

# A new family of metal borohydride guanidinate complexes: Synthesis, structures and hydrogen-storage properties



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## ABSTRACT

We report on a new class of complex hydrides: borohydride guanidinate complexes ( $\text{MBH}_4 \cdot n\text{CN}_3\text{H}_5$ ,  $\text{M}=\text{Li}$ ,  $\text{Mg}$ , and  $\text{Ca}$ ). They can be prepared via facile solid-state synthesis routes. Their crystal structures were successfully determined using a combination of X-ray diffraction, first-principles calculations and neutron vibrational spectroscopy. Among these compounds,  $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{CN}_3\text{H}_5$  is composed of large complex  $\text{Mg}[\text{CN}_3\text{H}_5]_6^{2+}$  cations and surrounding  $\text{BH}_4^-$  ions, while  $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{CN}_3\text{H}_5$  possesses layers of corner-sharing  $\text{Ca}[\text{BH}_4]_4(\text{CN}_3\text{H}_5)_2$  octahedra. Our dehydrogenation results show that  $\approx 10$  wt% hydrogen can be released from  $\text{MBH}_4 \cdot n\text{CN}_3\text{H}_5$  ( $\text{M}=\text{Li}$ ,  $\text{Mg}$ , and  $\text{Ca}$ ) at moderate temperatures with minimal ammonia and diborane contamination thanks to the synergistic effect of C–N bonds from guanidine and hydridic H from borohydrides leading to a weakening of the N–H bonds, thus impeding ammonia gas liberation. Further tuning the dehydrogenation with different cation species indicates that  $\text{Mg}(\text{BH}_4)_2 \cdot n\text{CN}_3\text{H}_5$  can exhibit the optimum properties with nearly thermally neutral dehydrogenation and very high purity hydrogen release.

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## 1. Introduction

Complex hydrides such as alkali and alkaline-earth metal borohydrides ( $\text{MBH}_4$ ) and amides ( $\text{MNH}_2$ ) have attracted much attention for hydrogen-storage applications due to their intriguing hydrogen-storage capacity and cycling ability [1–9]. Several systems, such as  $\text{Mg}(\text{BH}_4)_2$  [10–12], have achieved full reversibility, although the process conditions (pressure and temperature) for their dehydrogenation and hydrogenation are higher than the DOE requirements due to their thermal stability. For other systems, decomposition at high temperatures leads to side reactions with concomitant toxic gas by-products, such as diborane and ammonia, which further prevent complete rehydrogenation due to loss of the B or N components in the systems [5,6]. One effective way to weaken the chemical bonds (lower dehydrogenation temperature) and facilitate preferential  $\text{H}_2$  release (suppress by-product gases) is to develop systems with coexisting  $\text{H}^{\delta+}$  and  $\text{H}^{\delta-}$  because of the thermodynamically favorable recombination reaction of H's with opposite charges ( $\text{H}^- + \text{H}^+ \rightarrow \text{H}_2$ ,  $\Delta H = -17.37$  eV). For example, the  $\text{MNH}_2 + \text{MH}$  system [13–17] has demonstrated significant potential

for a reversible on-board hydrogen-storage material, albeit with some release of ammonia—a common difficulty of the amide compounds. Borohydride derivatives with coexisting  $\text{H}^{\delta+}$  and  $\text{H}^{\delta-}$  such as  $\text{M}_{m+n}(\text{BH}_4)_m(\text{NH}_2)_n$  and  $\text{MBH}_4 \cdot n\text{NH}_3$  have also been developed with intriguing diverse crystal structural arrangements [18–25]. The net effect of introducing protic hydrogen into a borohydride system is a combination of the strength and polarity of M–H bonds and the attractive interaction between H's. Hence, the thermal stability, decomposition temperatures and purity of the released gases for such complex systems vary largely, depending on the electronegativity and polarizing power of the associated metal species. Furthermore, the endothermic decomposition of borohydrides upon ammoniating is touted to be exothermic, albeit with a lowered decomposition temperature by the formation of a stable B–N decomposition product, preventing a direct re-hydrogenation. Although in some cases,  $\text{NH}_3$ , with a lone electron pair available for bonding, can help stabilize hydrides profitably e.g.,  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  [26], the enthalpy change as a result of stabilizing these compounds is not sufficient to be the game changer for an endothermic dehydrogenation.

As part of this endeavor in developing new  $\text{H}^{\delta+}$  and  $\text{H}^{\delta-}$  co-containing complex hydrides, herein, we report the syntheses and detailed structural and property characterization of a new family of borohydride guanidinate complexes  $\text{MBH}_4 \cdot n\text{CN}_3\text{H}_5$  ( $\text{M}=\text{Li}$ ,  $\text{Mg}$ , and  $\text{Ca}$ ),

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aiming to explore new high-hydrogen-content compounds with potential applications for hydrogen storage. Introducing borohydrides with various metal species is desirable to induce more reactive H<sup>-</sup> to combine effectively with H<sup>+</sup> in guanidine molecules as well as to adjust the N–H bond strength by metals with different electronegativities. Compared to CN<sub>3</sub>H<sub>5</sub>/MH or MCN<sub>3</sub>H<sub>4</sub>/MH composites in our previous study, these new borohydride guanidinate complexes with attractive hydrogen contents (> 10 wt%) exhibit high-purity hydrogen release at moderate temperatures. Particularly, compared to the previously reported borohydride ammoniates with exothermic dehydrogenation, Mg(BH<sub>4</sub>)<sub>2</sub>·2CN<sub>3</sub>H<sub>5</sub> and Ca(BH<sub>4</sub>)<sub>2</sub>·2CN<sub>3</sub>H<sub>5</sub> exhibit a nearly thermally neutral dehydrogenation, indicating that a full rehydrogenation is potentially promising.

## 2. Materials and methods

High-purity guanidine (CN<sub>3</sub>H<sub>5</sub>) and guanidinium borohydride ([CN<sub>3</sub>H<sub>6</sub>][BH<sub>4</sub>]) were prepared using a modified method reported in the literature [27,28]. For synthesis of high-purity guanidine, stoichiometric amounts of Na metal and guanidinium carbonate (2:1 molar ratio) were separately dissolved in anhydrous ethanol in a nitrogen-filled glove box. The two solutions were mixed and filtered to yield a colorless ethanol solution of guanidine. Solid guanidine was obtained by evaporating ethanol under vacuum, and the product was further purified by sublimation on a Schlenk line. The yield for the final purified product was about 60%. For synthesis of high-purity guanidinium borohydride, in a typical reaction, 30 mmol of sodium borohydride and 30 mmol guanidine hydrochloride were mixed with 20 mL of anhydrous Tetrahydrofuran (THF) in a flask under Ar flow on a Schlenk line. The mixture was stirred for 18 h at room temperature and subsequently filtered using a Buchner funnel under vacuum. Pure guanidinium borohydride was recovered by evaporating the collected filtrate under vacuum on a Schlenk line. The yield for the product was about 80%. Borohydride (LiBH<sub>4</sub>, Mg(BH<sub>4</sub>)<sub>2</sub> and Ca(BH<sub>4</sub>)<sub>2</sub>, > 95% purity) and metal hydride (LiH, MgH<sub>2</sub> and CaH<sub>2</sub>, > 99% purity) precursors were purchased from Sigma-Aldrich. The MBH<sub>4</sub>·nCN<sub>3</sub>H<sub>5</sub> compounds were then synthesized by grinding corresponding molar ratios of borohydride and guanidine in an agate mortar with a pestle or by ball milling the MH-CN<sub>3</sub>H<sub>6</sub>BH<sub>4</sub> powder mixtures using a Fritsch Pulverisette 7 planetary mill at 200 rpm for 3 h. All sample handling was performed in a He-filled glovebox due to the air-sensitivity of these complex hydrides.

Phase identification and equilibrium were monitored on samples sealed in glass capillaries using a Rigaku X-ray diffractometer with a Cu K<sub>α</sub> source. Data for structural studies were collected over 24 h at room temperature in the 2θ range of 5–70° with a step size of 0.02°. Rietveld structural refinements were done using the GSAS package [29]. Neutron vibrational spectra (NVS) were measured at 5 K using the BT-4 Filter-Analyzer Neutron Spectrometer (FANS) at the NIST Center for Neutron Research, with the Cu(220) monochromator under conditions that provided energy resolutions of 2–4.5% over the vibrational energy range probed.

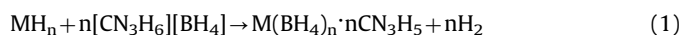
Thermogravimetric analysis (TGA) measurements with simultaneous differential scanning calorimetry (DSC) were made using a Netzsch (STA 449 F1 Jupiter) TGA-DSC instrument under He flow with Al sample pans and temperature ramp rates of 2 °C/min. Temperature readings were estimated to be accurate to within ± 1 °C. Temperature-programmed-desorption (TPD) measurements were performed on a Sieverts-type apparatus described previously [30]. Mass spectrometry (MS) measurements were conducted using a Hiden RGA mass spectrometer. TPD and MS measurements were performed from room temperature to 400 °C at a ramping rate of 2 °C/min.

First-principles calculations based on density-functional theory (DFT) were performed with the PWSCF package [31]. We used a Vanderbilt-type ultrasoft potential with Perdew–Burke–Ernzerhof exchange correlation. A cutoff energy of 544 eV was found to be enough for the total energy to converge within 0.5 meV/atom. Car–Parrinello molecular dynamics simulations [32] were used to help in searching for the most likely crystal structures. Structure optimizations on the candidate structures were further performed with respect to atomic positions, with the lattice parameters fixed at the experimental values. Lattice dynamics calculations were then performed on the relaxed structures using the supercell method with finite displacements [33].

## 3. Results and discussion

### 3.1. Syntheses and crystal structures of borohydride guanidates

Borohydride guanidates were first prepared by mixing LiBH<sub>4</sub>, Mg(BH<sub>4</sub>)<sub>2</sub> and Ca(BH<sub>4</sub>)<sub>2</sub> with guanidine (CN<sub>3</sub>H<sub>5</sub>) powder in 1:1, 1:2 and 1:2 molar ratios, respectively. Combination of CN<sub>3</sub>H<sub>5</sub> and LiBH<sub>4</sub> generates a translucent slurry with a featureless X-ray diffraction (XRD) pattern, indicating the formation of an amorphous phase, while mixing guanidine with Mg(BH<sub>4</sub>)<sub>2</sub> and Ca(BH<sub>4</sub>)<sub>2</sub> produces crystalline compounds. An alternative synthesis route was also conducted by mixing LiH, MgH<sub>2</sub> and CaH<sub>2</sub> with guanidinium borohydride ([CN<sub>3</sub>H<sub>6</sub>][BH<sub>4</sub>]) powders in 1:1, 1:2, and 1:2 molar ratios respectively. The 1:1 ratio of the LiH/[CN<sub>3</sub>H<sub>6</sub>][BH<sub>4</sub>] mixture again led to the formation of an amorphous slurry. No reaction was found after ball milling the 1:2 ratio of MgH<sub>2</sub>/[CN<sub>3</sub>H<sub>6</sub>][BH<sub>4</sub>] mixtures, whereas similar XRD patterns were observed for both the ball-milled product of CaH<sub>2</sub>/2[CN<sub>3</sub>H<sub>6</sub>][BH<sub>4</sub>] mixtures and the ground Ca(BH<sub>4</sub>)<sub>2</sub>/2CN<sub>3</sub>H<sub>5</sub>. The XRD peaks could be indexed using an orthorhombic *Pna*2<sub>1</sub> cell (No. 33) with lattice parameters of *a* = 8.329 Å, *b* = 8.413 Å, and *c* = 14.201 Å. With the indexed lattice parameters, the crystal structure of calcium borohydride guanidinate with a stoichiometry of Ca(CN<sub>3</sub>H<sub>5</sub>)<sub>2</sub>(BH<sub>4</sub>)<sub>2</sub> was then solved using combined direct space methods and first-principles molecular dynamics simulated annealing. The determined composition indicates that by ball milling CaH<sub>2</sub> and [CN<sub>3</sub>H<sub>6</sub>][BH<sub>4</sub>], the hydridic H<sup>-</sup> from CaH<sub>2</sub> could deprotonate the guanidinium cation [CN<sub>3</sub>H<sub>6</sub>]<sup>+</sup> to form the neutral guanidine molecule (CN<sub>3</sub>H<sub>5</sub>) with a release of H<sub>2</sub>. The remaining BH<sub>4</sub><sup>-</sup> anions and Ca<sup>2+</sup> cations in the system then combine with the guanidine molecules formed in-situ and produce Ca(CN<sub>3</sub>H<sub>5</sub>)<sub>2</sub>(BH<sub>4</sub>)<sub>2</sub> (Eq. (1)), which is the same product as starting directly from borohydride and guanidine (Eq. (2)).



Little reaction observed between MgH<sub>2</sub> and [CN<sub>3</sub>H<sub>6</sub>][BH<sub>4</sub>] is probably due to the less reactive MgH<sub>2</sub> precursor, while both synthetic routes from different precursors confirm the amorphous nature of LiBH<sub>4</sub>·CN<sub>3</sub>H<sub>5</sub>.

The major peaks of the XRD pattern (Fig. S1 in the appendix) for the crystalline product of Mg(BH<sub>4</sub>)<sub>2</sub>/2CN<sub>3</sub>H<sub>5</sub> (with a small amount of extra Mg(BH<sub>4</sub>)<sub>2</sub>) can be indexed into a hexagonal *R*-3 cell with *a* = 11.819 Å and *c* = 14.101 Å. By comparing to the lattice volumes of the precursors Mg(BH<sub>4</sub>)<sub>2</sub> and CN<sub>3</sub>H<sub>5</sub>, the stoichiometry of the new phase is evaluated to be Mg(CN<sub>3</sub>H<sub>5</sub>)<sub>6</sub>(BH<sub>4</sub>)<sub>2</sub>, assuming three formula units per unit cell, which is consistent with *R*-3 extinction. A further test on mixing a 1:6 molar ratio of Mg(BH<sub>4</sub>)<sub>2</sub> and CN<sub>3</sub>H<sub>5</sub> generates a pure Mg(CN<sub>3</sub>H<sub>5</sub>)<sub>6</sub>(BH<sub>4</sub>)<sub>2</sub> phase. While the quality and insensitivity of XRD do not allow accurate determination of atomic positions for lightweight H, the crystal structure

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