The First Crystallographic and Spectroscopic Characterization of a 3d-Metal Borohydride: Mn(BH$_4$)$_2$

Radovan Černý,*,† Nicolas Penin,† Hans Hagemann,‡ and Yaroslav Filinchuk*,§

Laboratory of Crystallography, University of Geneva, 1211 Geneva, Switzerland, Department of Physical Chemistry, University of Geneva, 1211 Geneva, Switzerland, and Swiss-Norwegian Beamlines at ESRF, BP-220, 38043 Grenoble, France

The first crystal structure of a 3d-metal borohydride is presented. Solvent-free homoleptic manganese borohydride Mn(BH$_4$)$_2$ forms at ambient conditions in ball-milled mixtures of alkali metal borohydrides and MnCl$_2$. It crystallizes in the trigonal crystal system with the space group symmetry $P3_112$ and is stable from 90 to 450 K, where the compound melts. Thermal expansion of Mn(BH$_4$)$_2$ between 90 and 400 K is highly anisotropic and strongly nonuniform. The structure of Mn(BH$_4$)$_2$ shows interesting similarity to α-Mg(BH$_4$)$_2$: the two structures are made of similar layers L with the composition M_4(BH$_4$)$_{10}$ per cell. The layers are stacked along the c-axis, and rotated by 120° by the 3$_1$ axis in Mn(BH$_4$)$_2$ and by 60° by the 6$_1$ axis in α-Mg(BH$_4$)$_2$. Three identical layers are stacked along one unit cell vector c in Mn(BH$_4$)$_2$, while six layers are stacked in α-Mg(BH$_4$)$_2$. In Mn(BH$_4$)$_2$ the layers L are connected directly, and share atoms. In α-Mg(BH$_4$)$_2$ the layers L are intercalated by a thin layer L′, which contains one Mg atom per layer per cell. The layer L is chiral, and both borohydrides crystallize in chiral space groups. Similar to α-Mg(BH$_4$)$_2$, the structure of Mn(BH$_4$)$_2$ is not densely packed and contains isolated voids with the estimated volume of 21 Å^3 each, which occupy in total 6% of the space. The resemblance between Mn(BH$_4$)$_2$ and α-Mg(BH$_4$)$_2$ is also reflected in their Raman and infrared spectra.

Introduction

Metal borohydrides are of interest for hydrogen storage in mobile applications.[1] Borohydrides of alkaline and alkaline earth metals desorb a large quantity of hydrogen (up to 20.8%), although the decomposition temperatures are usually high.[2] On the other hand, most of the known borohydrides of transition metals, especially of 3d-metals, are known[3,4] to be unstable, volatile, strong reducing agents, and inflammable on contact with air. The decomposition temperature of single cation borohydrides was recently empirically related (through the enthalpy of formation) to the Pauling electronegativity of the cation.[5] Tuning the decomposition temperature by alloying metal borohydrides by different cations seems to be an interesting way of tuning the thermodynamic properties of borohydride-based hydrogen storage materials.[6]

Contrary to the alkali or alkali earth metal borohydrides,[7] the details of crystal structures of homoleptic (i.e., where metal atoms are not coordinated to other ligands than BH$_4$) transition metal borohydrides M^{+n}(BH$_4$)$_n$ are sparse. Those which are satisfactorily characterized by diffraction methods on crystalline samples are Zr(BH$_4$)$_4$ at 113 K,[8] Hf(BH$_4$)$_4$ at 110 K,[9] and Y(BH$_4$)$_3$ at room temperature.[10] No crystal structure is known for 3d-metals homoleptic borohydrides, in spite of the fact that the synthesis has been reported for zinc,[11,12] titanium,[13] manganese,[14] iron,[15] cobalt,[16] and copper[17] borohydrides. No structure prediction was attempted for manganese borohydride. In

the case of alkaline or alkaline earth metal A−transition metal M double-cation homoleptic borohydrides A^{+m}M^{+n}(BH$_4$)$_{m+n}$ only the crystal structure of LiSc(BH$_4$)$_4$ was recently determined.[18] Here we report on the crystal structure and Raman and infrared spectra of solvent-free manganese borohydride Mn(BH$_4$)$_2$.

Structures of several solvated manganese borohydride complexes are known, like Mn(BH$_4$)$_2$(THF)$_3$[19] and manganese borane complexes.[20] Attempts to desolvate Mn(BH$_4$)$_2$(THF)$_3$ resulted in the decomposition.[19] Solvent-free Mn(BH$_4$)$_2$ can be prepared in the anhydrous ether solution[14] by the reaction between lithium borohydride and manganese chloride, which is insoluble in the ether. Manganese chloride cannot be replaced by a complex bromide Li$_2$MnBr$_4$ in the reaction, contrary to the iron and cobalt analogues.[21] Ether solution of Mn(BH$_4$)$_2$ is stable at room temperature.[21]

Experimental Section

Synthesis. A mixture of MBH$_4$ (M = Li, Na, 95% purity from Fluka) and anhydrous MnCl$_2$ (99.999% purity from Aldrich) with molar ratios of 2:1 and 3:1 was manually premixed by using an agate mortar and pestle, and then mechanically milled to promote the synthesis reaction. Precursors were handled in an argon-filled glovebox to avoid (hydro-)oxidation. The milling process was carried out in a Fritsch Pulverisette 7 high-energy planetary ball-milling system. A 25 mL stainless steel grinding bowl sealed with a lid having a Viton O-ring and three stainless steel balls of 15, 12, and 10 mm diameter were used as the milling medium. The rotational speed of milling was set at 600 rpm. The ball mass to powder mass ratio was fixed to 25:1. The milling was stopped for 5 min (cooling brake) every 10 min to avoid heating of the system as well as

* To whom correspondence should be addressed. R.C.: phone: +41 22 379 6450, fax: +41 22 379 6108, e-mail: radovan.cerny@unige.ch. Y.F.: phone: +33 47 688 2775, fax: +33 47 688 2694, e-mail: yaroslav.filinchuk@ esrf.fr.
† Laboratory of Crystallography, University of Geneva.
‡ Department of Physical Chemistry, University of Geneva.
§ Swiss-Norwegian Beamlines at ESRF.

agglomeration of the powder on the walls of the grinding bowl; the previous two-step process was repeated 35 times. The cooling break was shown[22] to be critical for successful synthesis of magnesium alanate by ball milling.

Reaction between alkali borohydride and manganese chloride in a molar ratio of 2:1 can be described as follows:

$$2M\text{BH}_4 + \text{MnCl}_2 \rightarrow 2M\text{Cl} + \text{Mn(BH}_4)_2 \qquad (1)$$

For reaction 1, using sodium borohydride instead of lithium resulted in the same product (+ NaCl) with broader diffraction peaks. The milling of mixtures in a molar ratio of 3:1 resulted in the same product + unreacted alkali borohydride. An attempt with potassium borohydride and manganese chloride in a molar ratio of 3:1 has shown a complex X-ray powder pattern without any diffraction peaks corresponding to $\text{Mn(BH}_4)_2$. The Raman spectrum of this sample presents also no bands pertaining to $\text{Mn(BH}_4)_2$, but several new bands in addition to those of unreacted KBH_4.

In Situ Synchrotron Powder Diffraction. A glass capillary (1 mm in diameter) with the sample was heated from 90 to 400 K at a rate of 60 deg/h, while synchrotron powder diffraction data (PXD) were collected. The temperature was controlled with the Oxford Cryostream 700. The in-house designed heat blower was used for temperatures above 400 K to follow the sample decomposition or melting. The data were collected at the Swiss-Norwegian Beamlines (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, using a MAR345 image plate detector at a sample-to-detector distance of 400 mm, using the radiation with the wavelengths $\lambda = 0.72846$ or 0.73475 Å. The capillary was oscillated by 60° during exposure to the X-ray beam for 60 s, followed by a readout for ~83 s.

Structure Solution. The PXD data showed LiCl as a major phase in the sample (~60 wt % = 75 mol %), and the second phase corresponded to the title compound. The 16 observed reflections of $\text{Mn(BH}_4)_2$ were indexed with DICVOL04[23] showing the hexagonal lattice with $a = 10.435(1)$ Å, $c = 10.835(2)$ Å, and $V = 1021.8(3)$ Å^3 at room temperature. A systematic extinction was observed only on $00l$ reflections, showing the presence of a screw axis along c; however, it was not easily recognizable. All possible screw axes, 3_1, 6_1, 6_2, and 6_3, were tried, and finally 3_1 was identified as the correct one. The structure was solved in the space group $P3_1$ with the direct space method program FOX,[24] and refined with the Rietveld method by using the program TOPAS.[25] Finally, the symmetry checking routine of the program PLATON[26] has identified the correct space group $P3_112$, which was then used for the final refinement providing two Mn atoms (positions 6c and 3a) and five BH_4 groups (two positions of the boron atom 3a, two 3b, and one 6c) within the asymmetric unit. The structure was solved and refined with the BH_4 groups as semirigid bodies with one common refined B–H distance. Two antibump distances were used: Mn–H of 1.9 Å and Mn–B of 2.4 Å. The displacement parameters were refined isotropically with three independent parameters (one for each type of atom); however, those of boron and hydrogen refined to the lower limit of 1. The uncertainties of crystallographic coordinates of hydrogen atoms were not available from the least-squares matrix, and were estimated by the bootstrap method.[27] The agreement factors are the following: R_{wp} (not corrected for background) = 5.07%, R_p (corrected for background) = 7.27%, $\chi^2 = 130$, $R_{Bragg} = 2.21\%$. The value of χ^2 seems to be too high, but it reflects mainly the extremely high counting statistics of the powder diffraction data obtained from modern 2D detectors. The structural drawing viewed along the c-axis is given in Figure 1. The table with atomic positions
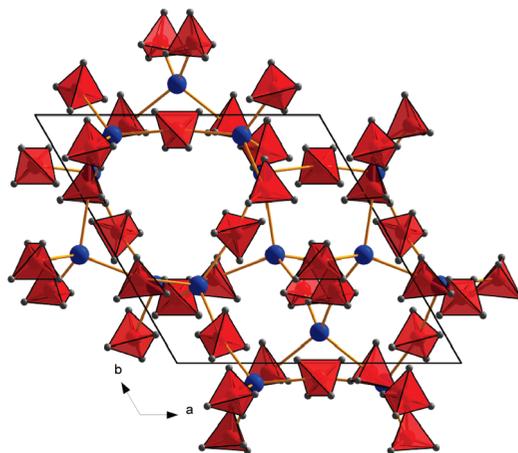
Figure 1. Crystal structure of $\text{Mn(BH}_4)_2$ viewed along the c-axis, showing the coordination of Mn atoms (blue) by BH_4 tetrahedra (red). The empty cavity is situated approximately at (0.304 2x 1/6) with the shortest distance of 2.47 Å to the nearest (hydrogen) atom.
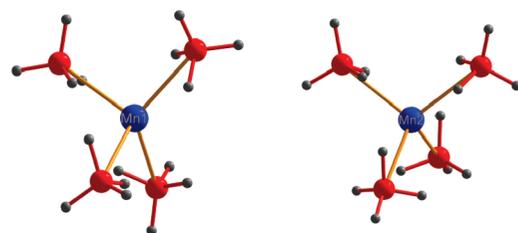
Figure 2. Coordination of Mn1 and Mn2 atoms (blue) by BH_4 tetrahedra (red).

is given in the Supporting Information as Table S1; the Rietveld plot is shown as Figure S1 in the Supporting Information.

Raman and Infrared Spectroscopy. Raman spectra were obtained with use of a Kaiser Holospec spectrometer equipped with a liquid nitrogen cooled CCD camera and a 488 nm laser. IR spectra were measured in a Specac "Golden Gate" ATR cell in a Biorad Excalibur FT-IR instrument. The resolution was set to 1 cm^{-1}.

Results and Discussion

Atomic Coordination. Both independent manganese atoms are surrounded by four BH_4 tetrahedra (Figure 2) in deformed tetrahedral coordinations (Mn–B distances within 2.39(1)–2.52(1) Å, B–Mn–B angles within 94.3(2)–127.19(3)°). A similar tetrahedral coordination of a cation by four $[\text{BH}_4]^-$ anions is known for Li$^+$ in three of the four known phases of LiBH$_4$[28−30] and in LiK(BH$_4$)$_2$,[31] for Zr^{4+} in zirconium borohydride at 113 K,[8] for Mg^{2+} in magnesium borohydride,[32−34] and for Sc^{3+} in lithium scandium borohydride.[18] On the other side, and similar to magnesium borohydride, each $[\text{BH}_4]^-$ is approximately linearly coordinated by two Mn^{2+} (Mn–B–Mn angles within 147.4(2)° to 170.0(2)°).

The coordination of manganese by hydrogen atoms cannot be determined unambiguously because of the limited accuracy of the $[\text{BH}_4]^-$ tetrahedra orientation, which is strongly affected by Mn–H and Mn–B antibump restraints used in the Rietveld refinement. The configuration resulting from such restraint refinement can be understood as the Mn–H$_2$BH$_2$–Mn bonding scheme giving 8-fold coordination of Mn by hydrogen atoms, with Mn–H distances varying within 1.86(4)−2.31(4) Å. A single B–H distance of 1.13(2) Å was refined for rigid BH_4 tetrahedra. It compares well with those in related borohydrides such as Mg(BH$_4$)$_2$ (1.08−1.22 Å[32,34]).

Characterization of Mn(BH₄)₂

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Unoccupied Void. By using a probe of 1.05 Å radius in PLATON[26] and assuming a 1.2 Å van der Waals radius of the hydrogen atom, a void was detected in the $P3_112$ structure. In the first approximation, the void is a one-dimensional infinite channel, occupying ~7.1% of the space of the structure. The shortest distance from the center of this void (1/3 2/3 0.810) to an atom (H22) is 2.02 Å, comparable with the metal–hydrogen distance in borohydrides. The use of a slightly larger probe of 1.1 Å splits up the infinite channel into three isolated voids, linked along c by the 3_1 symmetry axis. The distance from the center (0.304 $2x$ 1/6) of this isolated void to the nearest atom (H12) is larger than that for the channel, namely 2.47 Å, but its estimated volume of 21 Å³ is quite small. Although this void cannot be considered as accessible to small neutral molecules, the analysis clearly reveals that the structure of Mn(BH₄)₂ is not densely packed, as the three voids account for a total of 6% of the space. We should note also that the exact size of the pore depends on the accurate location of hydrogen atoms, and an uncertainty is related to the positions of H-atoms derived from our X-ray powder data.

It is remarkable that the low-temperature phase of Mg(BH₄)₂, crystallizing in the space group $P6_122$, contains an even larger unoccupied void, which may accommodate a small molecule, such as H₂O.[34]

Anisotropy of Thermal Expansion. Thermal expansion of Mn(BH₄)₂ between 90 and 400 K is highly anisotropic and strongly nonuniform (Figure 3.): lattice parameter a increases and c decreases and the cell volume first increases and then decreases with the maximum at ~325 K. This unexpected behavior resembles lattice expansion of β-Mg(BH₄)₂.[34] However, contrary to Mg(BH₄)₂, no phase transition is observed in Mn(BH₄)₂ between 90 and 400 K. A volume drop above ~325 K also might be related to a partial substitution of BH₄⁻ anions by the smaller Cl⁻ present in the Mn(BH₄)₂ + LiCl mixture, as was recently found for LiBH4 + LiCl mixtures.[35] Mn(BH₄)₂ melts at ~450 K without any visible reaction or formation of crystalline decomposition products.

Raman and Infrared Spectra. Figure 4 compares the IR and Raman spectra of Mn(BH₄)₂ and α-Mg(BH₄)₂. The spectra are very similar, the only difference is that the bands for the Mn compound are shifted to lower frequencies.

In Mn(BH₄)₂, there are five different BH₄⁻ units, and one expects thus a complex pattern of B–H stretching (around 2300 cm⁻¹) and bending (around 1200 cm⁻¹) modes in both IR and Raman spectra. However, in particular the bending mode region remains relatively simple. Indeed, for one single [BH₄]⁻ ion on a low-symmetry site (C_2 or C_1), one expects to observe five different deformation bands (which are both IR and Raman active) arising from splitting of the doubly degenerate v_2 and the triply degenerate v_4 modes of the free tetrahedral ion. However, as can be seen in Figure 4, much less than the 25 expected deformation bands (from the site group analysis) are observed. Low-temperature IR spectra (at 183K) do not reveal additional bands. These observations hold equally for α-Mg-(BH₄)₂. The absence of extensive splitting may be explained by similarity of the local structure of different [BH₄]⁻ groups remaining similar despite the complex packing in the crystal.

The comparison of the spectra of Mn(BH₄)₂ and α-Mg(BH₄)₂ shows that for the Mn compound, the vibrational frequencies are shifted about 20–30 cm⁻¹ to lower frequencies. In the case of the cubic alkali borohydrides,[36] this magnitude of frequency shifts reflects a B–H bond length increase of about 0.02 Å. Compared to the cubic alkali borohydrides the metal–boron distances are shorter for the divalent Mn(Mg) ions, and thus a
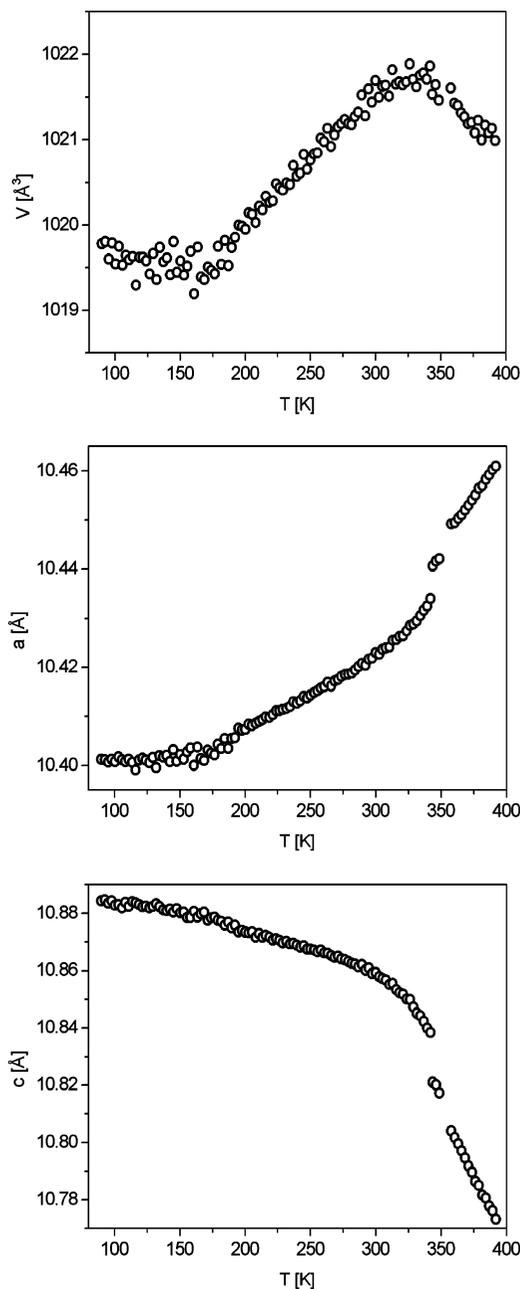
Figure 3. Unit cell volume and cell dimensions of Mn(BH₄)₂, refined from the in situ MAR345 powder diffraction data and plotted as a function of temperature.

frequency shift can be associated not only with a B–H bond length change, but also with a change of the force constant due to the interaction with the Mn(Mg) ion.

Structural Similarity to Mg(BH₄)₂. The structure of Mn-(BH₄)₂ shows interesting similarity to α-Mg(BH₄)₂. The lattice parameters a for manganese and magnesium borohydrides are essentially identical. The c parameters are related in the same 3:10 ratio as the number of formula units per unit cell ($Z = 9$ for manganese and 30 for magnesium borohydride). As already pointed out, Mn(BH₄)₂ and α-Mg(BH₄)₂ have the same coordination of cations and BH₄⁻ anions.

The structures of both borohydrides are made of similar layers L (Figure 5, top). The layers contain two independent M atoms (blue and violet). The layers are stacked along the c-axis, and rotated by 120° by the 3_1 axis in Mn(BH₄)₂ and by 60° by the 6_1 axis in α-Mg(BH₄)₂. Three identical layers are stacked along the unit cell vector c in Mn(BH₄)₂, and six layers are stacked
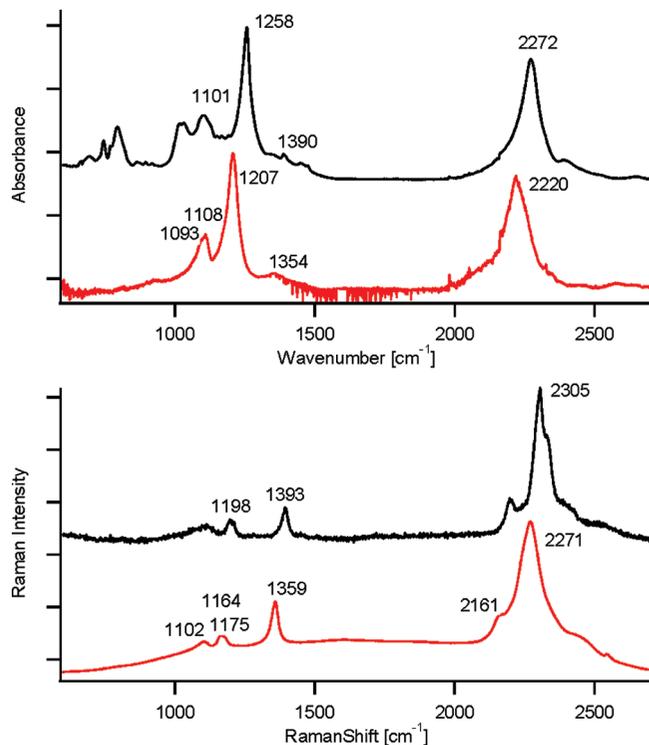
Figure 4. IR (top) and Raman (bottom) spectra of $Mn(BH_4)_2$ (in red) and $Mg(BH_4)_2$ (in black) at room temperature.
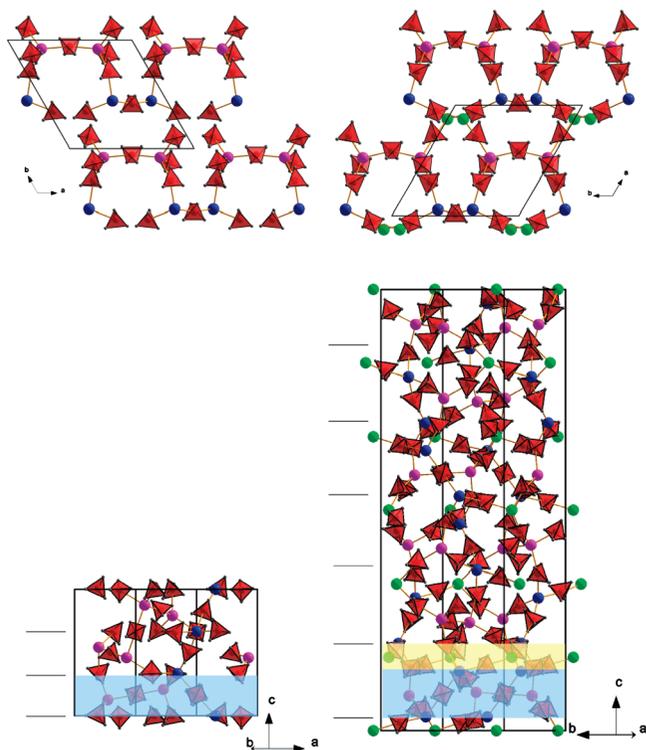
Figure 5. Crystal structure of $Mn(BH_4)_2$ (left) and α-$Mg(BH_4)_2$ (right) made from the similar layers L (top). The layers contain two independent *M* atoms (blue and violet). The layer of $Mn(BH_4)_2$ is shown here as a mirror image of the layer of α-$Mg(BH_4)_2$ (see text for more details). The layers are stacked along the *c*-axis (bottom), and rotated by 120° by the 3_1 axis in $Mn(BH_4)_2$ and by 60° by the 6_1 axis in α-$Mg(BH_4)_2$. In $Mn(BH_4)_2$, the layers L (light blue) are overlapping, sharing atoms. In α-$Mg(BH_4)_2$, the layers L (light blue) are intercalated by a thin layer L′ (yellow) containing the third independent Mg atom (green).

in α-$Mg(BH_4)_2$ (Figure 5, bottom). In $Mn(BH_4)_2$ the layers L (light blue) are connected directly, and share atoms. In α-Mg-

$(BH_4)_2$ the layers L (light blue) are intercalated by a thin layer L′ (yellow) containing the third independent Mg atom (green) in the structure.

The composition of the L layer is $M_4(BH_4)_{10}$ per unit cell in both borohydrides. The L′ layer contains one Mg atom per layer per cell. In α-$Mg(BH_4)_2$ the layer L is made up of Mg1 and Mg2 atoms and the layer L′ of Mg3 atoms. The composition of the basic crystal building block (L + L′) is then $Mg_4(BH_4)_{10}$ + Mg = $Mg_5(BH_4)_{10}$ per unit cell. In $Mn(BH_4)_2$ the layer L is made up of Mn1 and Mn2 atoms. As the layers L are in contact they share atoms Mn2, B1, B3, and B4 (including the hydrogen atoms) which leads to the correct composition of the basic crystal building block (L with shared boundaries) as $Mn_3(BH_4)_6$ per cell.

The building principle of $Mn(BH_4)_2$ and α-$Mg(BH_4)_2$ structures from identical layers can theoretically lead to a polytypism, which would be reflected in a strong anisotropic broadening of the powder diffraction peaks; however, this was not observed in our experimental data.

Structure Chirality. The layer L in α-$Mg(BH_4)_2$ and $Mn(BH_4)_2$ has the symmetry of the layer group *c*211 (no. 10).[37] The layer is built from nonchiral objects (tetrahedra), but the resulting layer structure is chiral. As both borohydrides crystallize in chiral space groups, one can imagine that the single crystals of each compound can exist in four different variants: left- or right-enantiomorph of the layer L stacked by one space group of the enantiomorphic pair ($P6_122-P6_522$ and $P3_112$ $P3_212$). This is, however, not true. As can be seen in Figure 5 (top), the screw axis that repeats the neighboring layers L, 3_1 for $Mn(BH_4)_2$ and 6_1 for $Mg(BH_4)_2$, is not on the same position in the layer. Moreover, careful examination of the layer L in both borohydrides shows that the layer L is of different handedness in $Mn(BH_4)_2$ than in α-$Mg(BH_4)_2$ (see Figure 5, top). This is certainly due to the different connectivity between the neighboring layers L in the two borohydrides: partial overlap in $Mn(BH_4)_2$, and L′ intercalation in α-$Mg(BH_4)_2$. This means that the handedness of the layer L is directly conditioned by the connectivity between the neighboring layers. Each crystal can then exist only in two variants: as left- or right-enantiomorph in one space group of the enantiomorphic pair. The structure of α-$Mg(BH_4)_2$ was refined on a single crystal;[34] however, the uncertainty of the Flack parameter, 0.0(6), did not allow the determination of the absolute structure consisting of relatively light atoms. As the structure of $Mn(BH_4)_2$ is determined by powder diffraction, no conclusion can be made about its absolute structure.

Topology of the Structure. Similar to the magnesium borohydride, $Mn(BH_4)_2$ shows a novel topology of the framework with four-connected Mn nodes (Supporting Information, Figure S2). The distances between the BH_4-bridged Mn atoms range from 4.71(1) to 4.86(1) Å. The topology of this tetrahedral framework contains 5-, 7-, and 8-membered rings of which 5- and 7-membered rings dominate.

As already pointed out for α-$Mg(BH_4)_2$,[32] the cation–anion framework of $Mn(BH_4)_2$, where the BH_4 group is considered as an anion B, resembles the frameworks of oxides and aluminosilicates: each tetrahedron AB_4 shares all of its vertices with other AB_4 tetrahedra.

Conclusions

The first crystal structure of a 3*d*-metal borohydride is presented. Solvent-free homoleptic manganese borohydride $Mn(BH_4)_2$ was prepared by a mechano-chemical synthesis by the reaction of lithium borohydride with manganese chloride

in a molar ratio of 2:1. The cooling break is important for its successful synthesis by ball milling. It crystallizes at ambient conditions in the trigonal crystal system with the space group symmetry $P3_112$. Its structure is stable from 90 to 450 K, where the compound melts. Thermal expansion of $Mn(BH_4)_2$ between 90 and 400 K is highly anisotropic and very nonuniform: lattice parameter a increases and c decreases. A volume drop above $\sim$325 K also might be related to a partial substitution of BH_4^- anions by the smaller Cl^- present in the $Mn(BH_4)_2$ + LiCl mixture. The structure of $Mn(BH_4)_2$ shows an interesting similarity to α-$Mg(BH_4)_2$: both structures are made of similar layers L stacked along the c-axis, and rotated by 120° by the 3_1 axis in $Mn(BH_4)_2$ and by 60° by the 6_1 axis in α-$Mg(BH_4)_2$. Three identical layers are stacked along one unit cell vector c in $Mn(BH_4)_2$, and six layers are stacked in α-$Mg(BH_4)_2$. In $Mn(BH_4)_2$, the layers L are overlapping, sharing atoms. In α-$Mg(BH_4)_2$ the layers L are intercalated by a thin layer L′ containing the third independent Mg atom in the structure. The layer L is chiral, and both borohydrides crystallize in chiral space groups. Similar to α-$Mg(BH_4)_2$, the structure of $Mn(BH_4)_2$ is not densely packed and contains isolated voids with the estimated volume of 21 Å³ each, occupying in total 6% of the space. The distance from the center of the void to the nearest atom (hydrogen) is 2.47 Å. The resemblance between $Mn(BH_4)_2$ and α-$Mg(BH_4)_2$ is reflected in the Raman and infrared spectra of both compounds.

Supporting Information Available: Table of atomic positions, representative Rietveld refinement profile, and crystal data (CIF file). This material is available free of charge via the Internet at http://pubs.acs.org.

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