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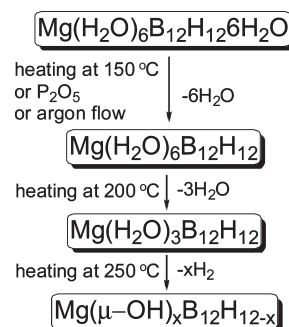
Thermal Decomposition Behavior of Hydrated Magnesium Dodecahydrododecaborates

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ABSTRACT $\text{MgB}_{12}\text{H}_{12}$ is an intermediate in the hydrogen desorption and sorption processes of magnesium borohydride, which is an important candidate material for hydrogen storage. It is thus highly desirable to synthesize anhydrous $\text{MgB}_{12}\text{H}_{12}$ in order to study its properties and its role in the hydrogenation and dehydrogenation of magnesium borohydride. Contrary to the literature claim, we find that anhydrous $\text{MgB}_{12}\text{H}_{12}$ cannot be obtained from simple thermal decomposition of $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12} \cdot 6\text{H}_2\text{O}$ (**1**) which has different thermal decomposition behavior from that of most hydrated alkali and alkaline earth salts of dodecahydrododecaborates. Thermal decomposition of **1** involves both dehydration and dehydrogenation processes in three steps, resulting in the formation of complexes $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12}$ (**2**), $\text{Mg}(\text{H}_2\text{O})_3\text{B}_{12}\text{H}_{12}$ (**3**), and $\text{Mg}(\mu\text{-OH})_x\text{B}_{12}\text{H}_{12-x}$ (**4**) that were characterized by XRD, IR, and ^{11}B NMR. Dehydrogenation was also confirmed by both the generation of hydrogen observed in TPD-MS spectra and the formation of polyhydroxylated complexes.

SECTION Energy Conversion and Storage



Magnesium borohydride, $\text{Mg}(\text{BH}_4)_2$, with a high hydrogen storage capacity (14.9 mass%) has recently attracted considerable attention as a potential hydrogen storage material.^{1–14} Recent theoretical and experimental results clearly show that an intermediate phase, $\text{MgB}_{12}\text{H}_{12}$, forms during hydrogen desorption from $\text{Mg}(\text{BH}_4)_2$ before the formation of the final products.^{15–18} Through the formation of this key intermediate, 6.1 % hydrogen can be reabsorbed into the final thermal decomposition product at appropriate (albeit a high pressure of hydrogen) conditions.¹⁸ It is thus very important to prepare an anhydrous and solvent-free compound of $\text{MgB}_{12}\text{H}_{12}$ and study its properties in order to elucidate its role as an intermediate in the hydrogen desorption and sorption processes of magnesium borohydride and to develop strategies for improved reversibility at moderate conditions.

While most anhydrous alkali and alkaline earth metal salts of dodecahydrododecaborates can be obtained through thermolysis of the hydrated salts,^{19,28} hydrated magnesium dodecahydrododecaborate, $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12} \cdot 6\text{H}_2\text{O}$ (**1**), has a different thermal decomposition behavior that produces polyhydroxylated boron cage compounds rather than the anticipated anhydrous $\text{MgB}_{12}\text{H}_{12}$. Here, we present the results of thermal treatment at different conditions and the corresponding products formed during the decomposition of the hydrated magnesium dodecahydrododecaborates.

The hydrated magnesium salt of dodecahydrododecaborate was prepared from the reaction of MgCO_3 with a free acid aqueous solution of dodecahydrododecaborate that was obtained through cation exchange from sodium or cesium salts

of dodecahydrododecaborate.²⁰ Single-crystal X-ray diffraction analyses indicate that 12 water molecules are present in the structure of the hydrated compound **1**. Six water molecules are directly coordinated to magnesium, and other so-called lattice waters are embedded in the lattice by hydrogen bonds.²⁰

The thermogravimetric analysis (TGA) of **1** in Figure 1 shows a three-step decomposition process. The weight losses of the first two steps correspond to elimination of six and three water molecules, respectively (curve a). On the basis of the weight loss, two intermediates $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12}$ (**2**) and $\text{Mg}(\text{H}_2\text{O})_3\text{B}_{12}\text{H}_{12}$ (**3**) were expected to form after the first and second steps. We were able to isolate compounds **2** and **3** by carefully controlling the experimental conditions.

The TGA curve of **1** revealed that the six lattice water molecules were removed rapidly at temperatures lower than 150 °C (Figure 1, curve a, first step, 28.0 % weight loss). These six water molecules could also be withdrawn by the presence of P_2O_5 at room temperature under a static vacuum condition or by pumping under a dynamic vacuum condition. It is surprising that these six waters could even be removed by an argon gas flow at room temperature (Figure 2S, Supporting Information). After the removal of six lattice water molecules, hexahydrated compound **2** was formed. For the remaining six water molecules directly bonded to magnesium, the weight

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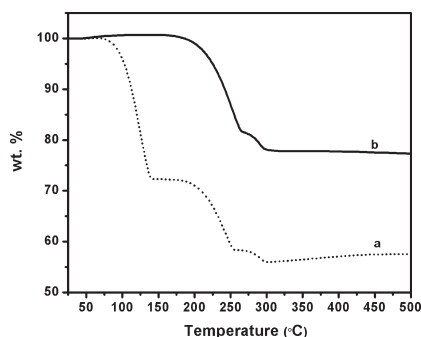
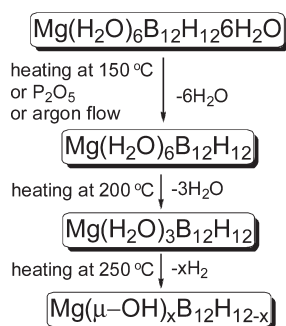


Figure 1. Thermogravimetric analyses of $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12} \cdot 6\text{H}_2\text{O}$ (1) (curve a, argon 40 mL/min, $10^\circ\text{C}/\text{min}$ temperature ramp) and $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12}$ (2) (curve b, argon 40 mL/min, $10^\circ\text{C}/\text{min}$ temperature ramp).

Scheme 1



loss started at about 200°C and ended at about 260°C , but only three of six waters were lost based on the weight loss values (curves a and b). Thus, after this step, trihydrated compound **3** was generated. In addition, both TGA curves displayed one more step with 2–3% weight loss that started at about 265°C (after the water loss). This small amount of weight loss was tentatively assigned to hydrogen release, and it resulted in the formation of polyhydroxylated compounds $\text{Mg}(\mu\text{-OH})_x\text{B}_{12}\text{H}_{12-x}$ (**4**). No more weight loss was observed at higher temperatures.

It should be noted that the literature claim of the formation of anhydrous $\text{MgB}_{12}\text{H}_{12}$ is incorrect.²⁰ A careful examination of the published TGA curve clearly shows that the authors miscalculated the weight loss (28.4% weight loss of $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12} \cdot 6\text{H}_2\text{O}$ corresponds to the weight of six rather than eight water molecules), which led the authors to erroneously claim that “thermal treatment eventually leads to the anhydrous magnesium dodecahydro *closo*-dodecaborate $\text{Mg}[\text{B}_{12}\text{H}_{12}]$ ”.²⁰

The complete thermal decomposition process of **1** includes three steps, and the products are **2**, **3**, and a mixture of **4**, as shown in Scheme 1.

The thermal decomposition products **2**, **3**, and **4** were characterized by XRD, IR, and ^{11}B NMR spectra. Products **2** and **3** produced different XRD patterns that are also different from that of **1**. In contrast, the XRD of **4** indicates that it is amorphous (see Figure 2). Crystal structure identification from XRD powder diffractions of compounds **2** and **3** is still in process, and preliminary results confirm six and three

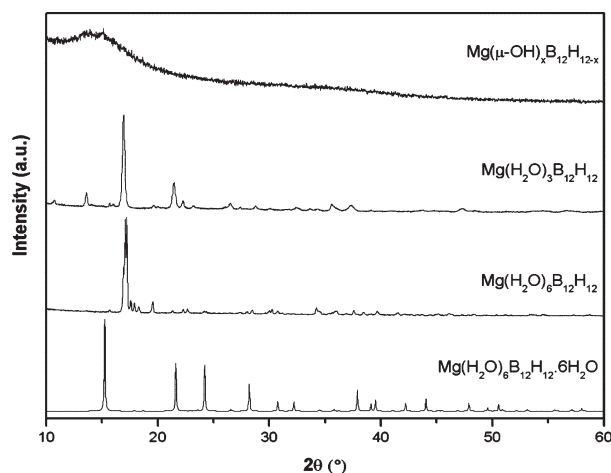


Figure 2. XRD patterns of $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12} \cdot 6\text{H}_2\text{O}$ (**1**) (from X-ray single-crystal diffraction²⁰), $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12}$ (**2**) (powder diffraction), $\text{Mg}(\text{H}_2\text{O})_3\text{B}_{12}\text{H}_{12}$ (**3**) (powder diffraction), and $\text{Mg}(\mu\text{-OH})_x\text{B}_{12}\text{H}_{12-x}$ (**4**) (powder diffraction).

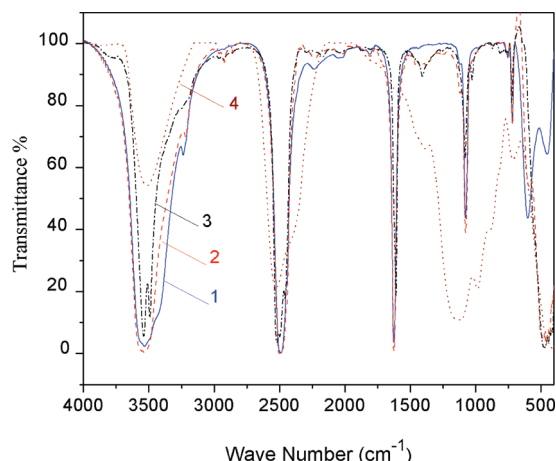


Figure 3. IR spectra of **1**, blue; **2**, red; **3**, black; and **4**, brown.

water molecules coordinated to magnesium in **2** and **3**, respectively. The structural results will be published separately.

The final thermal decomposition product **4** seems to be a mixture of a variety of polyhydroxylated derivatives of dodecahydrododecaborates rather than an anhydrous compound $\text{MgB}_{12}\text{H}_{12}$, as previously claimed.²⁰ The formation of polyhydroxylated compounds was confirmed by IR and ^{11}B NMR spectra. When **2** was heated at 250°C under dynamic vacuum for 36 h, it converted into **4** after all weight loss was completed. The IR spectrum of **4** still maintained a strong O–H stretching vibration band at about 3510 cm^{-1} . However, the characteristic band for the O–H bending vibration of water at 1610 cm^{-1} disappeared. This suggested that some hydroxyl groups but no water molecules remained in the complexes after the thermal treatment procedure (Figure 3). A sharp peak at about 1070 cm^{-1} in **1**, **2**, and **3**, assigned to a B–B bond in the boron cage, changed to a broad signal in **4**. This change is likely due to the substitution of hydroxyl group on the boron cage resulting in the formation of a mixture of mono- and polyhydroxylated derivatives of a polymeric product.

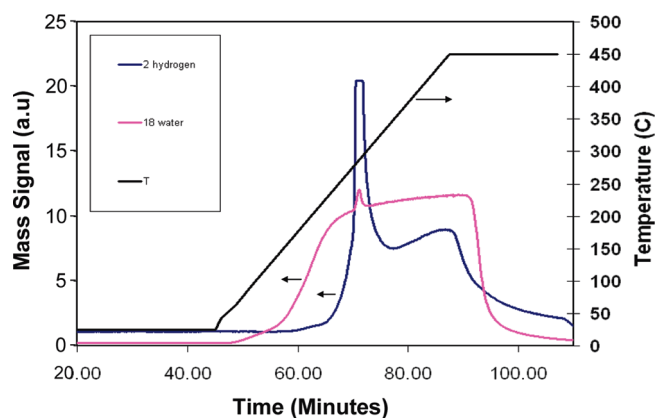


Figure 4. TPD-MS of compound 2.

The limited solubility of **4** in water provides an opportunity to confirm from ^{11}B NMR spectra that the final product **4** is a mixture of a variety of polyhydroxylated derivatives. Several signals appear at $\delta = 0$ ppm, assigned to the boron in the B–OH bonds, and several peaks from $\delta = -15$ to -27 ppm are assigned to the boron in B–H bonds. Comparing the ^{11}B and $^{11}\text{B}\{^1\text{H}\}$ NMR of **4** in water solution to the chemical shift of the di-, tri-, or more-fold hydroxylated derivatives previously reported, the final product **4** indeed contains multiple substituted hydroxylated derivatives.^{21–23} The existence of polyhydroxylated complexes is further supported by solution ^{11}B NMR spectra of the partially decomposed hydrated magnesium dodecahydride, which is completely soluble in water. In these spectra, several substituted product peaks related to B–O or B–H were clearly identified from their chemical shifts (Supporting Information).^{21–23}

It is rational to assume that the polyhydroxylated compounds are derived from dehydrogenation of the hydrated compounds. Dihydrogen bonds frequently appear between a proton and a hydride in many types of compounds,^{24–27} and hydrogen release from such compounds occurs when heated. Typical examples are ammonia borane and ammonia magnesium borohydride.^{3,29} With the dehydration process, the distance between magnesium and the boron cage decreases based on the preliminary structure results. Thus, it is reasonable to assume that dihydrogen bonds exist between a proton of water and a hydride of the boron cage in the hydrated compound **3**. Together with the strong oxyphilicity of magnesium, the O–H bond of water is weakened at high temperatures, and the water proton reacts with B–H hydrogen to release H_2 from the hydrated complexes to generate polyhydroxylated complexes **4**. The TPD-MS experimental results indicate that water (red line) is released first and then hydrogen (blue line) is produced at higher temperatures (Figure 4).

Thermal decomposition processes of hydrated magnesium dodecahydride involve both dehydration and dehydrogenation in three steps, resulting in the formation of hexahydrated complex **2**, trihydrated complex **3**, and polyhydroxylated complexes **4**. These products were characterized by XRD, IR, and ^{11}B NMR spectra. Dehydrogenation was confirmed by both the generation of hydrogen observed in TPD-MS spectra and the formation of polyhydroxylated

complexes. The existence of a dihydrogen bond between the proton of water and the hydride of the $\text{B}_{12}\text{H}_{12}^{2-}$ anion is considered to play an important role in the dehydrogenation process. Anhydrous magnesium dodecahydride cannot be obtained from simple thermal decomposition of the hydrated compound.

Experimental Section

All operations were carried out under nitrogen or argon atmosphere using a high-vacuum line or inside of a glovebox, unless otherwise stated. $\text{Cs}_2\text{B}_{12}\text{H}_{12} \cdot x\text{H}_2\text{O}$ was purchased from BASF and MgCO_3 from Aldrich, and both were used as received. DOWEX 50WX8-100 ion exchange resin was obtained from Aldrich. Infrared spectra (KBr pellets) were recorded on a Bruker Tensor 27 FT-IR spectrometer with 2 cm^{-1} resolution. ^{11}B NMR spectra were obtained at 160.42 MHz on a Bruker DRX-500 spectrometer, and ^{11}B NMR spectra shifts are reported in parts per million (ppm) when externally referenced to $\text{BF}_3 \cdot \text{OEt}_2$ at 0 ppm. TGA was carried out on a Perkin–Elmer TGA 7 analyzer, and samples were loaded on a quartz crucible by heating the samples at a rate of 10 or $1^\circ\text{C}/\text{min}$ under $40\text{ cm}^3/\text{min}$ of Ar flow. Temperature-programmed desorption (TPD) experiments were performed with a He flow of $30\text{ cm}^3/\text{min}$ using a Cirrus residual gas-analyzing mass spectrometer (RGA-MS). X-ray powder diffraction patterns of **2**, **3**, and **4** were collected at room temperature using a Bruker D8 Advance X-ray powder diffractometer (40 kV, 50 mA, $\text{Cu K}\alpha_1$ radiation) equipped with an incident beam Ge 111 Vario monochromator and a Lynxeye Super Speed detector. Samples were ground, loaded, and sealed in 1 mm Lindeman glass capillaries in a drybox under an argon atmosphere.

Hydrated magnesium dodecahydride dodecaborates **1** were prepared according to the published method^{20,28} with the modifications listed below. Starting with $\text{Cs}_2\text{B}_{12}\text{H}_{12}$, an aqueous solution of free acid $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12}$ was produced through cation exchange reaction. Solid MgCO_3 was immediately added to the above acid solution at room temperature to neutralize the acid until the pH value of the aqueous solution was close to 7. A small amount of additional MgCO_3 was added to ensure complete consumption of all of the acid. Filtration was used to remove the residual white MgCO_3 to produce a clear filtrate that was subsequently evaporated isothermally to form crystalline hydrates of **1**. Large single crystals of **1** were picked up from the mother solution for the investigation. Crystals of **1** were dried by P_2O_5 under static vacuum in a desiccator for several days to produce hexahydrated complex **2**. Complex **2** could also be obtained by drying **1** at room temperature under dynamic vacuum until there was no change in weight. Similarly, if **1** or **2** were dried at 100°C under dynamic vacuum until no change in weight, trihydrated complex **3** was formed. When hydrated complexes **1**, **2**, or **3** were heated at 250°C under vacuum until no weight loss, polyhydroxylated complex **4** was formed. Complexes **1**, **2**, **3**, and **4** were characterized by XRD, IR, ^{11}B NMR, and TGA.

SUPPORTING INFORMATION AVAILABLE Additional experimental results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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