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Metal Hydrides

Magnesium Borohydride: Synthesis and Crystal Structure**

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Owing to their light weight, complex p-metal hydrides are of interest for hydrogen storage in mobile applications.[1] Magnesium borohydride ($Mg(BH_4)_2$), which has been known since the 1950s,[2] has a theoretical hydrogen capacity of 14.8 wt%. Although this compound is thermally quite stable (decomposition temperature of ca. 300 °C) and, thus, less suitable for reversible storage applications, it is of interest as a complex p-metal hydride.[3] There have been several reports on the preparation and structure of solvates of $Mg(BH_4)_2$,[4] but few on the solvent-free compound.[5,6] Early work suggested the existence of two crystalline modifications of $Mg(BH_4)_2$, a tetragonal low-temperature (LT) phase and a cubic high-temperature (HT) phase.[7] The density of the LT phase was given as 0.989 $g\,cm^{-3}$ and the phase-transition temperature as 186 °C. No structural data were reported, owing to difficulties in obtaining crystalline products of sufficient quality for diffraction methods.

Various theoretical investigations have been performed in the recent past. Total-energy density functional theory (DFT) calculations of $Mg(BH_4)_2$ in 28 relatively simple structure types suggested that the most likely ion arrangement is that corresponding to the monoclinic $Cd(AlCl_4)_2$ type, albeit with a somewhat higher (orthorhombic) symmetry.[8] On the other hand, similar DFT calculations by other authors predicted two different modifications, one having a $Mg(AlH_4)_2$-like ion arrangement and trigonal symmetry, and the other having a novel ion arrangement and monoclinic symmetry.[9] Clearly, all these structure models differ substantially. Their only common features are their low dimensionality (sheet-like for the orthorhombic and trigonal models, and chain-like for the monoclinic model) and their simplicity (one symmetry-independent cation site and up to two symmetry-independent anion sites).

Herein, we present the crystal structure and Raman spectrum of solvent-free $Mg(BH_4)_2$. The compound was obtained by a hitherto unexplored synthetic method that avoids the use of diborane. The reaction involves the metathesis of $LiBH_4$ and $MgCl_2$ in diethyl ether, and is more efficient than the previously reported reaction from $NaBH_4$ and $MgCl_2$, which yields a solvated product that is rather amorphous.[5] In this way, $Mg(BH_4)_2$ and its deuteride were each obtained in approximately 30% yield (see the Experimental Section). We emphasize that drying at 145 °C was crucial for complete removal of the solvent and for obtaining a highly crystalline product suitable for high-resolution diffraction studies.

The structure of $Mg(BH_4)_2$ was solved and refined from data measured in synchrotron X-ray and neutron diffraction experiments on a multiphase powder sample (containing ca. 50 wt% of the main phase). The complexity of the structure is unprecedented for this type of compounds. In contrast to previous reports, the structure of $Mg(BH_4)_2$ has hexagonal symmetry (space group $P6_1$), and contains five symmetry-independent Mg^{2+} ions and ten symmetry-independent $[BH_4]^-$ ions. The Mg^{2+} and $[BH_4]^-$ ions are connected into a novel three-dimensional framework. All the cations have similar atomic environments. As shown in Figures 1 and S3

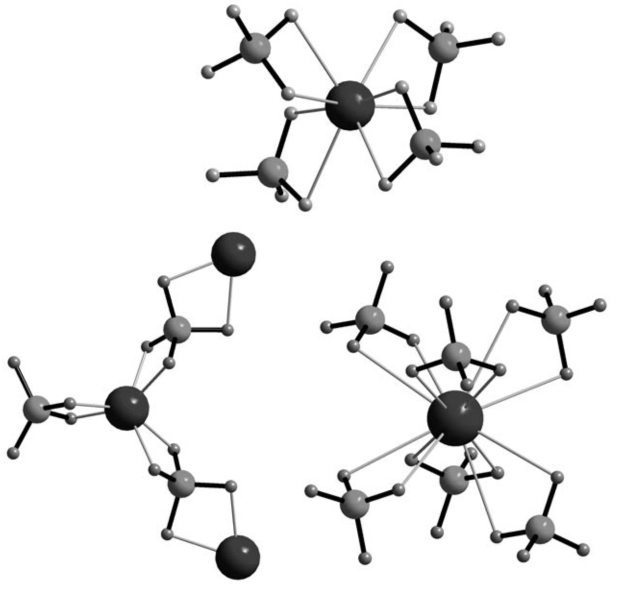

Figure 1. Comparison of the structures of $Be(BH_4)_2$ (bottom left), $Mg(BH_4)_2$ (top), and $Ca(BH_4)_2$ (bottom right), highlighting the coordination environments of the cations (Mg5 for $Mg(BH_4)_2$). $Be(BH_4)_2$ is a one-dimensional polymer; $Mg(BH_4)_2$ and $Ca(BH_4)_2$ are three-dimensional frameworks. Be/Mg/Ca large, B medium, H small spheres.

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(see the Supporting Information), each Mg^{2+} ion is surrounded by four $[BH_4]^-$ tetrahedra arranged in a deformed tetrahedron (Mg–B 2.31(3)–2.53(2) Å; B-Mg-B 83(2)–131(2)°). Each $[BH_4]^-$ ion is approximately linearly coordinated by two Mg^{2+} ions (Mg-B-Mg 148(1)–177(2)°). The orientation of the $[BH_4]^-$ tetrahedra is such that each Mg^{2+} ion is coordinated by tetrahedral edges only (called μ_2-H_2 bridges hereafter), resulting in an unusual eightfold, relatively irregular hydrogen coordination environment. In solid-state ternary alkali-metal and alkaline-earth hydrides, the hydrogen coordination environments of the cations are usually sixfold octahedral.[10] Only one example of sevenfold pentagonal bipyramidal coordination is known, and no examples of eightfold coordination or higher have been reported.

The Mg–D distances in $Mg(BD_4)_2$ are in the range 1.81(4)–2.25(5) Å, with the exception of one longer distance (Mg4–D64 2.46(8) Å). As expected for eightfold coordination, these distances are longer on average than those in binary MgD_2 (Mg–D 1.95 Å), where the Mg^{2+} ions have sixfold deuterium coordination environments. A single B–D distance of 1.18(1) Å was refined for all ten symmetry-independent rigid BD_4 tetrahedra. This distance compares well with those in related borohydrides such as $LiBH_4$ (1.04–1.28 Å),[11] $Be(BH_4)_2$ (1.07–1.19 Å),[12] and $Ca(BH_4)_2$ (1.11–1.12 Å).[13]

The beryllium and calcium analogues of $Mg(BH_4)_2$ have much simpler structures. For tetragonal $Be(BH_4)_2$, an X-ray diffraction experiment on a single crystal revealed a single Be^{2+} site that is connected to three $[BH_4]^-$ ions through μ_2-H_2 bridges, resulting in a sixfold, approximately trigonal-prismatic hydrogen configuration.[12] As shown in Figure 1, the Be^{2+} and $[BH_4]^-$ ions form a polymeric helical chain in which two out of eight hydrogen atoms are not bonded to beryllium. For orthorhombic $Ca(BH_4)_2$, X-ray powder diffraction suggested that the Ca^{2+} ion is octahedrally coordinated by six $[BH_4]^-$ ions through μ_2-H_2 bridges, forming a 12-fold, approximately icosahedral hydrogen coordination environment.[13] In this case, the Ca^{2+} and $[BH_4]^-$ ions form a three-dimensional framework (Figure 1). The increase of the hydrogen coordination number from six (for Be^{2+}) to eight (for Mg^{2+}) and twelve (for Ca^{2+}) suggests that cation size is one of the reasons that $Mg(BH_4)_2$ does not adopt one of the simpler structures of its alkaline-earth analogues.

Interestingly, the crystal structure of the zirconium analogue $Zr(BH_4)_4$ is completely different (at 113 K).[14] The Zr^{4+} ion is surrounded by four $[BH_4]^-$ units in a tetrahedral configuration; however, despite the facts that Zr^{4+} has an ionic radius similar to that of Mg^{2+} and that the Zr–B distances (2.34 Å) are similar to the Mg–B distances in $Mg(BH_4)_2$ (2.31(3)–2.53(2) Å), this hydride shows μ_3-H_3 bonding. This configuration leads to a 12-fold hydrogen coordination environment of zirconium and to a molecular structure.

An intriguing aspect of the $Mg(BH_4)_2$ structure is its complexity. Considering the cations (A) only, the Mg^{2+} network (Mg···Mg > 4.6 Å) resembles an amorphous state on a local level, with respect to both complexity and the local environments of the numerous building units. The topology of the Mg^{2+} network is novel for a three-dimensional framework. The network contains a variety of five-membered rings, which are more numerous than six- and eight-membered rings (Figure S4). If the tetrahedral anions (B) are included, the resulting three-dimensional framework (Figure S5), in which each tetrahedron AB_4 shares all of its vertices with another tetrahedron, resembles the frameworks of oxides and aluminosilicates, which generally display nearly linear A-B-A fragments.

Finally, it is worth pointing out that the structure of $Mg(BH_4)_2$ is significantly different from those predicted by theory.[8,9] Although the theoretical structures all display μ_2-H_2 bridges, the hydrogen coordination environments of the cations and the topologies of the networks differ.

The Raman spectra of $Mg(BH_4)_2$, $Mg(BD_4)_2$, $LiBH_4$, and $LiBD_4$ are shown in Figure 2. According to the spectral regions, the bands can be assigned to stretching modes, to bending and deformation modes, and to low-frequency lattice modes including librational motions of the anions (for assignments, see Table S1). As shown previously,[15,16] the stretching modes of the $[BH_4]^-$ ion are subject to important Fermi resonances. In the B–H stretching region (around 2300 cm^{-1}), the spectra of $Mg(BH_4)_2$ and $LiBH_4$ are similar, while those of the corresponding deuterides are more complex. In the bending region (1000–1400 cm^{-1}), the spectra of the hydrides and the deuterides show significant differences. By correlating the B–D stretching frequency with the B–D bond length, as was done for the cubic alkali-metal borohydrides,[17] a frequency of 1605 cm^{-1} suggests a bond length of 1.17 Å. However, for $LiBH_4$ and $Mg(BH_4)_2$, the stretching bands may be additionally shifted owing to a strong network of Li···H–B and Mg···H–B bonds. Theoretical calculations of lattice dynamics in the orthorhombic phase of $LiBH_4$[18] confirmed that B–H stretching vibrations are coupled with the thermal motion of the Li^+ ions. In the case of solid $Be(BH_4)_2$, the Raman spectra present two strong bands at 2509 and 2450 cm^{-1}, which were assigned to the B–H stretching modes of the two terminal B–H bonds.[19]

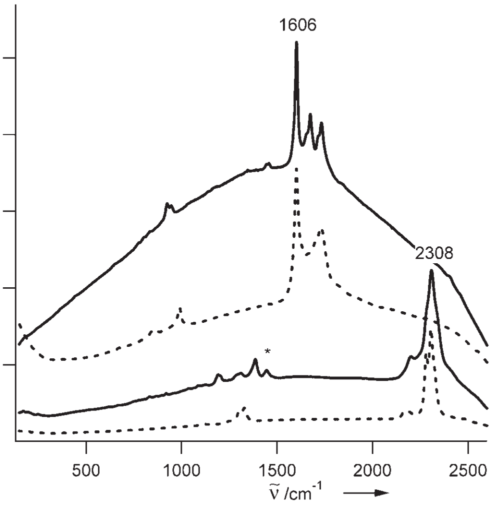

Figure 2. Lower curves: Raman spectra of the hydrides $Mg(BH_4)_2$ (——) and $LiBH_4$ (-----). Upper curves: Raman spectra of the deuterides $Mg(BD_4)_2$ (——) and $LiBD_4$ (-----). The asterisk indicates a band resulting from residual diethyl ether.

In conclusion, the structure of $Mg(BH_4)_2$ differs from those of its beryllium and calcium analogues, as well as from those predicted by theory. The structure is one of the most complex atom arrangements solved from powder diffraction data to date. Its solution required not only the best available experimental diffraction techniques and methodologies, but also highly crystalline samples, which were a challenge to synthesize.

Experimental Section

Synthesis: To fully exploit the metathesis reaction, we investigated different starting compounds and solvents. We first attempted to reproduce the preparation of $Mg(BH_4)_2$ through the reaction of $MgCl_2$ and $NaBH_4$ in diethyl ether, as reported in reference [5]. The yield from this method was less than 5%, even after heating the reaction mixture under reflux for 3 days. We then used $LiBH_4$ in the place of $NaBH_4$, because $LiBH_4$ is more soluble in ether.[20] Commercial $LiBH_4$ or $LiBD_4$ (2 g, 91.8 mmol; prepared according to references [21 and 22]) and anhydrous $MgCl_2$ (4 g, 42 mmol) were introduced into a 500-mL flask containing dry diethyl ether (300 mL). The mixture was heated under reflux for 3 days in a nitrogen atmosphere, and ether was repeatedly added to compensate for evaporation losses. The reaction mixture was allowed to cool for 1 h. Then the liquid phase was removed using a syringe equipped with a small filter and collected in a new flask. The ether was removed under vacuum (10^{-2}–10^{-3} mbar, liquid-nitrogen trap) at room temperature, leaving a white paste of solvated $Mg(BH_4)_2$ or $Mg(BD_4)_2$ and other compounds. Upon careful drying under vacuum at increasing temperatures (50, 70, 90, 110, 130, and 145 °C) over 3 or 10 days (in two different experiments), a dry solid was obtained. X-ray analysis revealed the presence of some LiCl, Li_2MgCl_4, and $LiBH_4$ or $LiBD_4$, in addition to the main phase $Mg(BH_4)_2$ or $Mg(BD_4)_2$ (yield ca. 30%). Above 150 °C, the sample started to decompose. For samples heated to only 120 °C, ether was detected in the Raman spectrum; these samples were not sufficiently well-crystallized for high-resolution diffraction studies.

Raman spectra: Raman spectra of powder samples in quartz capillaries were obtained at room temperature using 488-nm laser excitation and a HoloSpec monochromator (Kaiser Optical) equipped with a liquid-nitrogen-cooled CCD camera (Princeton Instruments).

Synchrotron X-ray and neutron diffraction: A powder synchrotron X-ray diffraction (S) pattern for $Mg(BD_4)_2$ was measured over 24 h at room temperature using synchrotron radiation ($\lambda = 0.400080(1)$ Å) at the Swiss–Norwegian Beam Line BM1B of the ESRF (Grenoble). A powder neutron diffraction (N) pattern was measured for the same sample at −100 °C using neutron radiation ($\lambda = 1.8857$ Å) on the HRPT at the Swiss Spallation Source (SINQ) of the PSI (Villigen). The S data were indexed in a hexagonal cell by using Dicvol96. The refined cell parameters for $Mg(BD_4)_2$ at 20 °C are $a = 10.3182(1)$, $c = 36.9983(5)$ Å, and $V = 3411.3(1)$ Å^3. The structure was solved jointly from the S and N data by direct-space methods (FOX[23]) in space group $P6_1$. Five magnesium atoms and ten BD_4 groups were refined jointly on the S and N data by using TOPAS-Academic.[24] The BD_4 tetrahedra were kept as semirigid bodies with ideal tetrahedral bond angles and a common refined B–D distance. In the final cycle, 186 parameters were refined, yielding the agreement factors of $R_{wp} = 0.048$, R_{Bragg}(main phase) $= 0.034$, and $\chi^2 = 16$ for the S data, and of $R_{wp} = 0.018$, R_{Bragg}(main phase) $= 0.008$, and $\chi^2 = 7.45$ for the N data.

In addition, nine S patterns were collected over the temperature range 100–200 °C to check for the phase transition reported in reference [7]. A transition to a HT phase was indeed observed at approximately 180 °C. The HT phase is possibly unstable above this temperature. Its diffraction peaks were not consistent with a cubic Cu_2O-type metal substructure (see the Supporting Information) nor with a face-centered cubic (fcc) structure ($a \approx 15.5$ Å) as reported in reference [7].

Experimental details, crystallographic data, interatomic distances, and Raman shifts are given in the Supporting Information.

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[1] F. Schüth, B. Bogdanovic, M. Felderhoff, *Chem. Commun.* **2004**, 2249–2258.
[2] E. Wiberg, R. Bauer, *Z. Naturforsch. B* **1950**, *5*, 397.
[3] A. M. F. R. Pinto, D. S. Falcão, R. A. Silva, C. M. Rangel, *Int. J. Hydrogen Energy* **2006**, *31*, 1341–1347.
[4] M. Bremer, H. Nöth, M. Warchhold, *Eur. J. Inorg. Chem.* **2003**, 111–119; and references therein.
[5] V. N. Konoplev, *Russ. J. Inorg. Chem.* **1980**, *25*, 964–966; and references therein.
[6] H. D. Batha, E. D. Whitney, T. L. Heying, J. P. Faust, S. Papeti, *J. Appl. Chem.* **1962**, *12*, 478–481; and references therein.
[7] V. N. Konoplev, V. M. Bakulina, *Russ. Chem. Bull.* **1971**, *20*, 136–138.
[8] P. Vajeeston, P. Ravindran, A. Kjekshus, H. Fjellvåg, *Appl. Phys. Lett.* **2006**, *89*, 071906.
[9] Y. Nakamori, K. Miwa, A. Ninomiya, H. Li, N. Ohba, S. Towata, A. Züttel, S. Orimo, *Phys. Rev. B* **2006**, *74*, 045126.
[10] K. Yvon, B. Bertheville, *J. Alloys Compd.* **2006**, *425*, 101–108.
[11] J.-P. Soulié, G. Renaudin, R. Černý, K. Yvon, *J. Alloys Compd.* **2002**, *346*, 200–205.
[12] D. S. Marynick, W. N. Lipscomb, *Inorg. Chem.* **1972**, *11*, 820–823.
[13] K. Miwa, M. Aoki, T. Noritake, N. Ohba, Y. Nakamori, S. Towata, A. Züttel, S. Orimo, *Phys. Rev. B* **2006**, *74*, 155122.
[14] P. H. Bird, M. R. Churchill, *Chem. Commun. (London)* **1967**, 403.
[15] S. Gomes, H. Hagemann, K. Yvon, *J. Alloys Compd.* **2002**, *346*, 206–210.
[16] P. Carbonnière, H. Hagemann, *J. Phys. Chem. A* **2006**, *110*, 9927–9933.
[17] G. Renaudin, S. Gomes, H. Hagemann, L. Keller, K. Yvon, *J. Alloys Compd.* **2004**, *375*, 98–106.
[18] K. Miwa, N. Ohba, S. Towata, Y. Nakamori, S. Orimo, *Phys. Rev. B* **2004**, *69*, 245120.
[19] J. W. Nibler, D. F. Shriver, T. H. Cook, *J. Chem. Phys.* **1971**, *54*, 5257–5266.
[20] B. E. Smith, B. D. James, R. M. Peachey, *Inorg. Chem.* **1977**, *16*, 2057–2062.
[21] H. I. Schlesinger, H. C. Brown, E. K. Hyde, *J. Am. Chem. Soc.* **1953**, *75*, 209–213.
[22] H. C. Brown, Y. M. Choi, S. Narasimham, *Inorg. Chem.* **1982**, *21*, 3657–3661.
[23] V. Favre-Nicolin, R. Černý, *J. Appl. Crystallogr.* **2002**, *35*, 734–743.
[24] A. A. Coelho, TOPAS-Academic, http://members.optusnet.com.au/alancoelho, **2004**.