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Thermal Desorption, Vibrational Spectroscopic, and DFT Computational Studies of the Complex Manganese Borohydrides $\text{Mn}(\text{BH}_4)_2$ and $[\text{Mn}(\text{BH}_4)_4]^{2-}$

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The mechanochemical reaction of LiBH_4 with MnCl_2 produces the neutral complex $\text{Mn}(\text{BH}_4)_2$. Thermal desorption studies show that the mechanochemical reaction of NaBH_4 with MnCl_2 produces a different species, apparently $\text{Na}_2\text{Mn}(\text{BH}_4)_4$, that undergoes dehydrogenation of a much lower weight percent H at a $\sim 20^\circ\text{C}$ higher temperature than the neutral $\text{Mn}(\text{BH}_4)_2$. Vibrational spectroscopy also reveals that a complex manganese borohydride(s) in addition to $\text{Mn}(\text{BH}_4)_2$ are formed from the mechanochemical reactions. Analysis of the vibrational spectra in conjunction with DFT calculations on a model $[\text{Mn}(\text{BH}_4)_4]^{2-}$ complex suggest bidentate binding of the $[\text{BH}_4]^-$ ligands to the Mn center in the anionic complex. The calculated highest frequencies of the B–H stretching modes (corresponding to the “free” B–H bonds) agree well with the experimental frequencies and support the presence of this structural feature.

Introduction

The widespread practical utilization of hydrogen as an energy carrier awaits the development of high-capacity, hydrogen storage materials that can be recharged under moderate conditions. A viable onboard hydrogen storage material must have the following properties: high gravimetric and volumetric hydrogen capacities; thermodynamic properties that are within rather stringent limits; and dehydrogenation and rehydrogenation kinetics that allow hydrogen cycling at moderate temperatures and pressures.¹ To date, no directly reversible hydrogen material has been identified that meets all of these criteria. Borohydrides have among the highest theoretical hydrogen storage capacities of all known compounds and their hydrogen storage properties have recently been the subject of intensive investigations.^{2–28} Studies of Group I and II borohydrides have shown that high temperatures (ca. $>400^\circ\text{C}$) and/or high pressures (~ 700 bar) are required for their recharging^{6,8,15,18,19} and thus they are of limited interest for practical solutions.²

Homoleptic transition metal borohydride complexes have been known since the days of the Manhattan project.²¹ Unlike Group I and II borohydrides which evolve hydrogen only upon heating to temperatures above 250°C ,^{2–9,11,13–15,17–19} the transition metal borohydride compounds evolve high weight percentages of hydrogen upon moderate heating.^{10,22–24} This suggests their possible application as onboard hydrogen storage materials and has led to renewed interest in these compounds. The hydrogen storage properties of these compounds were initially studied without detailed consideration of their molecular structure, which resulted in confusion about their formulation.^{10,22–24} Structural studies utilizing X-ray diffraction,^{16,25–28} NMR,^{25,28} and vibrational spectroscopy^{16,25,26} have now clearly established that, unlike Group I and II borohydrides, there are coordinative bonding interactions between the $[\text{BH}_4]^-$ ligands and the metal

centers. Additionally these studies have shown that there are two subclasses of homoleptic transition metal borohydride complexes: neutral^{20,21,26} and anionic.^{16,25,27} The anionic character of these compounds has been found to generally result in an increased stability and a reduced volatility when compared to neutral transition metal borohydride complexes.

The manganese borohydride complexes $\text{Mn}(\text{BH}_4)_2(\text{THF})_3$ and $[\text{Mn}(\text{BH}_4)(\text{THF})]^{2-}$ can be prepared in THF solution.^{29,30} However, these compounds hold very little potential as hydrogen storage materials as elimination of the THF “solvate” occurs at nearly the same temperature that hydrogen is evolved, leading to the irreversible decomposition of the complex. This led us to explore the solvent-free synthesis of the materials through mechanochemical (ball milling) techniques. This preparation of the manganese borohydride complexes involves a metathesis reaction between MBH_4 ($\text{M} = \text{Li}$ or Na) and MnCl_2 . High throughput screening studies of borohydride complexes of the first transition metal series that were prepared by this mechanochemical synthesis showed that the manganese borohydride complexes were stable at room temperature and eliminated hydrogen at temperatures relevant to on-board hydrogen storage applications.^{31,32} These findings were confirmed and supplemented by Choudhury et al.²² Additionally, the high throughput screening studies also showed that while an unacceptably high, 1:1 ratio of H_2 to B_2H_6 is evolved upon thermal analysis of zinc borohydride,¹⁰ a much lower 1:50 ratio is observed for manganese borohydride. Choudhury et al.²² formulated the compound that they obtained through the mechanical milling of LiBH_4 and MnCl_2 as the anionic borohydride $\text{LiMn}(\text{BH}_4)_3$. However, a recent structural study by Cerny et al. showed that the compound resulting in their mechanical milling reaction in their laboratory is $\text{Mn}(\text{BH}_4)_2$.²⁶ To clarify the nature of the products resulting from the mechanochemical reaction between MBH_4 ($\text{M} = \text{Li}$ or Na) and MnCl_2 , we have carried out vibrational spectroscopic and DFT computational studies on the resulting complexes to elucidate the structures of these materials and correlate them with their observed dehydrogenation hydro- genation kinetics.

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TABLE 1: Synthesis Conditions for Manganese Borohydride Complexes

reactants	synthesis method	ball-to-powder ratio	milling time (h)
$\text{MnCl}_2 + 2\text{LiBH}_4$	ball milling	42:1	1.5
$\text{MnCl}_2 + 3\text{LiBH}_4$	ball milling	16:1	3
$\text{MnCl}_2 + 2\text{NaBH}_4$	ball milling	43:1	5
$\text{MnCl}_2 + 3\text{NaBH}_4$	ball milling	49:1	7
$\text{MnCl}_2 + 2\text{LiBH}_4$	ether solution		
$\text{MnCl}_2 + 3\text{LiBH}_4$	ether solution		
$\text{MnCl}_2 + 2\text{NaBH}_4$	THF solution		
$\text{MnCl}_2 + 3\text{NaBH}_4$	THF solution		

Experimental Section

Sample Preparation. Anhydrous manganese chloride (Alfa Aesar, 96.5%) and LiBH_4 (Sigma Aldrich, 95%) or NaBH_4 (Sigma Aldrich, 99%) were placed in 65 mL containers with

TABLE 2: Calculated Bond Length and Angles of the $\text{Mn}(\text{BH}_4)_2^{2-}$ Complex

bond	Å	angle	deg
Mn–B	2.17	Mn–B–H1	55
B–H1	1.29	Mn–B–H2	102
B–H2	1.22	Mn–B–H3	140
B–H3	1.22	B–Mn–B _{min}	106
B–H4	1.30	B–Mn–B _{max}	113

steel balls. The MnCl_2 to MBH_4 molar ratio were either 1:2 or 1:3, respectively. The mixtures were milled with a Fritsch Pulverisette planetary mill at 350 rpm. All sample handling was done in an argon-filled glovebox. Table 1 shows the optimized reaction conditions for the ball-to-powder ratio and milling rates used.

Solvent synthesis reactions were carried out with a modification of the procedure reported by Makhaev et al.²⁹ This synthesis

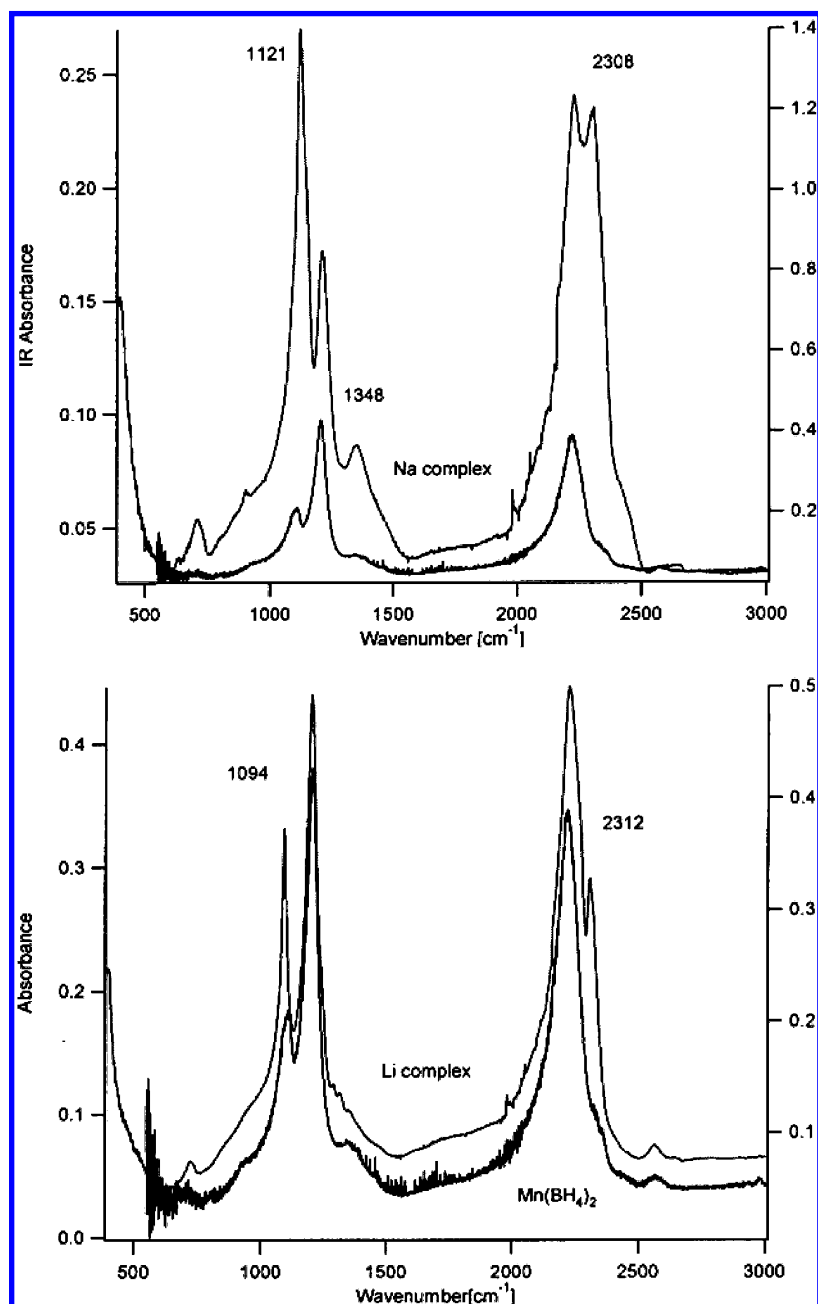


Figure 1. IR spectra (top traces) of the product mixture obtained from the mechanochemical reactions of NaBH_4 and LiBH_4 with MnCl_2 compared with the spectrum of $\text{Mn}(\text{BH}_4)_2$ (lower traces) which were approximately scaled to the spectra of the ball milled samples.

TABLE 3: IR Bands (in cm^{-1}) Observed in Different Borohydrides^a

compd	deformation modes	bridging bending mode	B–H stretching modes + Fermi resonances	terminal B–H stretching modes
LiBH ₄	1090 vs, 1219, 1232, 1289, 1318		2276 vs, 2303	
NaBH ₄	1110 vs		2218 s, 2282 vs, 2394 w	
Mn(BH ₄) ₂ ²⁶	1093 sh, 1106, 1205	1349	2223 br	
Na–Mn complex	1121, 1211	1348	2230, 2308	
Li–Zn complex ²⁴		1404	2090, 2223, 2290	2400, 2450
LiSc(BH ₄) ₄ ¹⁶	1113, 1194	1325	2199, 2242 w, 2259	2464
NaSc(BH ₄) ₄ ²⁵	1105, 1187	1340 w	2240, 2392	2459, 2486
Zr(BH ₄) ₄ ³⁸	1057, 1180, 1221, 1284		2123, 2180	2576

^a Key: s strong, vs very strong, w weak, sh shoulder, br broad.

was done in order to compare the hydrogen storage properties of solvent synthesized samples with those of ball milled samples. Tetrahydrofuran was used for the NaBH₄ precursor complexes and diethyl ether for LiBH₄ precursor complexes. Mixtures of approximately 4 g of MnCl₂ and stoichiometric amounts of MBH₄ for molar ratios of 1:2 or 1:3, respectively, were put in Schlenk flasks. About 80 mL of solvent was added. The mixtures were stirred for 48 h at room temperature on the Schlenk line under N₂ flow. The insoluble alkali metal chloride salts from the metathesis reactions were filtered. The solvents in the solutes were evaporated and trapped using the Schlenk line resulting in yellow solid products which were stored at –20 °C inside the Ar glovebox. The different preparations are listed in Table 1.

Thermal Desorption. Thermal desorption studies were done isothermally with a Suzuki Shokan PCT-2SDWIN sievert type apparatus at 100, 120, and 150 °C. Precise temperature control was achieved by using a silicon oil bath. Desorption was performed into an initially evacuated fixed volume chamber.

Vibrational Spectroscopy. IR spectra were obtained with a Perkin-Elmer Spectrum One instrument in conjunction with a “Golden Gate” ATR setup. The spectral resolution is 2 cm^{-1} for the IR experiments. Raman spectra were obtained by using an Ar ion laser (488 nm) with a Kaiser Optical Instruments Holospec Monochromator and a liquid nitrogen cooled CCD camera. The spectral resolution was 3–4 cm^{-1} . The samples were handled in a glovebox and were sealed in glass capillaries for the Raman experiments.

DFT Calculations. The Kohn–Sham³³ DFT calculations (PBE³⁴ exchange-correlation functional and TZP basis set) were applied to optimize the geometry of the studied complexes. For the obtained minima, the vibrational frequencies were calculated in the harmonic approximation. All the computations were performed with the ADF^{35,36} program package.

Results and Discussion

All the Mn borohydride complexes that were prepared in this study were amorphous and could not be detected by X-ray diffraction. However, IR spectra confirmed that reactions had taken place, as the bands of the starting LiBH₄ or NaBH₄ nearly disappeared in the milled samples. The formation of complex Li and Na manganese borohydrides is manifested by the spectral differences seen in samples obtained from LiBH₄ and NaBH₄, as shown in Figure 1. Very recently, the compound Mn(BH₄)₂ could be prepared and characterized without formation of other manganese borohydrides.⁸ The corresponding IR spectrum is also shown in Figure 1. Comparison of the two spectra clearly shows that the main product of the reaction with LiBH₄ is Mn(BH₄)₂. A similar IR spectrum was reported by Choudhury et al. but assigned to LiMn(BH₄)₃.²² Their reported spectrum also contained a feature at 1603 cm^{-1} , which although assigned

a Mn–Cl stretching mode, is more likely a water bending mode as their spectrum also contains a broad band at 3536 cm^{-1} , which is characteristic of the O–H stretch of H₂O.

Figure 1 also shows that the spectrum of the products obtained from the reaction with NaBH₄ is significantly different from that of Mn(BH₄)₂. In this context it is important to note also that these IR spectra are quite different from those reported for ball milled Zn borohydride complexes.²⁴ These Zn compounds present a complex IR spectrum with five strong bands at 2450, ca. 2400, 2290, 2223, and 2090 cm^{-1} in the B–H stretching region, as well as a strong BH₂ deformation band at 1404 cm^{-1} . This B–H stretching pattern with multiple bands is in agreement with the presence of several different types of B–H bonds as shown by the crystal structures of the Zn complexes.²⁷ Table 3 provides a comparison of the IR bands that are observed for the Mn borohydride complexes with those of other borohydrides.

To obtain more insight on the structure of the Mn borohydrides, we have performed DFT calculations on an isolated Mn(BH₄)₄^{2–} ion. The optimized structure, shown in Figure 2, shows that the manganese ion is tetrahedrally surrounded by the four borohydride groups which form bidentate hydride bonds with the central ion. Characteristic structural data (bond length and angles) are summarized in Table 2. In our previous studies on MSc(BH₄)₄ (M = Li, Na),^{16,25} a tridentate binding to the central Sc ion was obtained. The crystal structure of (Ph₄P)(Mg(BH₄)₄)³⁷ presents isolated Mg(BH₄)₄^{2–} units. In this

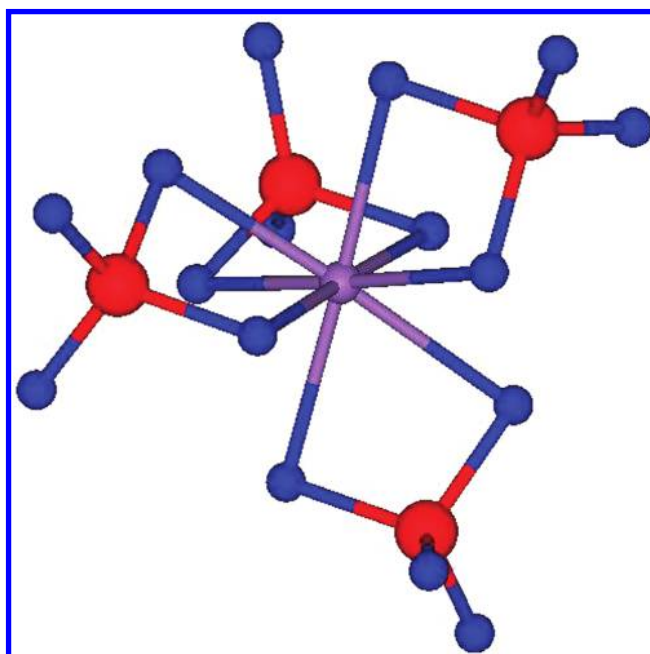


Figure 2. Theoretical structure of the isolated Mn(BH₄)₄^{2–} ion, showing the bidentate bonding to the central ion.

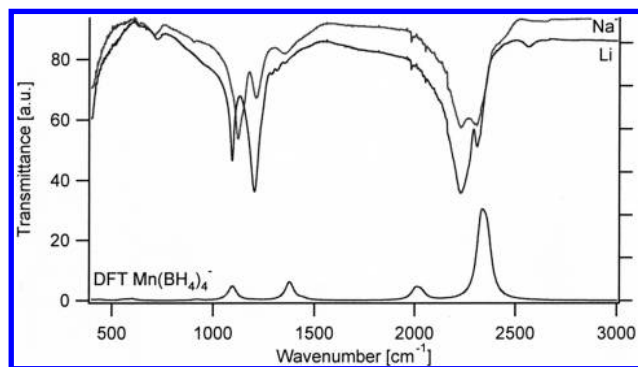


Figure 3. Experimental IR transmission spectra of the ball milled samples compared with the theoretical (DFT) IR spectrum of isolated $\text{Mn}(\text{BH}_4)_4^{2-}$. The upper traces are of the product mixture obtained from the mechanochemical reactions of NaBH_4 and LiBH_4 with MnCl_2 and the bottom trace is the calculated absorption spectrum of the isolated $\text{Mn}(\text{BH}_4)_4^{2-}$ ions.

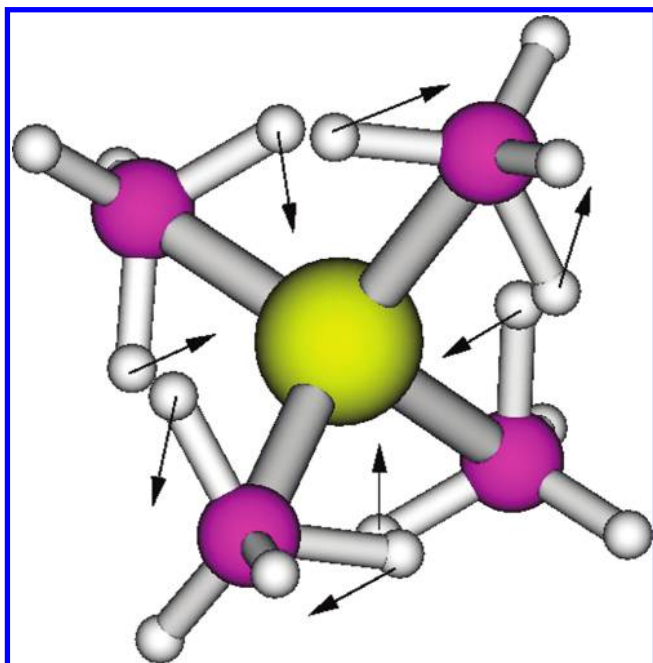


Figure 4. Illustration of the inner BH_2 bending motion.

case, two BH_4^- ions form bidentate H binding to the metal, and the two other tridentate bonds. The $\text{Mg}-\text{B}$ bond is about 2.42 Å, which is much larger than the calculated value of the isolated $\text{Mn}(\text{BH}_4)_4^{2-}$ complex (2.17 Å).

The calculated IR spectrum of the isolated $\text{Mn}(\text{BH}_4)_4^{2-}$ complex is compared with the experimental IR spectra in Figure 3. Following the identification of the contributions from $\text{Mn}(\text{BH}_4)_2$ (see Figure 1), one observes some similarities between the remaining bands in the Na sample and the calculated spectrum (at ca. 2350 cm^{-1} and the band around 1350 cm^{-1}), but also some differences (relative intensity at ca. 1200 cm^{-1} , other features around 2200 cm^{-1}).

Figure 4 illustrates the inner BH_2 bending motion (bridging bending mode in Table 3) (calculated at 1376 cm^{-1}), while Figure 5 illustrates an outer B–H stretching mode (terminal B–H stretching mode in Table 3), which is at 2332 cm^{-1} in the calculated spectrum. In considering the data seen in Table 3, it is interesting to note that the highest experimental B–H stretching mode is found at a significantly lower frequency (ca. 100 cm^{-1}) than those of $\text{LiSc}(\text{BH}_4)_4$, $\text{NaSc}(\text{BH}_4)_4$, and $\text{Zr}(\text{BH}_4)_4$ (2468, 2470, and 2576 cm^{-1} , respectively) in which the $[\text{BH}_4]^-$

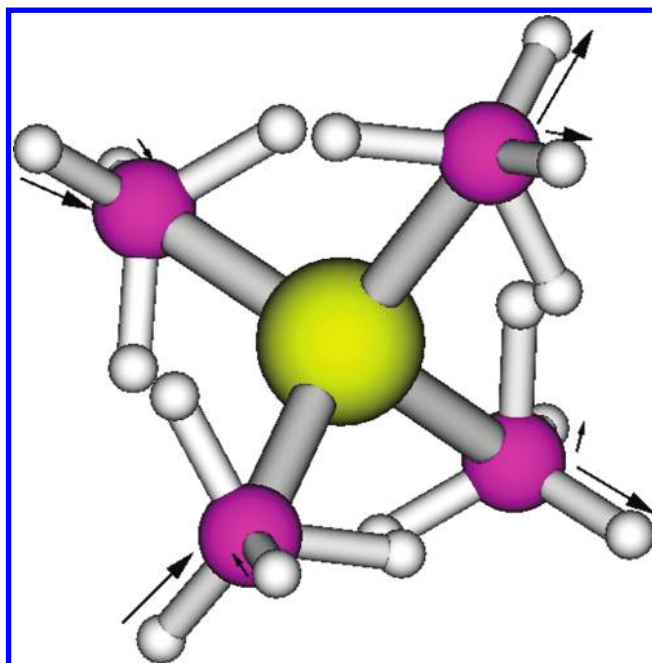


Figure 5. Illustration of the outer B–H stretching mode.

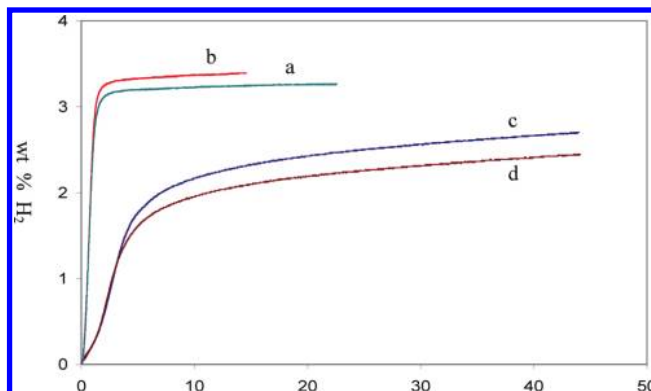


Figure 6. Isothermal decomposition at 100 °C of (a) 1:3 LiMn , (b) 1:3 LiMn doped with TiF_3 , (c) 1:2 NaMn , and (d) 1:2 NaMn .

ligands exhibit tridentate coordination to the transition metal as well as the stretches observed for Zn borohydrides in which the $[\text{BH}_4]^-$ ligands exhibit more complicated coordination modes.²⁴ Apparently, the bidentate coordination that has been found for $\text{Mn}(\text{BH}_4)_2$ is also present in the product obtained from the reaction with NaBH_4 . The spectral differences are therefore apparently indicative of variation in the $[\text{BH}_4]^-$ coordination modes. The finding of divergent coordination modes is not unexpected given the widely varied d electron configuration of the transition metal centers in the borohydride complexes.

Thermal Desorption Studies. The thermal desorption studies were carried out on a Sievert type apparatus. As seen in Figure 6, all of the samples showed an initial fast step followed by a much slower second step. Thus the manganese borohydride compounds clearly undergo dehydrogenation through a multistep process as has been observed for other metal borohydrides.^{9,19} The materials prepared from LiBH_4 (1:2 LiMn and 1:3 LiMn) were observed to undergo rapid elimination of over 3 wt % H_2 at 100 °C. As seen in Figure 4b, the addition of 4 mol % titanium fluoride as dopant to 1:3 LiMn results in a slight increase in the evolved weight percent of H_2 but does not increase the kinetics of the desorption process. The materials prepared from NaBH_4 (1:2 NaMn and 1:3 NaMn) can readily be seen to have much slower dehydrogenation kinetics at 100

TABLE 4: Comparison of the Weight Percent of H₂ Evolved from Manganese Borohydride Compounds upon Thermalysis

entry	reactants	synthesis method	desorption temp/°C	obsd H ₂ wt %	assumed product	H ₂ wt % evolved from Mn complex
1	MnCl ₂ + 2LiBH ₄	ball milling	120	3.7	Mn(BH ₄) ₂	7.4
2	MnCl ₂ + 3LiBH ₄	ball milling	100	3.3	Mn(BH ₄) ₂	7.4
3	MnCl ₂ + 2NaBH ₄	ball milling	120	2.9	Na ₂ Mn(BH ₄) ₄	6.9
4	MnCl ₂ + 3NaBH ₄	ball milling	150	2.8	Na ₂ Mn(BH ₄) ₄	5.5
5	MnCl ₂ + 2LiBH ₄	ether solution	100	3.4	Mn(BH ₄) ₂ [O(C ₂ H ₅) ₂] ₂	2.3
6	MnCl ₂ + 3LiBH ₄	ether solution	150	4.0	LiMn(BH ₄) ₃ [O(C ₂ H ₅) ₂]	3
7	MnCl ₂ + 2NaBH ₄	THF solution	100	2.9	Mn(BH ₄) ₂ (thf) ₃	1.3
8	MnCl ₂ + 3NaBH ₄	THF solution	120	3.8	Mn(BH ₄) ₂ (thf) ₃	2.6

°C. They were found to require heating to temperatures up to 150 °C to achieve rates of dehydrogenation that match **1:3 LiMn**.

The materials generated in all reactions with LiBH₄ as well as the those produced in all reactions with NaBH₄ show nearly identical dehydrogenation kinetics and dehydrogenation profiles at 100 °C regardless of the stoichiometry employed in the ball milling reaction. This indicates that the same manganese borohydride species are obtained in both cases regardless of the stoichiometry of the reactants. It has been previously reported that ball milling mixtures of LiBH₄ and MnCl₂ produce Mn(BH₄)₂ + LiCl regardless of the reactant stoichiometry.²⁶ Thus difference in the weight percent of H₂ that is eliminated is apparently the result of the difference in the ratio of reactants. Our data support that a 1:2 ratio is the most efficient reaction stoichiometry for the preparation of Mn(BH₄)₂. It is evident from the observed dehydrogenation behavior that a product other than Mn(BH₄)₂ is produced from the reaction with NaBH₄. The agreement that was found between the calculated spectrum for [Mn(BH₄)₄]²⁻ and the spectrum for the product of the reaction with NaBH₄ indicates that the product is Na₂Mn(BH₄)₄. However, other formulations such as NaMn₂(BH₄)₅ cannot be ruled out at this point. Assuming the formation of only Mn(BH₄)₂ or Na₂Mn(BH₄)₄, the stoichiometric complement of LiCl or NaCl, and the requisite amount of unreacted starting materials, we have calculated the weight percent of H₂ losses for the manganese borohydrides complexes that appear in the final column of Table 4.

The solvent synthesized materials are known to eliminate coordinated solvent upon heating.^{29,30} Taking the weight loss due to the elimination of the established²⁹ number of solvent molecules, the thermal desorption data indicate that these materials evolve significantly lower (1.3–3.0) weight percent of H₂ at low temperatures. The large discrepancy seen in Table 4 between the weight percent of H₂ that is obtained from the balling milled and solvent synthesized materials indicates that they undergo dehydrogenation through distinctively different pathways.

Conclusion

In conclusion, our results confirm that the mechanochemical reaction of LiBH₄ with MnCl₂ produces mainly the neutral complex Mn(BH₄)₂ rather than the anionic complex LiMn(BH₄)₃.¹⁶ However, thermal desorption studies show that the mechanochemical reaction of NaBH₄ with MnCl₂ produces a species that is chemically distinct from Mn(BH₄)₂, which is apparently Na₂Mn(BH₄)₄. Unfortunately, structural characterization of the resulting manganese complex is problematic as the material is amorphous, precluding structural determination by X-ray diffraction, and paramagnetic, precluding characterization through NMR studies. Vibrational spectroscopy also reveals that a complex manganese borohydride(s) in addition to Mn(BH₄)₂

are formed from the mechanochemical reactions. Analysis of the vibrational spectra in conjunction with DFT calculations on a model Mn(BH₄)₄²⁻ complex suggest bidentate binding of the [BH₄]⁻ ligands to the Mn center. The calculated highest frequencies of the B–H stretching modes (corresponding to the “free” B–H bonds) agree well with the experimental frequencies and support this structural feature.

Recently, it was found that the mechanical milling of ScCl₃ with LiBH₄ results in the formation of LiCl,¹⁶ while milling with NaBH₄ gives Na₃ScCl₆.²⁶ This work shows that the chemical sensitivity to the Group I cation extends to mechanical milling reactions MnCl₂ with Group I borohydrides. In the present case we have seen that the composition of the resulting borohydride product is profoundly affected. Our findings should help guide investigators in further efforts to prepare envisioned manganese borohydrides which could possibly couple their demonstrated, favorable hydrogen storage properties of low dehydrogenation temperatures and low diborane contamination of the evolved hydrogen with the desired rechargeability.

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