

Synthesis and Properties of Calcium Alanate and Two Solvent Adducts

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Several ways to synthesize solvated and desolvated calcium tetrahydroaluminate by wet-chemical and mechanochemical methods are presented. The products were characterized by elemental analysis, X-ray diffraction (XRD), and infrared spectroscopy (FTIR). The crystal structure of $\text{Ca}(\text{AlH}_4)_2 \cdot 4\text{THF}$ was determined. After desolvation, an ultrafine powder was obtained. IR data and the mass balance suggest a compound with the composition $\text{Ca}(\text{AlH}_4)_2$, containing tetrahedral $[\text{AlH}_4]$ groups.

1. Introduction

Complex aluminum hydrides have been considered promising materials for reversible hydrogen storage, since it was found that transition-metal dopants can considerably lower kinetic barriers for both hydrogen absorption and desorption.¹ Of the light representatives of alkaline-earth-metal tetrahydroaluminates, or alanates, magnesium tetrahydroaluminate was investigated recently with respect to hydrogen storage purposes, and its structure was determined.^{2,3} However, little is known about calcium tetrahydroaluminate, which contains 7.9 wt % hydrogen and has not yet been investigated as a material for hydrogen storage.

The compound was first synthesized by Schwab and Wintersberger⁴ by the following route in tetrahydrofuran (THF) as solvent:



The purified and dried product contained 40% calcium tetrahydroaluminate, the rest being THF. It was not possible to desolvate the material without decomposing the tetrahydroaluminate.

Finholt⁵ et al. reported a similar synthesis procedure in dimethyl ether, but with a ratio of 1.3 mol of CaH_2 to 3 mol of AlCl_3 . After 8 days of reaction, the product was extracted

with THF. From the elemental composition, the formula $\text{Ca}(\text{AlH}_4)_2 \cdot \text{THF}$ was proposed. However, the yield varied considerably, and the results were “erratic” according to the authors.

In a later work, the compound was synthesized by adding 10 mol of CaH_2 to 1 mol of AlCl_3 in a mixture of 75% THF and 25% diethylene glycol dimethyl ether,⁶ with stirring under reflux. Catalytic amounts of LiAlH_4 and a trace of iodine were added to increase the reaction rate. The tetrahydroaluminate formed was kept in solution and used as a reducing agent. No attempt was made to isolate the compound.

Maltseva⁷ et al. described the formation of calcium tetrahydroaluminate by reaction 1 in a ball mill and measured the desorption of hydrogen from milled and unmilled mixtures in various compositions. No attempt was made to isolate the tetrahydroaluminate from the calcium chloride.

Robinson⁸ described the preparation of calcium tetrahydroaluminate by a metathetical reaction involving CaCl_2 and NaAlH_4 . However, the properties of the product were not reported.

In this work, several methods to synthesize solvated and desolvated calcium tetrahydroaluminate by wet-chemical, mechanically assisted, and mechanochemical processes shall be presented. The products were characterized by elemental analysis, single-crystal and powder X-ray diffraction, and infrared spectroscopy.

2. Experimental Section

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

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to use. Solids were handled in an argon-filled glovebox equipped with a recirculation and regeneration system. Both the water and oxygen concentrations were kept below 1 ppm during operation.

2.1. Reagents. Tetrahydrofuran (THF) and diethyl ether (DEE) (both p.a., Merck) were distilled over sodium before use. Pure sodium tetrahydroaluminate was obtained from an industrial product (purity >95%, Albemarle Corp.) by Soxhlet extraction with THF. The solvent was drawn off the extract until a residual pressure of 2×10^{-3} mbar was reached, and a dry white powder was obtained. According to XRD measurements, the material was phase-pure. The hydrogen content determined by elemental analysis was 7.5 ± 0.1 wt % (theoretical 7.6 wt % H), and the C content amounted to 0.2 wt %. Calcium chloride (98%, Sigma-Aldrich) was used as received.

2.2. Instrumentation and Analyses. Mechanically assisted chemical synthesis was accomplished in an inertized 500 mL flat flange vessel, which was used as a glass ball mill reactor. A PTFE stirrer was used to move 20 glass balls (diameter 10 mm). The typical rotation speed was 150 rpm.

High-energy ball milling was performed by a Fritsch P6 planetary mill at 600 rpm using an 80 mL silicon nitride vial and balls. The vial was filled and sealed in the glovebox. Typical milling times were 4 h. Every 15 min, the ball mill was stopped for 5 min, and the rotation direction was reversed in the subsequent cycle.

Elemental analysis of carbon and hydrogen was done with a CE Instruments Flash EA 1112 series analyzer using helium as the purge gas. The powder samples were wrapped in tin capsules in the glovebox and stored in gastight containers until weighing and measuring, which took place immediately after sample preparation. The typical amount of a sample was 4–6 mg. For calibration, benzoic acid and purified LiAlH_4 were used as standards. Control measurements were made before and after the tetrahydroaluminate samples were measured.

Solid-state infrared spectra of the tetrahydroaluminates (as KBr pellets) were recorded in the range of $4000\text{--}370$ cm^{-1} under a nitrogen atmosphere and ambient conditions by using a Perkin-Elmer Spectrum GX FTIR spectrometer. The evaluation was done with the Perkin-Elmer Spectrum v. 2.00 software.

X-ray fluorescence analysis was performed by means of a wavelength-dispersive Siemens SRS 3000 spectrometer. The tetrahydroaluminate samples were slowly oxidized in air to obtain an oxidic matrix before the measurements. Evaluation was done with the SemiQuant software package from SpectraChem Analytical.

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, a Mo $\text{K}\alpha$ radiation source, and an Oxford Cryostream LT at 200 K) to avoid any oxidation or exposure to moisture. The determination of the unit cell and the solution and refinement of the crystal structure were performed using the SHELXL97 software.

Powder X-ray diffraction patterns were obtained with a Philips X'PERT diffractometer (Cu $\text{K}\alpha$ radiation, 2 kW, with an X'Celerator RTMS detector, automatic divergence slit). The powder was measured on a Si single crystal and sealed in the glovebox by an airtight hood made of Kapton foil, the foil being mounted out of the focus of the spectrometer. The software for data acquisition and evaluation was X'PERT 1.3e and ProFit 1.0c. PowderCell Vers. 2.4 was used to calculate the powder diffraction pattern of $\text{Ca}(\text{AlH}_4)_2 \cdot 4\text{THF}$ from the single-crystal data.

CCDC 256633 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and Discussion

All syntheses of calcium tetrahydroaluminate were based on the same metathesis reaction:



Various procedures based on wet-chemical, mechanically assisted, and mechanical synthesis were used to prepare solvated and solvent-free calcium tetrahydroaluminate.

3.1. Synthesis Procedures. 3.1.1. Wet-Chemical Synthesis. The reaction was performed in DEE as solvent in a first attempt, with stirring under reflux, as had been described earlier for the synthesis of $\text{Mg}(\text{AlH}_4)_2$.⁹ However, after 4 days, no formation of a product was observed.

THF was used as solvent in a second attempt. In this case, a conversion was observed after 4 days. According to XRD analysis of the product, it still contained fair amounts of residual NaAlH_4 , which had not been converted. As the sodium tetrahydroaluminate possesses a solubility similar to that of the desired product, it could not be separated to a satisfactory extent.

Further attempts were aimed at driving the reaction to completion to avoid separation of NaAlH_4 from the calcium tetrahydroaluminate.

3.1.2. Mechanically Assisted Synthesis. Synthesis was performed in a glass ball mill reactor to create fresh particle surfaces during the reaction. Additionally, THF was used as a solvent with a high dissolution capacity for NaAlH_4 .

A 0.1 mol sample of CaCl_2 (11.33 g) and 0.2 mol of NaAlH_4 (10.9 g) were dispersed in 400 mL of THF, and the mixture was heated under reflux. During the reaction, the gray solid precipitate was milled by the glass balls. After 16 h of stirring and reflux, the precipitate was allowed to settle, the clear solution was drawn off, and the solvent was partly evaporated under vacuum until colorless crystals were formed. The crystals were allowed to grow overnight. Some of them were taken for single-crystal X-ray diffraction measurements. The yield was 24.3 g. This high value was due to the formation of a solvent adduct, which had also been reported earlier.^{4,5} In consideration of the fact that $\text{Ca}(\text{AlH}_4)_2 \cdot 4\text{THF}$ (molar mass 288.4 g/mol) was produced (see below), the yield was 84%.

Once produced, the crystals were not stable under ambient conditions. After 3 months of storage under argon in the glovebox, the formerly clear crystals had changed into an opaque white powder. According to elemental analysis, its content was then 39.9% C and 9.7% H, which is close to the theoretical composition of $\text{Ca}(\text{AlH}_4)_2 \cdot 2\text{THF}$ (39.1% C, 9.8% H).

The solvent could be removed almost completely from a freshly prepared product under vacuum (1×10^{-3} mbar) 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

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was kept for 4 h. According to elemental analysis, the product contained 7.1 ± 0.1 wt % H and 0.7 ± 0.3 wt % C (theoretical 7.9 wt % H).

Heating at 110 °C led to a partial decomposition of the tetrahydroaluminate, which was indicated by an increasingly gray color of the product and a growing Al signal in the XRD pattern.

3.1.3. Mechanical Synthesis. The observations made during the wet-chemical and mechanically assisted experiments led to the conclusion that the formation of fresh surfaces is necessary to obtain full conversion at a satisfactory reaction rate. As a consequence, the reaction was performed in a planetary ball mill under inert conditions.

a. With DEE. A 2.27 g sample of CaCl_2 (20 mmol) and 2.18 g of NaAlH_4 (40 mmol), together with 5 mL of DEE and 10 silicon nitride balls with a total weight of 42 g, were filled into the milling vial and sealed under an argon atmosphere (ball-to-powder ratio 10:1). The mixture was milled for 14 cycles, each cycle consisting of 15 min ball milling at 600 rpm and a subsequent intermission of 5 min. The direction of rotation was reversed after each cycle. A light gray powder was obtained as the reaction product. It was extracted for 12–16 h using a Soxhlet apparatus with DEE as solvent.

To remove the solvent, a drying procedure was used similar to the one described in section 3.1.2. After the final temperature was kept at 90 °C for 2 h, the product was obtained as a fine white powder. The yield was about 45%, relating to $\text{Ca}(\text{AlH}_4)_2$, and increased with longer extraction times.

According to XRF analysis, the dried product oxidized in air contained 17.9% Ca, 35.1% Al, 3.4% Cl, 4.3% Na, and 0.2% Si. Calculation was based on an oxidic matrix. Hence, the Al:Ca ratio was 1.96.

b. With THF. The same synthesis procedure was used as described in section a, except for the solvent, which was THF in this case. The product was a dry white, voluminous powder. Soxhlet extraction with THF as solvent was applied to separate the tetrahydroaluminate from the byproduct NaCl. Due to the good solubility of the THF adduct obtained, however, it is also possible to digest the raw product with warm THF and separate the dissolved tetrahydroaluminate by filtering. The solvent was removed using the drying procedure described in section 3.1.2. After drying, the yield was 70%, relating to $\text{Ca}(\text{AlH}_4)_2$.

The results of the XRF analysis revealed that the dried and oxidized product contained 17.1% Ca, 34.6% Al, 4.5% Cl, 4.9% Na, and 0.3% Si. Calculation was based on an oxidic matrix. The Al:Ca ratio was 2.03.

c. Without Solvent. The same procedure was used as described in section a, except that no solvent was added. The product was a light gray powder and represented a mixture of NaCl and calcium tetrahydroaluminate according to XRD data. Again, the tetrahydroaluminate was separated from the chloride by Soxhlet extraction (12–16 h) using THF as solvent. During extraction, which was slow, the solvent adduct was formed. Hence, the calcium tetrahydroaluminate could not be separated in a solvent-free form. Once obtained,

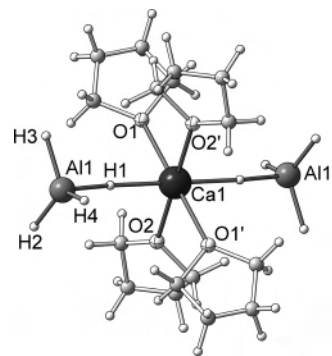


Figure 1. Molecular structure of $\text{Ca}(\text{AlH}_4)_2 \cdot 4\text{THF}$.

Table 1. Crystal Data, X-ray Collection, and Structure Refinement of $\text{Ca}(\text{AlH}_4)_2 \cdot 4\text{THF}$

cryst syst	monoclinic
space group	$P2_1/n$
cell constants	
a (Å)	8.267(2)
b (Å)	10.477(2)
c (Å)	14.677(3)
β (deg)	91.57(3)
cell vol (Å ³)	1270.7(4)
no. of formula units per cell	2
color	colorless
composition	$\text{C}_{16}\text{H}_{40}\text{Al}_2\text{CaO}_4$
molar weight	390.52
$F(000)$	428
density(calcd) (g cm ⁻³)	1.021
temp (K)	230
abs coeff, μ (mm ⁻¹)	0.328
2θ range (deg)	5.6–52.1
scan type	W
no. of data collected	4130
no. of unique data, R_{INT}	2292, 0.0312
no. of obsd data with $F \geq 4\sigma(F)$	1180
no. of params	131
R1 (for $F \geq 4\sigma(F)$), R1 (all data)	0.0917, 0.1219
wR2 (for $F \geq 4\sigma(F)$), wR2 (all data)	0.2838, 0.3156
GOF	1.150
largest difference peak, hole (e Å ⁻³)	0.314, -0.274
CCDC registration number	256633

the solvent could be removed from the adduct using the drying procedures described above.

XRF analysis yielded 17.7% Ca, 34.8% Al, 3.2% Cl, 4.0% Na, and 0.2% Si. Calculation was based on an oxidic matrix. The Al:Ca ratio was 1.97.

3.2. Structure of $\text{Ca}(\text{AlH}_4)_2 \cdot 4\text{THF}$. From the reaction mixture produced by mechanically assisted synthesis (section 3.1.2), crystals were obtained in the form of colorless bars. The compound $\text{Ca}(\text{AlH}_4)_2 \cdot 4\text{THF}$ crystallized in the monoclinic space group $P2_1/n$ with two formula units per unit cell ($a = 8.267$ Å, $b = 10.477$ Å, $c = 14.677$ Å, $\beta = 91.57^\circ$). The crystallographic data are summarized in Table 1.

The molecular structure of $\text{Ca}(\text{AlH}_4)_2 \cdot 4\text{THF}$ (see Figure 1) is similar to that of the corresponding magnesium compound $\text{Mg}(\text{AlH}_4)_2 \cdot 4\text{THF}$.^{9,10} It consists of a central calcium ion occupying a crystallographic inversion center which is octahedrally coordinated by two hydrogen atoms of two $[\text{AlH}_4]$ units and four oxygen atoms from four THF molecules. The carbon atoms of these THF molecules are highly disordered, even at low temperatures. Those belonging

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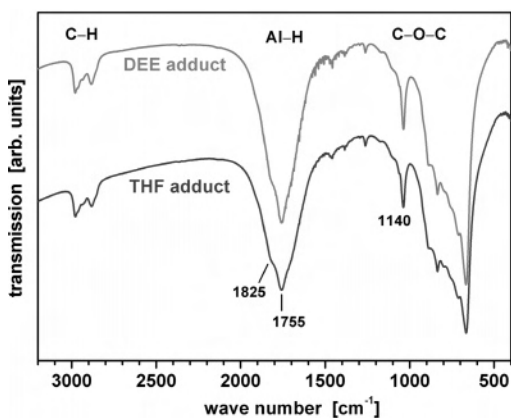


Figure 2. FTIR spectra of the DEE and THF adducts of calcium tetrahydroaluminate.

to O1 were split over two positions; those belonging to O2 were split over three different positions. The bridging hydrogen atom H1 was refined without restraints (Ca1–H1, 1.92 pm; Al1–H1, 1.65 pm). The positions of the atoms H2, H3, and H4 were fixed by bonding parameters, assuming that the tetrahedral AlH_4 units in $\text{Ca}(\text{AlH}_4)_2 \cdot 4\text{THF}$ are similar to those in $\text{Mg}(\text{AlH}_4)_2 \cdot 4\text{THF}$.

Several crystals were investigated by single-crystal X-ray analysis, but all of them exhibited very low refraction intensities, which is consistent with the powder diffraction data discussed in section 3.4 and with the fact that the C atoms of the THF molecules were disordered. Only for Al, Ca, and O no disorder was found. Hence, the final structure parameters were only poor ($R1 = 0.0917$, $wR2 = 0.2838$).

3.3. Infrared Spectroscopy. FTIR spectra were taken from the products produced by mechanically assisted and mechanical synthesis. Figure 2 shows two solid-state IR spectra of DEE and THF solvated products. In addition to the fingerprint region, strong bands appear for the solvent adducts in the regions around 1000–1200, 1600–2000, and 2850–3050 cm^{-1} . Whereas the first and the last bands can be attributed to aliphatic ether and C–H vibrational transitions from the solvent molecules, the broad band around 1800 cm^{-1} is assigned to Al–H vibrations. Peak shoulders in the Al–H bands indicate that there are H atoms in different binding states.

The data suggest that the raw product synthesized by ball milling in the presence of THF already had the same molecular configuration as the product dissolved in THF and recrystallized. Comparison of the Al–H bands of samples prepared by mechanical synthesis with THF and DEE (according to sections 3.1.3.a and 3.1.3.b) reveals a shift of the main peak to higher wavenumbers when the substance is dried; see Figure 3b) and Table 2.

Main contributions to the Al–H vibrational transition are found at 1755 and 1830 cm^{-1} , with a shoulder around 1900 cm^{-1} . The position of the signals indicates the presence of $[\text{AlH}_4]$ tetrahedra in the structure, as the absorption maximum of the octahedral $[\text{AlH}_6]$ group in Na_3AlH_6 , prepared by thermal decomposition of NaAlH_4 , is at lower wavenumbers (1435 cm^{-1}). The shape of the signal of the THF adduct remained up to a state where the material was dried for 30

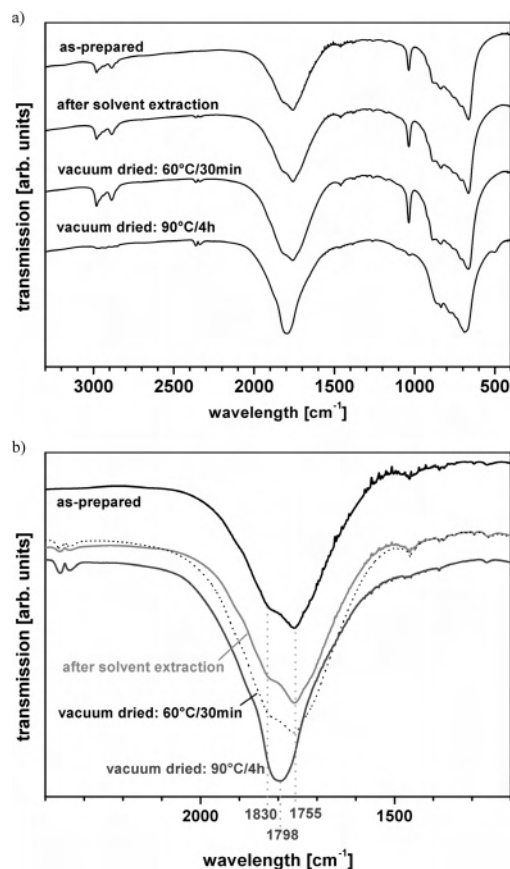


Figure 3. FTIR spectra of $\text{Ca}(\text{AlH}_4)_2 \cdot 4\text{THF}$ during the drying procedure: (a) overview, (b) region of the Al–H vibrational transition.

Table 2. Fundamental Frequencies (cm^{-1}) of the AlH_4 Group in Calcium Tetrahydroaluminate, Magnesium Tetrahydroaluminate, and Sodium Tetrahydroaluminate

M =	Ca	M = Mg	M = Na
$\text{M}(\text{AlH}_4)_2 \cdot 4\text{THF}$	1755	1731	
$\text{M}(\text{AlH}_4)_2 \cdot \text{DEE}$	1755	1795	
$\text{M}(\text{AlH}_4)_2$	1798	1835	1675

min at 60 °C. At higher drying temperatures, both contributions disappeared at the expense of a single peak at 1798 cm^{-1} and a minor contribution around 1650 cm^{-1} . Such a shift can be explained by a change in the covalent character of the Al–H bonds in the material, e.g., by the formation of H bridges.¹¹ This was also found in the case of magnesium tetrahydroaluminate,⁹ where a $\text{Mg}(\text{AlH}_4)_2$ sheet structure developed from the THF adduct when the solvent was released.

In the case of magnesium tetrahydroaluminate, the differences in the binding situation of the AlH_4 group of the THF adduct (1 bridging H atom, 3 terminal H atoms), the DEE adduct (2.5 bridging H atoms, 1.5 terminal H atoms), and the $\text{Mg}(\text{AlH}_4)_2$ itself (3 bridging H atoms, 1 terminal H atom) were clearly reflected in the spectra. In contrast, both the DEE and THF adducts of the calcium tetrahydroaluminate exhibit a similar absorption spectrum, which suggests that both compounds have a similar structure.

The shoulder at 1600–1700 cm^{-1} of the dry calcium tetrahydroaluminate coincides with the region of the Al–H

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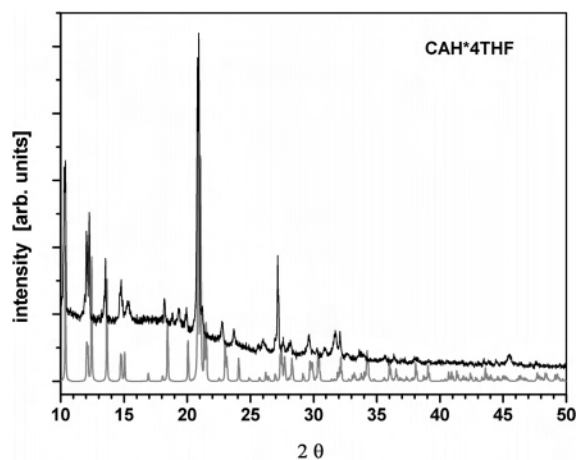


Figure 4. Observed (upper) and calculated (lower) X-ray powder diffraction pattern of $\text{Ca}(\text{AlH}_4)_2 \cdot 4\text{THF}$.

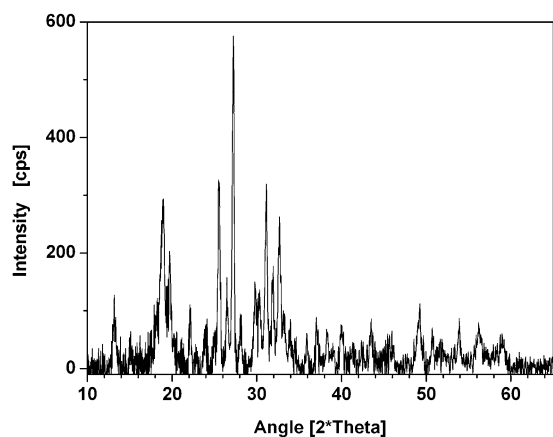


Figure 5. Background-subtracted X-ray powder diffraction pattern of $\text{Ca}(\text{AlH}_4)_2$.

stretching vibration of pure NaAlH_4 . However, no detectable amount of sodium tetrahydroaluminate could be found in DSC measurements, and the elemental composition and mass balance of the different samples also did not indicate any NaAlH_4 .

3.4. Powder X-ray Diffraction. Powder X-ray measurements of samples indicated a poor crystallinity of the product in any stage of the synthesis procedure. The main reflections of an as-prepared sample according to section 3.1.3.b were only weak and originated from NaCl and the tetrahydroaluminate having a crystallite size in the range of 50–80 nm, which was estimated from the fwhm values using the Scherrer formula. The remaining material was supposed to be either in an amorphous state or in the form of crystallites with sizes in the lower nanometer range.

Once separated from the byproduct NaCl , $\text{Ca}(\text{AlH}_4)_2 \cdot 4\text{THF}$ decomposed slowly under the X-ray beam at room temperature, leading to a broadening and decreasing intensities of the reflections. Hence, measurements were performed with exposure times of not longer than 15 min. An experimental X-ray pattern of the solvate is compared with a powder pattern calculated on the basis of the single-crystal data in Figure 4.

Figure 5 shows an experimental pattern of dry $\text{Ca}(\text{AlH}_4)_2$. The pattern of the product looks similar irrespective of the

Table 3. Powder Diffraction Pattern of $\text{Ca}(\text{AlH}_4)_2$ Prepared by Mechanically Assisted Synthesis (Section 3.1.2), Including d Spacing, 2θ Values (for $\text{Cu K}\alpha$ Radiation), and Relative Signal Intensities

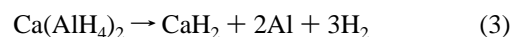
d (Å)	$I(\text{rel})$	2θ (deg)	d (Å)	$I(\text{rel})$	2θ (deg)
4.53	5	9.78	1.24	11	38.35
3.38	18	13.17	1.22	5	39.07
2.97	6	15.06	1.2	11	40.04
2.37	43	18.95	1.17	5	41.37
2.28	30	19.73	1.14	4	42.43
2.04	15	22.14	1.12	12	43.48
1.9	9	23.88	1.09	5	45.20
1.82	8	24.99	1.07	6	45.90
1.78	53	25.58	1.02	17	49.23
1.73	21	26.51	1.0	9	50.76
1.68	100	27.26	0.98	5	51.67
1.64	12	28.12	0.95	13	53.91
1.55	25	29.84	0.93	12	56.26
1.53	22	30.34	0.9	8	59.04
1.49	53	31.14	0.85	2	65.64
1.46	28	31.92	0.84	2	67.07
1.43	42	32.69	0.83	3	69.06
1.4	14	33.29	0.81	3	71.22
1.38	11	33.93	0.81	3	72.85
1.36	6	34.57	0.79	3	77.05
1.31	8	35.95	0.78	1	79.16
1.28	11	37.06			

synthesis method. However, the absolute intensities and line widths vary depending on the method and from batch to batch. A list of the reflections and their relative intensities is given in Table 3.

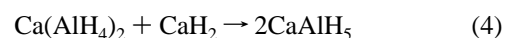
4. Discussion

The results show that the DEE and THF adducts of calcium tetrahydroaluminate can be prepared by ball milling under inert conditions or by mechanically assisted wet-chemical synthesis. For each process, the same metathesis reaction 2 can be applied. After separation from the byproduct by digestion or Soxhlet extraction, the organic solvent can be removed almost completely in a drying procedure under vacuum at elevated temperatures. Thus, gram amounts of calcium tetrahydroaluminate with a purity of >90% are obtained.

Of the alkaline-earth-metal tetrahydroaluminates, the lighter $\text{Mg}(\text{AlH}_4)_2$ exhibits a sheet structure consisting of octahedrally coordinated Mg atoms interconnected by tetrahedral $[\text{AlH}_4]$ groups.³ BaAlH_5 as the next heavier compound after calcium tetrahydroaluminate contains one-dimensional zigzag chains of distorted $[\text{AlH}_6]$ octahedra.¹² $\text{Sr}_2\text{Al}_7\text{H}_{14}$ structurally contains edge-sharing $[\text{DSr}_4]$ tetrahedra as well as isolated $[\text{AlH}_6]$ octahedra.¹³ In the case of calcium tetrahydroaluminate, IR data and the mass balance, including the impurities, such as NaCl and residual organic solvent, suggest a compound with the composition of $\text{Ca}(\text{AlH}_4)_2$ similar to $\text{Mg}(\text{AlH}_4)_2$. The IR data did not indicate any formation of a hexahydride or pentahydride structure. Moreover, a partial decomposition would be required for the formation of a pentahydride from the isolated $\text{Ca}(\text{AlH}_4)_2 \cdot 4\text{THF}$ according to



and



In this case, the formation of Al should be detectable, for example, by a gray coloring of the sample and Al signals in the X-ray pattern, which, however, were not observed.

Both the single-crystal data of $\text{Ca}(\text{AlH}_4)_2 \cdot 4\text{THF}$ and the powder X-ray data of $\text{Ca}(\text{AlH}_4)_2$ show a material with a high disorder in the lattice, which is not observed with the lighter and heavier homologues of the tetrahydroaluminate. As the crystalline THF adduct decomposes into an ultrafine powder upon drying, the structure is not accessible by single-crystal

methods. Hence, determination of the structure remains a challenge. To learn more about the local ordering, theoretical studies and neutron diffraction measurements will be carried out.

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