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Synthesis and structures of magnesium alanate and two solvent adducts

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Abstract

A synthesis and purification method for $Mg(AlH_4)_2$ is presented, which is based on a metathesis reaction of $NaAlH_4$ and $MgCl_2$ in diethyl ether and subsequent purification procedure leading to a high yield of the monoether adduct of $Mg(AlH_4)_2$. After removal of the solvent, the alanate has been obtained as a nanocrystalline material with a yield of 81% and a purity of 95%. Crystal structures were determined and discussed for the solvent adducts $Mg(AlH_4)_2$. 4THF and $Mg(AlH_4)_2$. Et_2O . A proposition is made for the structure of $Mg(AlH_4)_2$.

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1. Introduction

In search of suitable materials for reversible hydrogen storage, the group of alkali alanates $MAlH_4$, with M=Li or Na, has become a matter of topical interest, mainly due to their high weight content of hydrogen and the low dissociation temperatures. However, the process of hydrogen uptake by the dehydrogenated compound is very slow and can only be realized under drastic conditions. Whereas all these properties have been known for decades (e.g. Refs. [1–5]), it was the work of Bogdanovic and Schwickardi in 1996, which showed that the decomposition of sodium alanate, NaAlH₄, can be made reversible by the addition of Ti or Fe compounds as catalysts [6].

Efforts have been made in the meantime to improve the reversible properties of sodium alanate mostly by ball milling and combination catalysts [7–9]. Recently, researchers at the Sandia National Laboratory reached a reversible amount of 5.5 wt.% of hydrogen in a number of absorption and desorption cycles [10]. This value is close to the theoretical value of 5.6 wt.% for the dissociation steps in the applied temperature range. In the work, a 'scale-up' reactor was studied, which contained 100 g of ball-milled NaAlH₄ together with a Ti–Al catalyst. Further

work was published about lithium alanate-based composite materials with reversible amounts in excess of 6–6.5 wt.% of hydrogen [11], a value which was defined by the US-DOE and the Japanese MITI to be a 'commercialization barrier' for hydrogen storage materials in mobile applications.

Whereas all activities described above dealt with alkali metal alanates, magnesium alanate as a representative of the earth alkali metal alanates could be a promising candidate as well. The compound was first synthesized in 1950 by Wiberg and Bauer [12] and contains 9.3 wt.% of hydrogen. Furthermore, the alanate decomposes readily below 200 °C [13,15]. In these early papers, several ways were reported for the synthesis of Mg(AlH₄)₂ (Eqs. (1)–(3)). However, sometimes only few experimental details were given.

$$4 \operatorname{MgH}_2 + 2 \operatorname{AlCl}_3 \to \operatorname{Mg}(\operatorname{AlH}_4)_2 + 3 \operatorname{MgCl}_2$$
(1)

$$MgH_2 + 2 AlH_3 \rightarrow Mg(AlH_4)_2$$
⁽²⁾

$$2 \operatorname{LiAlH}_{4} + \operatorname{MgBr}_{2} \rightarrow \operatorname{Mg}(\operatorname{AlH}_{4})_{2} + 2 \operatorname{LiBr}$$
(3)

In the period following, Ashby et al. [14] and Claudy et al. [15] reported about similar methods for the synthesis of magnesium alanate, but made differing observations, mainly concerning the solubility and thermal properties of the

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product. Moreover, every group reported about difficulties to obtain the substance without impurities.

As magnesium alanate is not available commercially and little is known about its properties, the aim of this work is to present a synthesis procedure for gram amounts of sufficiently pure material and to investigate the structure of the products, including two solvent adducts of the alanate.

2. Experimental

All synthesis operations were carried out on the bench using Schlenk tube techniques. The glassware was evacuated down to a pressure of 10^{-3} mbar and flushed with dry and oxygen-free nitrogen prior to use. Handling of the solids was done in an argon-filled glove box equipped with a recirculation system. Both the water and oxygen concentrations were kept below 1 ppm during operation.

2.1. Reagents

Tetrahydrofuran (THF), diethyl ether (Et₂O), and nheptane (all reagents p.a., Merck) were distilled over sodium before use. Sodium alanate (purum, Sigma-Aldrich) was used in a 1 M THF solution as received. Solvent-free NaAlH₄ was obtained by drawing the THF off under vacuum and heating the dry white solid to 50 °C until a residual pressure of 2×10^{-3} mbar was reached, which lasted several hours. FTIR measurements of the product indicated a hydrocarbon content below the detection limit of the method. Lithium alanate (97%, Merck) was used after determination of the hydrogen content by elemental analysis. Magnesium bromide diethyl etherate (99%, Sigma-Aldrich) was dissolved in diethyl ether before use. Magnesium chloride (98%, Sigma-Aldrich) and magnesium iodide (98%, Sigma-Aldrich) were used as received.

2.2. Instrumentation and analyses

Solid state infrared spectra of the alanates (as KBr pellets) were recorded in the range of $5000-370 \text{ cm}^{-1}$ at ambient conditions in air using a Perkin-Elmer Spectrum GX FTIR spectrometer. No significant change was observed between two subsequently taken spectra, effects caused by the ambient humidity were therefore excluded. The evaluation was done with the Perkin-Elmer Spectrum v. 2.00 Software.

Elemental analysis of carbon and hydrogen was done using a CE Instruments Flash EA 1112 Series analyser with helium as purge gas. The powder samples were wrapped in tin capsules in the glove box and stored in gas-tight containers until weighing and measuring, which was done immediately after sample preparation. The typical amount of a sample was 4–6 mg. For calibration, benzoic acid and a standardized $LiAlH_4$ were used as standards. Control measurements were made before and after measuring the alanate samples.

Halogen analysis was carried out by the Mohr method using a 0.01-M AgNO₃ solution.

For structure analysis, single crystals of the products, which are known to be highly reactive in air, were rapidly stuck on top of a glass filament using perfluorinated oil and mounted in an X-ray diffractometer (STOE IPDS II, equipped with a graphite monochromator, Mo K α radiation source and an Oxford Cryostream LT at 200 K), to avoid any oxidation or exposure to moisture. The determination of the unit cell, the solution and refinement of the crystal structure were performed using the Bruker SHELXL97 software.

Powder X-ray diffraction patterns of the THF and diethyl ether adduct were obtained with a STOE STADI P diffractometer (Cu Ka radiation, 1 kW, with Ge monochromator). The powder was measured under exclusion of air in a sealed rotating glass tube. Evaluation of the diffraction patterns was performed with the STOE WinXPow32 software. The same software was used to calculate powder diffraction patterns from the single crystal data. Powder X-ray diffraction patterns of the magnesium alanate were obtained with a PHILIPS X'PERT diffractometer (Cu Ka radiation, 2 kW, with X'Celerator RTMS detector, automatic divergence slit). The powder was covered by mineral oil, spread, and measured on a Si single crystal. The software for data acquisition and evaluation was X'PERT 1.3e and ProFit 1.0c.

Thermogravimetric analysis was performed in an argon atmosphere between room temperature and 350 °C at 2 K/min using a NETZSCH STA 409C analyser equipped with a skimmer and a BALZERS quadrupole mass spectrometer for evolved gas analysis. Typical sample amounts were 10 mg.

3. Results and discussion

The synthesis of magnesium alanate proceeds via the formation of a solvent adduct which precipitates from the solvent and which must be dried in order to obtain the pure substance. The magnesium alanate as well as the solvent adducts with THF and diethyl ether were synthesized and investigated.

3.1. Synthesis of $Mg(AlH_4)_2$ and two solvent adducts

As reaction type for the syntheses, we chose metathesis reactions of halide and alanate anions, similar to Eq. (3).

The following reactions have been investigated in particular:

 $2 \operatorname{NaAlH}_{4} + \operatorname{MgJ}_{2} \rightarrow \operatorname{Mg}(\operatorname{AlH}_{4})_{2} \cdot 4\operatorname{THF} + 2 \operatorname{NaJ}$ (in THF) (5)

 $2 \operatorname{NaAlH}_{4} + \operatorname{MgCl}_{2} \rightarrow \operatorname{Mg(AlH}_{4})_{2} \cdot 4\operatorname{THF} + 2 \operatorname{NaCl}$ (in THF) (6)

$$2 \operatorname{LiAlH}_{4} + \operatorname{MgBr}_{2} - \operatorname{dietherate} \rightarrow \operatorname{Mg}(\operatorname{AlH}_{4})_{2} \cdot \operatorname{Et}_{2}O +$$

2 LiBr (in Et₂O) (4)

$$2 \operatorname{LiAlH}_{4} + \operatorname{MgCl}_{2} \rightarrow \operatorname{Mg(AlH}_{4})_{2} \cdot \operatorname{Et}_{2}O + \operatorname{LiCl}$$

(in Et₂O) (7)

$$2 \operatorname{NaAlH}_{4} + \operatorname{MgCl}_{2} \rightarrow \operatorname{Mg(AlH}_{4})_{2} \cdot \operatorname{Et}_{2}O + 2 \operatorname{NaCl}$$
(in Et₂O) (8)

Whereas instructions for reactions (4)–(7) can be found in the literature, reaction (8) has not yet been investigated, according to our knowledge. The following procedures were carried out in detail.

3.1.1. Reaction (4): 2 LiAlH₄+MgBr₂dietherate \rightarrow Mg(AlH₄)₂·Et₂O + 2 LiBr/in Et₂O

This synthesis procedure is based on a short description by Wiberg and Bauer [12]. According to the authors, the product can be recovered from the product solution.

13.0 g MgBr₂-dietherate (0.05 mol) and 4.0 g LiAlH₄ (0.105 mol) were dissolved in 50 ml diethyl ether, respectively. The MgBr₂-dietherate solution was added to the alanate solution, which led to the formation of a white precipitate. The suspension was stirred under reflux for 3 h and filtered. The residue was dried under vacuum at ambient temperature and investigated by XRD, as was the white residue, obtained from the diethyl ether solution which was evaporated to dryness. According to the spectra, both powders contained considerable amounts of LiBr. 30 wt.% LiBr were determined in the residue from the ether solution.

Several propositions were made in the literature for obtaining the alanate free from coprecipitating halides. Regarding the next reaction (5), it was claimed [14] that the solubility of the sodium iodide in THF was sufficiently high to keep it in solution, while the alanate precipitated and could be recovered almost free from halide. For reaction (6), it was proposed to conduct the reaction by a stepwise addition of the magnesium chloride solution in THF to the sodium alanate and subsequent filtering as fast as possible [15]. This would prevent the initial colloidal NaCl particles from growing so that they could be washed through the filter cake.

3.1.2. Reaction (5): 2 NaAlH₄+MgJ₂ \rightarrow Mg(AlH₄)₂· 4THF+2 NaJ/in THF

The synthesis procedure is based on a modified description by Ashby et al. [14].

 MgJ_2 (24.6 g; 0.09 mol) was suspended in 500 ml THF and stirred for 30 min at ambient temperature. Two hundred millilitres of a 1 M NaAlH₄ solution in THF (0.2 mol) were added, leading to the formation of a white precipitate. Another 200 ml of THF were added and the suspension was stirred under reflux for 2 h. The fine white solid was filtered and dried under vacuum at ambient temperature, the yield was 19.6 wt.%.

XRD measurements of the filter cake showed a diffraction pattern similar to the one detected for $Mg(AlH_4)_2$. 4THF by French workers [15] plus signals indicating a content of NaJ, which was 40.5 wt.%, as determined by the Mohr method. The residue obtained from the filtrate contained 7 wt.% NaJ.

The product which was recrystallized from THF contained 47.3 ± 1.4 wt.% C and 9.2 ± 0.6 wt.% H (theoretical values for Mg(AlH₄)₂·4THF are 51.1 wt.% C and 10.7 wt.% H).

3.1.3. Reaction (6): 2 NaAlH₄+MgCl₂ \rightarrow Mg(AlH₄)₂· 4THF+2 NaCl/in THF

The synthesis procedure is based on the description by Claudy et al. [15].

 $MgCl_2$ (3.8 g; 0.04 mol) was dissolved in 150 ml THF at 65 °C under reflux (2 h). At room temperature, 75 ml of the solution were added to 175 ml of a NaAlH₄ solution in THF (0.1 mol). The white and milky precipitate was quickly removed by filtering. The second half of the MgCl₂ solution was added to the filtrate and the precipitate again removed by filtering.

The residue was dried in a Schlenk tube under vacuum at two different temperatures. At about 70 °C, the major amount of the solvent evaporated and the fine white powder formed a fluidized bed. When the gas generation subsided, the temperature was raised to 100 °C and kept there, until the residual pressure had reached 1×10^{-3} mbar. A light-gray powder was obtained with a yield of 74%. XRD measurements indicated a content of NaCl in the product. Elemental analysis showed a content of 0.8 wt.% C and 6.3 wt.% H (theoretical amount: 9.3 wt.% H). The product contained 6 wt.% NaCl.

The results indicate that the attempts described above led to products which contained about 7 (NaJ) or 6 (NaCl) wt.% of halide, which has not been considered a satisfying purity. Therefore, two additional reactions were carried out to obtain sufficiently pure magnesium alanate with a high yield. Their products were subjected to a purification procedure which was mainly a Soxhlet extraction of the alanate from the coprecipitated halide.

3.1.4. Reaction (7): 2 $LiAlH_4 + MgCl_2 \rightarrow Mg(AlH_4)_2$. $Et_2O + LiCl/in Et_2O$

Diethyl ether (100 ml) was added to a mixture of 10.2 g $MgCl_2$ (0.105 mol) and 8.2 g $LiAlH_4$ (0.21 mol). The suspension was heated and stirred under reflux for 6 h and

allowed to stand overnight. The ether was drawn off, leaving 24 g of a rigid gray residue which contained the ether adduct of Mg alanate and LiCl, as was determined by XRD measurements and the Mohr method (34 wt.% LiCl). The gray color was due to Al impurities in the educt LiAlH_4 .

The product was subjected to a purification procedure by several Soxhlet extractions with 200 ml diethyl ether, respectively. The residue of the first extraction contained 9–14 wt.% LiCl. For a further reduction of the halide content, the residue was subjected to a second extraction which led to a product containing 5.3–6.8 wt.% LiCl. A third extraction reduced the LiCl content to 2.8–3 wt.%, relative to Mg(AlH₄)₂·Et₂O, which is a theoretical content of about 5.2–5.6 wt.%, relative to Mg(AlH₄)₂. This value was not considered to be sufficiently low for a further use of the material. However, recrystallization from the second extract solution yielded some colorless, crystalline material, which was pure and could be used for structural investigations.

The high LiCl contents in the extracts were probably due to a relatively high solubility of LiCl compared to the alanate, or the LiCl crystallites were sufficiently small so that they were able to run through the filter tube of the extractor. As a consequence, a metathesis reaction was chosen, where a halide less soluble than LiCl is formed. This is the case, e.g. for NaCl, which has a free energy of solution of -9 kJ/mol, compared to -42 kJ/mol for the LiCl [16], see reaction (8).

3.1.5. Reaction (8): 2 NaAlH₄+MgCl₂ \rightarrow Mg(AlH₄)₂ \cdot Et₂O +2 NaCl/in Et₂O

Diethyl ether (150 ml) was added to a mixture of 9.5 g $MgCl_2$ (0.1 mol) and 10.8 g $NaAlH_4$ (0.2 mol). The suspension was heated and stirred under reflux for 8 h and allowed to stand overnight. The next day, the ether was drawn off, leaving a rigid gray residue which contained 38 wt.% NaCl. In a Soxhlet apparatus, the product was extracted with diethyl ether, which took several days. The white, crystalline residue from the extract was $Mg(AlH_4)_2$. Et₂O, as was confirmed by XRD measurements (see Section 3.3). According to elemental analysis, the product contained 28.5±2 wt.% C and 10.6±0.9 wt.% H (theoretical: 29.9 wt.% C and 11.3 wt.% H). The yield of the ether adduct was 81.5%. It contained only traces (0.9 wt.%) of NaCl.

When the diethyl ether of a magnesium alanate solution was drawn off under vacuum, the dissolved product became gel-like at first, forming viscous bubbles, which indicates a polymer-like structure of the material. The continued procedure led to a firm white solid which became brittle upon further drying at 50 °C. Under these conditions, the product lost a large part of the bound diethyl ether, as was confirmed by FTIR measurements. Obviously, there are coherent structural changes which lead to a less rigid material that can be removed easily from the flask and pulverized.

The solvent was removed from the product under vacuum in a glass oven with a rotating flask, yielding a fine white powder. During the drying process, the temperature was gradually increased from room temperature to 90 °C, which was kept until a residual pressure of 1×10^{-3} mbar was reached (after ~6 h). The product was Mg(AlH₄)₂, as was confirmed by XRD measurements (see Section 3.4). According to elemental analysis, the product contained 9.02±0.08 wt.% H and 2.3±0.2 wt.% C (theoretical: 9.34 wt.% H). The residual content of NaCl was 1.7 wt.%.

Although it is mentioned in the literature that $NaAlH_4$ was 'insoluble' in diethyl ether [17], it is obviously practicable to accomplish a reaction with $MgCl_2$ as described above. Probably, precipitation of sodium chloride and magnesium alanate is a driving force which leads to a steady state apart from the equilibrium of solution. Therefore, the reaction can proceed until the $NaAlH_4$ is consumed.

Thermogravimetric measurements of the $Mg(AlH_4)_2$ showed that the maximum decomposition temperature was 175 °C, which is a value between the observations of Wiberg and Bauer, who mentioned that the decomposition would start at 140 °C [13] and Claudy et al., who found about 200 °C [15] for the maximum decomposition temperature. However, a detailed analysis of the evolved gas by mass spectrometry revealed that the alanate starts to decompose at about 110 °C already. This explained experimental difficulties to get Mg(AlH₄)₂ from the THF adduct without losses of hydrogen. In the adduct, THF is strongly bound to the Mg atoms and temperatures around 100 °C have to be applied in a vacuum to remove the solvent molecules. This was a reason why the more volatile diethyl ether was preferred as solvent and $Mg(AlH_4)_2$ was prepared from the ether adduct.

3.2. THF adduct

Colorless, coffin-lid shaped single crystals of the THF adduct were obtained by crystallization from a cooled and concentrated Mg alanate THF solution. They were investigated by single crystal X-ray diffraction analysis. The structure determined confirmed the structure proposed by Noeth et al. [18]. The tetrakis THF adduct, Mg(AlH₄)₂· 4THF (1), crystallizes in the orthorhombic space group *Pcbn* ($\alpha = \beta = \gamma = 90^{\circ}$, a = 10.198 Å; b = 16.484 Å; c = 14.064 Å). Fig. 1 shows the molecular packing of 1 in the lattice.

In the solid state, compound **1** consists of discrete molecules. The central atom of each molecule, Mg, is octahedrally coordinated by four THF molecules and two



Fig. 1. Molecular packing of the THF adduct, Mg(AlH₄)₂·4THF, in the lattice.

hydrogen atoms. The latter serve as μ_2 bridges for two Al atoms, the coordination sphere of which is complemented by three terminal H atoms, respectively, completing the AlH₄ tetrahedrons. The Al–H bond length in the H bridge is 1.5 Å, the mean length of the terminal Al–H bonds is 1.52 Å, the Mg–H bond length is 2.1 Å.

The reflection pattern of a single crystal measurement

was used to calculate a corresponding powder diffraction pattern. In Table 1, the calculated pattern is compared to the measured intensities of a powder sample. As can be seen in the table, the calculated diffractogram was similar to the one obtained from powder XRD measurements. Furthermore, the data are in fair agreement with a diffraction pattern published previously by French workers [15].

Calculated and measured powder diffraction patterns for $Mg(AlH_4)_2$. 4THF, including the *d*-spacing, the 2θ -values (for Cu K α radiation), and the relative signal intensities. Signals weaker than 1% of the maximum intensity were omitted

Calculated			Measured		
d (Å)	2θ (°)	<i>I</i> (rel)	<i>d</i> (Å)	2θ (°)	<i>I</i> (rel)
8.67	10.20	28	8.72	10.14	32
7.37	12.00	18	7.42	11.92	48
7.12	12.42	9	7.16	12.36	32
7.04	12.57	10	7.07	12.51	50
5.81	15.23	5	5.87	15.09	12
5.46	16.21	11	5.82	15.21	11
5.09	17.40	2	5.49	16.13	18
4.84	18.31	1	4.87	18.19	4
4.60	19.29	2	4.62	19.18	4
4.13	21.49	100	4.16	21.36	100
4.08	21.79	52	4.10	21.65	38
4.00	22.22	12	4.02	22.10	3
-	-	-	3.99	22.27	2
3.78	23.49	10	3.81	23.34	17
3.69	24.11	2	3.72	23.93	2
3.56	25.01	4	3.58	24.83	1
3.52	25.31	2	3.54	25.15	1
-	_	_	3.39	26.28	2
3.33	26.78	3	3.34	26.636	3
_	-	_	3.28	27.185	6
3.24	27.48	5	3.25	27.383	6
3.21	27.82	2	3.23	27.612	4
_	-	-	3.20	27.839	7
-	-	_	3.10	28.756	4
3.08	28.97	6	3.08	28.94	4
_	-	-	2.98	29.921	2
2.92	30.62	9	2.94	30.398	7
2.89	30.89	6	2.91	30.7	4
2.71	32.99	5	2.73	32.842	5
2.70	33.19	4	2.68	33.411	2
2.67	33.51	2	2.61	34.395	3
_	_	_	2.59	34.59	2
2.57	34.84	1	2.58	34.769	2
2.44	36.81	4	2.47	36.289	2
2.42	37.17	2	2.46	36.536	2
2.37	37.97	3	2.39	37.67	1
2.30	39.23	2	2.32	38.874	4
2.26	39.82	2	2.28	39.459	2
_	_	_	2.20	40.992	2
2.06	43.87	2	2.08	43.508	2
1.92	47.36	2	2.01	44.993	2
1.84	49.39	2	1.84	49.47	1
			-		

3.3. Diethyl ether adduct

Crystals were obtained as colorless needles from a saturated etherate solution by layering the solution with n-heptane. The needles were investigated by single crystal X-ray diffraction analysis.

The compound Mg(AlH₄)₂·Et₂O (**2**) crystallizes in the monoclinic space group $P2_1/n$ with four formula units per unit cell of the lattice (a = 5.181 Å, b = 17.278 Å, c = 12.488 Å, $\alpha = \gamma = 90^{\circ}$, $\beta = 95.74^{\circ}$). The crystallographic data are summarized in Table 2. The coordinates of the

Table	2
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Crystal data, X-ray collection and structure refinement of $Mg(AlH_4)_2 \cdot Et_2O$

Crystal system		Monoclinic
Space group		$P2_1/n$
Cell constants,	a (Å)	5.181(1)
	b	17.278(4)
	с	12.488(3)
	$oldsymbol{eta}$ (°)	95.74(3)
Cell volume		1112.3(4)
Number of formula uni	ts per cell	4
Colour		Colourless
Composition		C ₄ H ₁₈ Al ₂ MgO
Molar weight		160.45
<i>F</i> (000)	352.0	
Calc. density $(g \text{ cm}^{-3})$	0.958	
Temperature (K)	200	
Absorption coefficient, μ (mm ⁻¹)		0.256
2θ range (°)		6-49
Scan type		Ω
Data collected		1779
Unique data; $R_{(INT)}$		1112; 0.0386
Observed data, $F \ge 4\sigma$	(F)	798
Number of parameters		107
R_1^{a} (for $F \ge 4\sigma(F)$); R	(all data)	0.0459; 0.0662
$wR(F^2)^{\rm b}$; Goof ^c		0.1324; 0.989
Largest difference peak	; hole (eA^{-3})	0.29; -0.15
CCDC registration number		182 771

$${}^{a}R_{1} = \frac{\sum_{hkl} ||F_{o}| - |F_{c}||}{\sum_{hkl} |F_{o}|}.$$

$${}^{b}wR(F^{2}) = \sqrt{\frac{\sum_{hkl} w(F_{o}^{2} - F_{c}^{2})^{2}}{\sum_{hkl} w(F_{o}^{2})^{2}}} \text{ where } 1/w = \sigma^{2}F_{o}^{2} + (aP)^{2} + bP \text{ with}$$

 $P = (\max(F_o^2, 0) + 2F_c^2)/3$, as coefficients *a* and *b* the values were chosen that were suggested by SHELXL97.

^c
$$Goof = \sqrt{\frac{\sum_{hkl} w(F_o^2 - F_c^2)^2}{n - m}}$$
, where *n* is the number of unique data and *m* is the number of parameters.

atoms and the isotropic thermal parameters are listed in Table $3.^{1}$

In contrast to the THF adduct, where the solid state consists of discrete molecules, **2** has a polymeric, ribbonlike structure. A part of the structure in the crystal is shown in Fig. 2. The Mg atoms are octahedrally coordinated by five H atoms and the O atom from one diethyl ether molecule. The bond lengths between Mg and its neighbors (mean Mg–H bond length: 2.0 Å) correspond to those found with the THF adduct **1**. The bond angles deviate only slightly from an ideal octahedron. Similar to **1**, each Al atom is tetrahedrally coordinated by four H atoms, the Al–H bond lengths in the H bridges of **1** and **2**

¹Further details of the crystal structure determination can be requested from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK stating the CCDC registration number 182 771, the authors, and the journal.

Table 3 Atomic positions and thermal parameters ($\times 10^3$ Å) of Mg(AlH₄)₂·Et₂O

Atom	Coordinates	Coordinates			
	x/a	y/b	z/c		
Al(1)	1.2275(2)	0.3936(1)	0.9846(1)	4.2(1)	
Al(2)	1.1840(2)	0.5681(1)	0.7455(1)	5.1(1)	
Mg(1)	0.6982(2)	0.4592(1)	0.8224(1)	4.3(1)	
H(1)	1.251(10)	0.318(6)	1.022(3)	8.2(16)	
H(2)	1.256(8)	0.447(4)	1.082(3)	5.9(12)	
H(3)	0.954(7)	0.401(3)	0.921(2)	3.5(9)	
H(4)	1.409(8)	0.415(4)	0.903(3)	5.0(11)	
H(5)	1.206(10)	0.603(5)	0.854(3)	6.5(13)	
H(6)	1.143(11)	0.614(5)	0.647(3)	8.1(16)	
H(7)	1.442(10)	0.523(5)	0.734(3)	7.3(15)	
H(8)	0.986(9)	0.496(4)	0.746(3)	5.3(11)	
O(1)	0.6587(6)	0.3677(2)	0.7195(2)	5.0(1)	
C(1)	0.6465(11)	0.3760(5)	0.6034(3)	7.4(2)	
C(2)	0.3850(13)	0.3739(7)	0.5479(4)	11.2(4)	
C(3)	0.6403(12)	0.2865(6)	0.7542(4)	7.6(2)	
C(4)	0.8875(11)	0.2456(6)	0.7628(4)	7.8(2)	

are comparable (mean Al–H bond length for **2**: 1.55 Å). The tetrahedron bond angles are bent to a mean value of about 102° between the H bridges which are lying in the plane perpendicular to the ether–ether axis.

Unlike in compound **1**, where the AlH₄ tetrahedrons can be regarded as terminal ligands, they act rather as bridging units in **2**. As can be seen in Fig. 2, the AlH₄ group around Al(1) serves as μ_3 -, the group around Al(2) serves as μ_2 -bridging unit. The bond lengths of the terminal Al–H bonds differ from those of the H bridges and are 1.47 Å for a μ_2 - and 1.55 Å for a μ_3 -unit. The connection pattern leads to a ribbon structure with its edges shielded by two rows of ether molecules. Fig. 3 shows the parallel arrangement of the alanate ribbons in the lattice.

Based on the single crystal data above, the X-ray powder diffraction pattern was calculated for $Mg(AlH_4)_2 \cdot Et_2O$ and compared to the measured signals of a powder sample (see Table 4). The pattern is complex, caused by a comparably low symmetry in the crystal. The few mea-



Fig. 2. Crystal structure of the diethyl ether adduct, Mg(AlH₄)₂·Et₂O. The coordinates of the specified atoms are shown in Table 3.



Fig. 3. Packing of the ribbons of the ether adduct in the lattice.

sured signals, which are missing in the calculated pattern were not due to impurities of the reactands $NaAlH_4$ and $MgCl_2$ in the sample.

3.4. $Mg(AlH_4)_2$

A structure analysis of the solvent-free $Mg(AlH_4)_2$ by single crystal X-ray diffraction was not possible, because single crystals could not be obtained by drying crystals from the solvent adducts. Nevertheless, X-ray powder diffractograms were obtained from $Mg(AlH_4)_2$ (see Table 5). The measured diffractogram resembles a pattern published by French workers [15] where the alanate was produced via the THF adduct. Moreover, evidence is given for a structure in the next section.

The signals in our diffractogram were obviously

Table 4

Calculated and measured powder diffraction pattern for Mg(AlH₄)₂·Et₂O including the *d*-spacing, the 2θ values (for Cu K α radiation) and the relative signal intensities. Signals weaker than 1% of the maximum intensity were omitted

Calculated		Measured			
d (Å)	2θ (°)	<i>I</i> (rel)	<i>d</i> (Å)	2θ (°)	<i>I</i> (rel)
10.08	8.76	92	10.14	8.71	28
8.64	10.22	9	8.74	10.12	19
7.09	12.47	4	7.16	12.36	48
-	-	_	6.77	13.06	9
6.21	14.24	61	6.24	14.19	43
_	_	_	5.88	15.06	11
-	_	_	5.41	16.38	12
5.04	17.59	6	5.28	16.77	12
4.94	17.94	75	4.97	17.84	35
4.6	19.28	5	4.57	19.39	8
4.44	19.96	2	4.43	20.02	31
4.29	20.67	19	4.37	20.29	16
4.22	21.02	9	4.32	20.55	15
_	_	_	4.13	21.51	18
_	_	_	4.1	21.65	26
4.07	21.81	13	4.05	21.91	11
3.84	23.14	5	3.86	23.02	14
3.76	23.65	100	3.8	23.39	100
_	_	_	3.69	24.09	25
3.59	24.75	28	3.6	24.71	45
3.55	25.09	71	3.58	24.83	46
_	_	_	3.53	25.21	35
3.47	25.68	15	3.46	25.74	41
3.39	26.29	19	3.39	26.28	19
3.36	26.47	24	3.33	26.72	13
3.33	26.74	63	3.31	26.9	17
3.31	26.89	21	_	_	_
3.25	27.4	3	3.25	27.41	19
_	_	_	3.23	27.62	20
3.15	28.27	45	3.16	28.18	17
_	_	_	3.12	28.56	21
3.04	29.39	6	3.05	29.24	18
3	29.74	42	3.03	29.48	28
_	_	_	2.96	30.13	21
2.92	30.6	2	2.92	30.61	13
2.88	31.06	9	2.85	31.31	17
2.84	31.46	3	_	_	_
2.83	31.61	4	_	_	_
2.81	31.87	2	2.77	32.29	13
2.76	32.43	3	2.73	32.76	12
2.66	33.69	2	2.68	33.39	21
2.58	34.79	11	2.58	34.8	19
2.55	35.19	30	2.56	35.08	27
2.52	35.65	18	2.52	35.65	10
2.49	36.08	3	2.47	36.3	12
2.46	36.47	3	2.44	36.77	19
2.38	37.69	2	2.41	37.24	12
2.35	38.21	2	2.33	38.58	11
2.33	38.59	1	2.31	39.02	8
2.29	39.25	3	2.28	39.54	10
2.27	39.6	6	2.23	40.34	9
2.22	40.54	4	2.22	40.59	10
2.21	40.77	4	_	-	_
2.21	40.82	5	_	_	_
2.2	41.06	4	2.19	41.23	8
2.17	41.49	10	2.17	41.58	8
2.13	42.37	5	2.13	42.35	7
2.07	43.79	4	2.08	43.4	12
2.07	13.17	т	2.00	13.4	14

Calculated			Measured		
d (Å)	2θ (°)	<i>I</i> (rel)	d (Å)	2θ (°)	<i>I</i> (rel)
2.05	44.04	7	2.05	44.09	7
2.01	45.04	2	2.01	44.98	10
1.99	45.5	3	1.96	46.2	10
1.98	45.82	3	_	_	_
1.93	47.04	2	1.92	47.38	8
1.92	47.31	4	1.9	47.87	10
1.88	48.36	6	1.87	48.74	8
1.85	49.27	3	1.85	49.28	8
1.83	49.83	3	1.82	50.18	8
1.82	50.03	3	_	_	_
1.79	50.86	3	1.79	50.89	7
1.72	53.06	2	1.73	52.83	7
1.71	53.5	8	_	_	_
1.7	53.94	4	1.69	54.36	7
1.69	54.16	1	1.66	55.36	8
_	_	_	1.61	57.07	8
_	_	_	1.6	57.46	8
_	_	_	1.59	57.77	9
_	_	_	1.55	59.56	7
_	_	_	1.51	61.15	8

Table 5

X-ray powder diffraction pattern for Mg(AlH₄)₂, including the *d*-spacing, the 2θ values (for Cu K α radiation), and the relative signal intensities

d (Å)	2θ (°)	<i>I</i> (rel)
3.556	25.02	1000
2.923	30.56	25
2.815	31.76	27
2.591	34.59	282
2.449	36.67	178
2.096	43.14	74
1.946	46.64	16
1.782	51.22	54
1.631	56.37	52
1.56	59.18	27
1.498	61.89	18
1.47	63.20	25
1.394	67.09	5
1.298	72.80	5
1.2206	78.26	9
1.188	80.84	7
1.146	84.47	5

broadened. An analysis of the peak shapes was performed and the volume-weighted mean grain size from Bragg-peak broadening, corrected for strain, was computed [19,20]. The method assumes Cauchy size broadening and Gauss strain broadening. The calculations indicated that after the drying procedure the mean crystallite size was only 30 ± 4 nm, and the lattice strain was about $0.2\pm0.09\%$, whereas the crystallite size of the ether adduct was much higher (in the range of 3 µm), and the strain was lower (<0.1%).

Probably, a partial collapse or breakage of the structure occurred during the drying process, the collapse being induced by internal stresses in the crystal when the solvent molecules were released at elevated temperatures.

3.5. FTIR measurements

Fig. 4a shows three solid-state IR spectra of the products. In addition to the fingerprint region which includes Al–H deformation vibrations, strong bands appear in the regions around 1000–1200, 1600–2000, and 2850–3050 cm⁻¹. Whereas the first and the last band can be attributed to aliphatic ether and C–H vibrational transitions from the bound solvent molecules, the broad band around 1800 cm⁻¹ may be assigned to Al–H vibrational transitions. The peak shoulders in the Al–H bands indicate that there are H-atoms in different binding states.

Comparison of the three Al-H bands (see Fig. 4b) indicates a plain shift of the peak values in the order of

$$\nu_{Al-H}(Mg(AlH_4)_2 \cdot 4THF) < \nu_{Al-H}(Mg(AlH_4)_2 \cdot Et_2O)$$

$$< \nu_{Al-H}(Mg(AlH_4)_2).$$

This shift can be explained by an increasing covalent character of the Al–H bonds in the compounds. Indeed, there is an increasing number of bridging H-atoms in the THF adduct (two bridging H-atoms per molecule) and the diethyl ether adduct (five bridging H-atoms), leading to stronger terminal Al–H bonds. Furthermore, samples taken in advanced stages of the drying procedure exhibited a ν_{Al-H} peak shift towards higher wavenumbers up to the peak value of Mg(AlH₄)₂, which is similar to the observations of Ashby et al. [14].

If the shift is caused by a further bridging of H-atoms in the structure, the structural changes in connection with the transformation of Mg(AlH₄)₂·Et₂O into Mg(AlH₄)₂ might be explained as follows: the release of a diethyl ether molecule leads to a free position in the octahedral coordination sphere of a Mg atom. The freed position may be occupied by an unbridged H atom of a μ_2 bridging AlH₄



Fig. 4. (a) FTIR spectra of magnesium alanate and the two solvent adducts, (b) region of the Al-H vibrational transitions.

tetrahedron of a neighboring alanate ribbon in the crystal. When this happens with every ether position, the transformation may result in a sheet structure of the magnesium alanate with six bridging H atoms per molecular unit. However, this remains to be proved by further investigations.

4. Conclusion and outlook

A synthesis and purification method for $Mg(AlH_4)_2$ was presented which is based on a metathesis reaction of NaAlH₄ and MgCl₂ in diethyl ether. The purification was done by Soxhlet extraction leading to the ether adduct of Mg(AlH₄)₂ with a yield of 81.5%. After removal of the solvent, the magnesium alanate was obtained with about 95% purity, with traces of organics and NaCl. Thermogravimetric investigations of the compound showed that the peak decomposition temperature was 175 °C.

Crystal structures were determined for the solvent adducts $Mg(AlH_4)_2 \cdot 4THF$ and $Mg(AlH_4)_2 \cdot Et_2O$. A direct determination of the structure of $Mg(AlH_4)_2$ was not possible, because no single crystals could be obtained from the substance. An analysis of the signals of a powder X-ray diffraction pattern showed that the crystallites were in the range of 30 nm which supports the assumption that the structure breaks when the solvent is released.

An interpretation of FTIR measurements led to a first hypothesis that starting from the ether adduct, a removal of the solvent molecules allows a progressive connection of the ether adduct ribbons which would result in a sheet structure of Mg(AlH₄)₂.

Further work will concentrate on the crystal structure of magnesium alanate as well as on its thermal and reversible properties for hydrogen storage.

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