH₄)₂, γ-Mg(BH₄)₂, Mg(BH₄)₂·1/2S(CH₃)₂ and its manganese counterparts (right) are shown.

Several manganese and magnesium borohydride polymorphs are isostructural and display similar diffraction patterns. The slightly larger manganese ion (r(Mn²⁺) = 0.66 Å) compared to the magnesium ion (r(Mg²⁺) = 0.57 Å) accounts for a larger unit cell and thus a slight shift of diffraction patterns towards lower Bragg angles. The initially isolated solvate product Mn(BH₄)₂·1/2S(CH₃)₂ (A) is transformed under vacuum at RT into γ-Mn(BH₄)₂ (B) upon prolonged treatment, while the magnesium analogue Mg(BH₄)₂·1/2S(CH₃)₂ (a) transforms into its γ-Mg(BH₄)₂ polymorph (b) upon heating in vacuo much faster. Formation of α-Mn(BH₄)₂ (C) proceeds by heating of Mn(BH₄)₂·1/2S(CH₃)₂ in vacuo. The structural parameters of the isostructural magnesium and manganese borohydride polymorphs are tabulated in Table 1 to provide an overview underlining their similarities.

Spectroscopic analysis of manganese and magnesium borohydride polymorphs

The spectra for Mn(BH₄)₂·1/2S(CH₃)₂, γ-Mn(BH₄)₂ and α-Mn(BH₄)₂ were examined by ATR-FTIR, and compared to the corresponding spectra of magnesium borohydride (Fig. 3). The spectrum for Mn(BH₄)₂·1/2S(CH₃)₂ exhibits vibrational modes from both borohydride B–H and C–H bonds (stretching 2983–2848 cm⁻¹ and bending 1424–683 cm⁻¹), the latter disappearing gradually as the solvent is lost from RT to 110 °C. B-H stretching in Mn(BH₄)₂ is observed from 2600–2200 cm⁻¹, while further stretching, bending and combination bands are observed in the range from 1500 cm⁻¹ and below. The close structural relation between magnesium and manganese borohydride is easily recognizable in Fig. 3. It should be emphasized that the similarities are unique; seen in the perspective that spectra for other metal borohydrides are significantly different.
different,

thus underlining that these materials are structurally very much alike. Unidentified bands are observed in the spectra for γ-Mn(BH4)2. These bands could arise from residual solvent or amorphous impurities present.

Thermal decomposition behavior of manganese borohydride

As seen from the temperature dependent in situ SR-PXD (Fig. 4) Mn(BH4)2·1/2S(CH3)2 transforms directly to α-Mn(BH4)2 in the temperature range 70 to 95 °C (see inset in Fig. 4) while losing the solvated DMS.

Further heating results in the thermal decomposition of α-Mn(BH4)2 and loss of diffraction as no crystalline decomposition products were observed at any time.

For Mn(BH4)2·1/2S(CH3)2 the TGA shows a total weight loss of 37.8 wt%, in two overlapping steps, in the temperature range 50 to 170 °C, see Fig. 5, A. The calculated contribution from loss of dimethylsulfide is 26.9 wt%. The remaining mass loss corresponds to hydrogen, ρH2(Mn(BH4)2) = 9.53 wt% H2, and loss of some diborane. The decomposition of α-Mn(BH4)2 is seen as an endothermic event at ~160 °C in the DSC curves [Fig. 5A and C] in good agreement with the in situ SR-PXD data (Fig. 4). A mass loss of 14.8 wt%, in the temperature range 125 to 175 °C, is observed for the sample of α-Mn(BH4)2 (Fig. 5C), which corresponds well to the observations for the solvate. The mass spectroscopy data reveals the presence of a substantial amount of diborane in the evolved hydrogen. In lieu of accurate gas quantification methods, relating the experimentally observed weight loss of 10.9 wt% to a table of fixed H2/B2H6 ratios provides a useful estimate of the relative ratio of H2 and B2H6 (see ESI†). In this manner a ratio of H2 to B2H6 of 16:1 is estimated. This is in contrast to previous observations made in a study involving nano-Ni doping of Li–Mn–B–H complexes,27 wherein they observed a significantly higher proportion of hydrogen in the desorbed gases. The decomposition products was suggested to be elemental boron and manganese metal for the reaction releasing mainly hydrogen. Slightly different decomposition patterns were suggested in a study involving materials obtained from mechanochemical treatment of 2–3 equivalents of LiBH4 and 1 equivalent MnCl2.54 The following decomposition pathway was suggested (eqn (1));

\[
2\text{Mn(BH}_4\text{)}_2 \rightarrow \text{Mn} + \text{MnB}_2 + 5\text{H}_2 + \text{B}_2\text{H}_6 \quad (1)
\]

however, this decomposition entails the loss of 22.4 wt% which is higher than our findings of 14.8 wt%. We further investigated the decomposition of α-Mn(BH4)2 by temperature dependent in situ SR-PXD experiments under different conditions; in vacuum (Fig. S4.1a†), under a backpressure of hydrogen (p(H2) = 10 bar, Fig. S4.1b†) and in argon (p(Ar) =

Fig. 2 Powder X-ray diffraction patterns for Mg(BH4)2 and Mn(BH4)2 polymorphs: (left) (a) Mg(BH4)2·1/2S(CH3)2, (b) γ-Mg(BH4)2, (c) ζ-Mg(BH4)2 shown in comparison to (right) (A) Mn(BH4)2·1/2S(CH3)2, (B) γ-Mn(BH4)2 and (C) α-Mn(BH4)2. Experimental details of X-ray data for the Mg(BH4)2 polymorphs presented here are found in the ESI†.
Fig. 4  *In situ* synchrotron radiation powder X-ray diffraction measured from room temperature to 200 °C of Mn(BH₄)₂·1/2S(CH₃)₂ (λ = 0.696713 Å, p(Ar) = 1 bar). Inset: Integrated intensities (wt%) of Mn(BH₄)₂·1/2S(CH₃)₂ and α-Mn(BH₄)₂ as a function of temperature. Filled circles: α-Mn(BH₄)₂, filled squares: Mn(BH₄)₂·1/2S(CH₃)₂.

Fig. 5  Thermogravimetry and differential scanning calorimetry (TGA-DSC, left, A, C) in combination with mass spectroscopy (MS, right, B, D) for Mn(BH₄)₂·1/2S(CH₃)₂ (top) and α-Mn(BH₄)₂ (bottom). Mass spectroscopy data for H₂, B₂H₆ and S(CH₃)₂ (ΔT/Δt = 5 °C min⁻¹, 65 mL min⁻¹ (Ar).
In this work we have demonstrated a solvent based synthesis method providing solvent and halide free Mn(BH₄)₂. The reaction affords a mixture of LiCl and Mn(BH₄)₂, from which three polymorphs of Mn(BH₄)₂ are extracted. The initially isolated product is a new solvate material, Mn(BH₄)₂·1/2S(CH₃)₂, isostructural to Mg(BH₄)₂·1/2S(CH₃)₂. The soluble content is removed upon treatment in vacuo at elevated temperatures, providing α-Mn(BH₄)₂, which is shown to be isosctructural to a new Mg(BH₄)₂ polymorph denoted ζ-Mg(BH₄)₂. Gently extracting the solvent from Mn(BH₄)₂·1/2S(CH₃)₂ and maintaining the structural integrity, yields another polymorph, γ-Mn(BH₄)₂ which is isosctructural to γ-Mg(BH₄)₂ and provides a direct structural link between manganese and magnesium borohydrides. Mn(BH₄)₂ decomposes at temperatures significantly lower than Mg(BH₄)₂ (140–160 °C vs. 280–290 °C), which was extensively investigated. In addition, the discovery of a porous γ-Mn(BH₄)₂ polymorph may prompt further work on e.g. physisorption of H₂ in the porous cavities. Deducing detailed reaction schemes for the decomposition of Mn(BH₄)₂ under various conditions is highly desirable. This is particularly important for future, prospective work aiming at tailoring or tuning the properties towards rehydrogenating the material, especially considering the low decomposition temperature observed for this material.

Notes

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Conclusions

In this work we have investigated the conditions, α-Mn(BH₄)₂ is observed to decompose as early as 140 °C (vacuum), and up to 160 °C (p(Ar) = 1 bar). The decomposition of α-Mn(BH₄)₂ and Mn(BH₄)₂·1/2S(CH₃)₂ at T > 125 °C follows the same pathway, i.e. TGA/DSC/MS results correspond to one another and in situ SR-PXD reveals amorphous decomposition products. In situ SR-PXD experiments were also conducted for γ-Mn(BH₄)₂ and diffraction disappears at T > 110 °C (p(Ar) = 1 bar, Fig. S4.1d†), giving rise to an amorphous hump in the background, similar to that observed for γ-Mg(BH₄)₂, i.e. heating the porous structure results in its collapse into amorphous Mn(BH₄)₂. Diffraction patterns measured at RT after decomposition were not assigned to any known crystalline compounds (Fig. S5.1†). However, manganese metal, magnesium borohydrides and/or elemental boron may be involved in an overall reaction pathway for the decomposition of Mn(BH₄)₂·1/2S(CH₃)₂ and Mn(BH₄)₂. Formation of polyboranes, such as MnB₂H₂H₁₂, can also be envisioned on the basis of reports that diborane can react with LiBH₄ at elevated temperatures. The low decomposition temperature observed for this material.

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