DOI: 10.1002/ejic.201000119

Mixed-Anion and Mixed-Cation Borohydride $KZn(BH_4)Cl_2$: Synthesis, Structure and Thermal Decomposition

Dorthe B. Ravnsbæk,[a] Lise H. Sørensen,[a] Yaroslav Filinchuk,[a,b] Daniel Reed,[c] David Book,[c] Hans J. Jakobsen,[a] Flemming Besenbacher,[d] Jørgen Skibsted,[a] and Torben R. Jensen*[a]

Keywords: Hydrides / X-ray diffraction / Solid-state structures / Solid-phase synthesis / Transition metals

$KZn(BH_4)Cl_2$, synthesized for the first time, contains a heteroleptic complex anion $[Zn(BH_4)Cl_2]^-$, extending the structural diversity of metal borohydrides. In-situ synchrotron powder diffraction, NMR and Raman spectroscopy were used to characterize $KZn(BH_4)Cl_2$ and to evaluate the mechanism for its thermal decomposition. The title compound decomposes at a significantly lower temperature than KBH_4 and may be used for inspiration for the design of novel hydrogen storage materials. Combining different ligands in modified metal borohydrides is proposed as a way to adjust stability with respect to hydrogen desorption.

Introduction

The increasing demand for clean energy and the negative environmental influence caused by the present carbon-based fossil fuels make the development and utilization of clean and sustainable energy a compelling challenge for the future. Hydrogen has been suggested as a future carrier of renewable energy; however, a safe, compact and efficient hydrogen-storage method still remains to be identified.[1] Borohydride-based materials currently receive great interest as potential hydrogen-storage systems due to their high gravimetric hydrogen densities. Unfortunately, many of the well-known borohydrides, such as $LiBH_4$, $NaBH_4$ and KBH_4, exhibit poor thermodynamic and kinetic properties, which hamper their utilization in technological applications.[2,3] Thermodynamic and kinetic properties have successfully been improved by the formation of reactive hydride composites, such as $2LiBH_4/MgH_2$, whose enthalpy of decomposition is reduced, whilst they are still capable of storing hydrogen reversibly.[4,5] Recently, a mixed-cation borohydride, $LiK(BH_4)_2$, was prepared and characterized. It structurally resembles $LiBH_4$ and possesses high thermodynamic stability comparable to the average of the two compounds, $LiBH_4$ and KBH_4.[6] Other examples of mixed-cation borohydrides are $MZn_2(BH_4)_5$ and $MSc(BH_4)_4$ (M = Li or Na), which consist of isolated $[Zn_2(BH_4)_5]^-$ and $[Sc(BH_4)_4]^-$ units, respectively, counterbalanced by M^+ cations.[7–10] Partial anion substitution was recently demonstrated by the preparation of $Li(BH_4)_{1-x}Cl_x$.[11,12]

Here, we present the synthesis, crystal structure, MAS NMR spectroscopic data and an investigation of the thermal decomposition for a novel compound, $KZn(BH_4)Cl_2$ (**1**), which is the first report on a mixed-anion and mixed-cation borohydride. The decomposition temperature for $KZn(BH_4)Cl_2$ is found to be significantly lower than that for KBH_4, hence this study provides inspiration for the design and preparation of novel materials, which may be suitable for hydrogen storage applications. Furthermore, two other new borohydrides, **2** and **3**, are identified.

Results and Discussion

Compound **1** was synthesized by a mechano-chemical method, that is, ball milling, which is a commonly used method for the preparation of borohydride-based hydrogen-storage materials. Usually, metathesis reactions occur in mixtures of metal borohydride and metal halide, but this study reveals a less common addition reaction [Equation (1)].

$$KBH_4 + ZnCl_2 \rightarrow KZn(BH_4)Cl_2 \qquad (1)$$

The high degree of crystallinity of the synthesized compound allows detailed diffraction studies of the crystal structure and of the chemical reactions occurring during synthesis and decomposition.

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[a] Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University,
Langelandsgade 140, 8000 Aarhus C, Denmark
Fax: +45-8619-6199
E-mail: trj@chem.au.dk
[b] Swiss-Norwegian Beam Lines at ESRF,
B. P. 220, 38043 Grenoble, France
[c] School of Metallurgy and Materials, The University of Birmingham,
Edgbaston, Birmingham, B15 2TT, UK
[d] Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, Aarhus University,
8000 Aarhus C, Denmark

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201000119.

The monoclinic structure ($P2_1/m$) of $KZn(BH_4)Cl_2$ was solved and refined from synchrotron radiation powder X-ray diffraction (SR-PXD) data measured on an almost pure sample of the title compound (Figure 1). The new structure of **1** consists of isolated $[Zn(BH_4)Cl_2]^-$ anions and octacoordinated K^+ cations, associated with the anions by weak K–Cl and K–BH_4 interactions (Figure 2). One Zn^{2+}, one K^+, two Cl^- and one BH_4^- ion are all located on the mirror plane. The Zn^{2+} ion has a trigonal-planar environment by two Cl^- and one BH_4^- ion, the latter acting as an η^2 ligand. The low coordination number for Zn explains the short Zn–B and Zn–H bond lengths [Zn–B 2.162(11), Zn–H 1.78(3) Å; Table 1]. The K^+ ion has a somewhat unusual coordination, forming a distorted square antiprism by five Cl^- and three BH_4^- ions, which are acting as η^2 ligands. The K–Cl [3.159(14)–3.66(2) Å] and K–B [3.274(13)–3.781(10) Å] distances in **1** are slightly longer than in KCl [3.130(2) Å[13]] and KBH_4 [3.364(11) Å[2]], where the K^+ ion has an octahedral environment by six BH_4^- ions. Significantly different bond lengths and coordination numbers for the Zn and K atoms allow us to describe **1** as $K[Zn(BH_4)Cl_2]$.

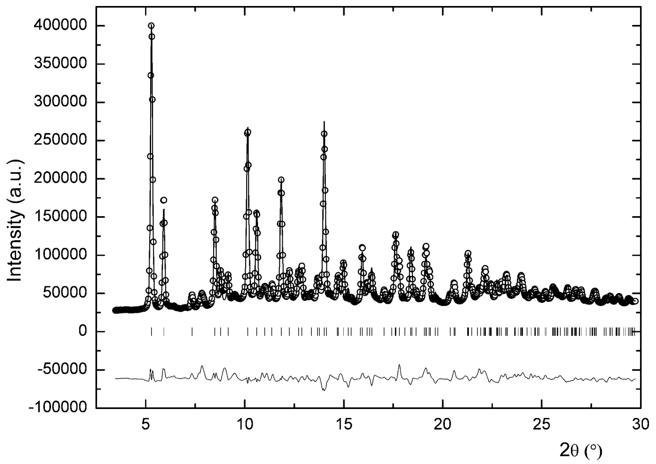

Figure 1. Rietveld refinement profile for $KZn(BH_4)Cl_2$ from SR-PXD data measured at BM01A, ESRF (λ = 0.703511 Å) at 82 °C on the ball-milled $KBH_4/ZnCl_2$ (1:1) sample.

The two Cl^- anions have different coordination: one is trigonal-planar with one Zn^{2+} and two K^+ ions, the other is tetrahedral with one Zn^{2+} and three K^+ ions in the nearest coordination sphere. The BH_4^- ion has a saddle-like coordination consisting of one Zn^{2+} and three K^+ ions. The two nearest neighbours (Zn^{2+} and K^+) define an almost linear Zn–BH_4–K coordination with an angle of 177.2(5)°, similar to the Mg–BH_4–Mg angle in the $Mg(BH_4)_2$ structures.[14–16] Hydrogen positions can be accurately obtained from X-ray powder diffraction for the light-element systems only, except some particular cases, e.g. when heavy atoms are in special positions.[16] In the presence of Zn, Cl and K atoms, H atoms in $KZn(BH_4)Cl_2$ are determined only tentatively. The BH_4^- ion is coordinated to Zn^{2+} via its tetrahedral edge (η^2 ligand), while the opposite edge is pointing towards K^+. Coordination of the BH_4^- anion via the edge is typical for metal borohydrides.[2] Thus, the orientation of the BH_4^- ion is determined here by the coordination via the short Zn–B and the long K–B contacts. Interestingly, the volume of the $KZn(BH_4)Cl_2$ formula unit (V/Z = 149.5 Å^3) is nearly equal to the sum of formula volumes for the reactants $ZnCl_2$ (V/Z = 74.3 Å^3)[17] and KBH_4 (V/Z = 76.2 Å^3).[2]

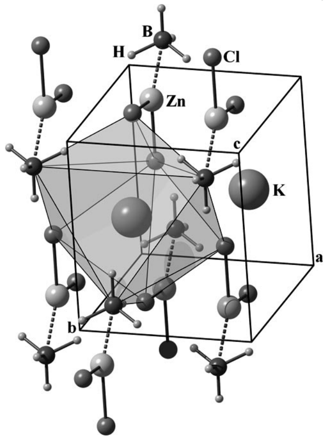

Figure 2. Crystal structure of $KZn(BH_4)Cl_2$. The complex $[Zn(BH_4)Cl_2]^-$ anions and eightfold coordination polyhedron for the K atom are highlighted.

Table 1. Selected interatomic distances in $KZn(BH_4)Cl_2$ at about 82 °C (for further details see Supporting Information, Table S2).

Atom 1	Atom 2	Distance [Å]
Zn	H	1.78(3)
Zn	B	2.162(11)
Zn	Cl	2.219(11)–2.338(13)
K	H	2.74(2)–2.84(2)
K	B	3.274(13)–3.781(10)
K	Cl	3.159(14)–3.665(16)
B	H	1.117(12)–1.13(3)

In the Raman spectrum for $KZn(BH_4)Cl_2$ measured at room temp. (Figure 3, b) the bidentate B–H$_{terminal}$ and B–H$_{bridge}$ stretching modes are observed at 2420, 2398 and 2144 cm^{-1}, respectively. Weaker bands are observed at 1401 and 1190 cm^{-1}, corresponding to the bidentate bridge stretching and BH_2 bending modes of the bridging hydrogen atoms, respectively.[18] From 400 to 100 cm^{-1}, several sharp bands are observed, suggesting well-defined lattice modes, which underlines the high degree of crystallinity of $KZn(BH_4)Cl_2$. The Raman spectroscopic data measured at –196 °C (Figure 3, a) in general exhibits the same features as the data measured at room temp., suggesting that no phase transition has occurred upon cooling. However, lowering of the temperature results in a decrease of the line widths of the Raman bands, hence several additional Raman shifts are resolved around the shift frequencies observed in the data measured at room temp. The Raman spectrum measured at 200 °C (Figure 3, c) shows no bands from vibration due to BH_4, suggesting that $KZn(BH_4)Cl_2$ is fully decomposed, which is in accordance with the TGA/DSC and in situ PXD measurements discussed later. The strong band at 290 cm^{-1} might be related to a Zn–Cl vibration of the tetrahedral $[ZnCl_4]^{2-}$ ion in K_2ZnCl_4, which is the main decomposition product.[19]

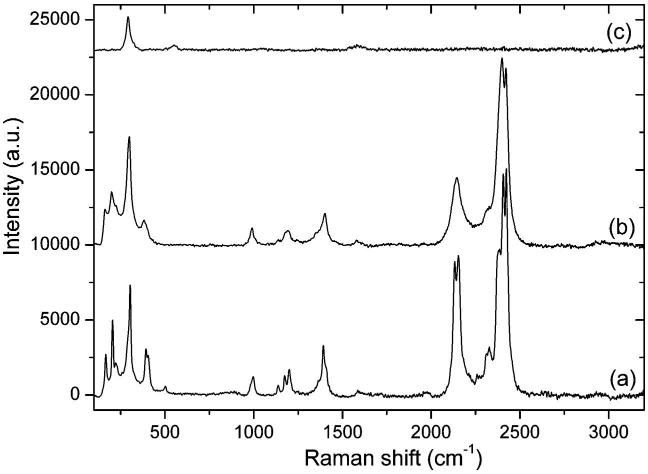

Figure 3. Raman spectrum for $KZn(BH_4)Cl_2$ measured at (a) –196 °C (liquid nitrogen), (b) room temp. and (c) 200 °C.

The ^{11}B MAS NMR spectrum of the central and satellite transitions for **1** (Figure 4, a) reveals a single centreband resonance and the corresponding manifold of spinning sidebands from the satellite transitions for the unique BH_4^- site in this compound. The least-squares optimization of simulated to experimental spinning sideband intensities[20] provides the isotropic chemical shift, $\delta_{iso}(^{11}B)$ = –43.6(2) ppm, and the quadrupole coupling parameters, C_Q = 0.648(15) MHz, η_Q = 0.51(2). The excellent agreement between the simulated and experimental ^{11}B MAS NMR spectra (Figure 4) demonstrates that $KZn(BH_4)Cl_2$ is present as a highly ordered phase. The isotropic chemical shift is observed at a frequency about 5 ppm lower than the corresponding resonance of KBH_4 [$\delta_{iso}(^{11}B)$ = –37.8(2) ppm], which may reflect the presence of Zn^{2+} ions in near coordination to the boron atoms in **1**.

The decomposition of $KZn(BH_4)Cl_2$ was investigated by in-situ SR-PXD (Figure 5). Diffraction from $KZn(BH_4)Cl_2$ is visible in the powder patterns up to about 110 °C, where the compound decomposes into an intermediate phase (denoted **2**), metallic Zn and K_2ZnCl_4. Phase **2** exists in a narrow temperature interval and also decomposes to zinc and K_2ZnCl_4 at about 130 °C. Hence the decomposition temperatures for **1** and **2** are significantly lower than that of KBH_4 (T_{dec} = 500 °C).[21] The intermediate phase **2** was indexed from the SR-PXD pattern, obtained at about 112 °C, in a monoclinic unit cell with cell parameters: a = 8.88, b = 23.74, c = 8.91 Å and β = 102.46°.

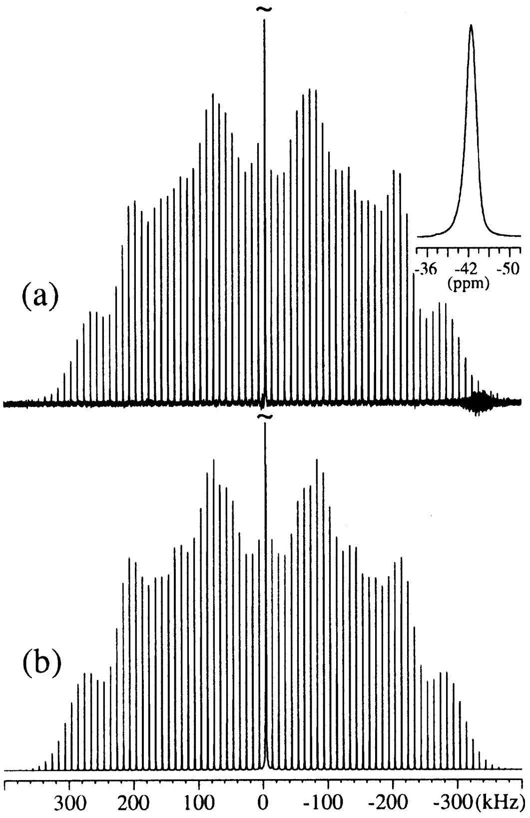

Figure 4. (a) ^{11}B MAS NMR spectrum (7.05 T) of the central (inset) and satellite transitions for $KZn(BH_4)Cl_2$ obtained with a spinning speed of 10.0 kHz and high-power ^1H decoupling. (b) Optimized simulation of the satellite transitions in (a), resulting in the isotropic chemical shift, $\delta_{iso}(^{11}B)$ = –43.6 ppm, and the quadrupole coupling parameters, C_Q = 0.648 MHz, η_Q = 0.51, for the unique ^{11}B site in $KZn(BH_4)Cl_2$.

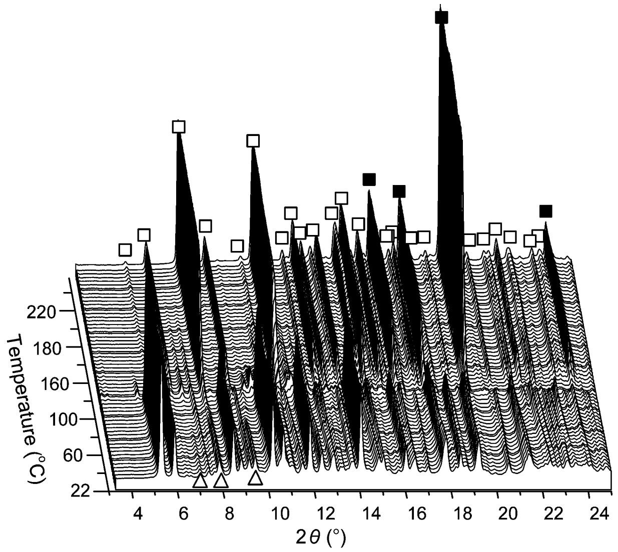

Figure 5. In-situ SR-PXD for the sample containing $KZn(BH_4)Cl_2$ measured at BM01A, ESRF (λ = 0.701135 Å) from room temp. to 200 °C, $\Delta T/\Delta t$ = 1 °C/min. Symbols: black squares: Zn; open squares: K_2ZnCl_4; triangles: unidentified phase; unmarked reflections at room temp. to about 110 °C are due to $KZn(BH_4)Cl_2$. At temperatures between approximately 110 and 130 °C, diffraction from the intermediate is observed.

Thermogravimetric analysis (TGA) confirms that **1** and **2** decompose in the temperature range from 110 to 160 °C (Supporting Information, Figure S1), giving an observed mass loss of 6.5 wt.-%. Because hydrogen represents only 2.1 wt.-% of $KZn(BH_4)Cl_2$, this indicates that some $(BH_3)_n$ gases are also lost during the decomposition. The calculated mass loss according to the reaction according to Equation (2) is 7.8 wt.-%.

$$2\ KZn(BH_4)Cl_2 \rightarrow K_2ZnCl_4 + Zn + 2/n\ (BH_3)_n + 2\ H_2 \qquad (2)$$

The loss of $(BH_3)_n$ gases indicates an irreversible character of the hydrogen release from **1** and **2**. Furthermore, we mention that ball-milled samples of KBH_4 and $ZnCl_2$ in higher molar ratios, i.e. 2:1, 3:1 and 4:1, have also been prepared and investigated. SR-PXD data for these samples reveal a diffraction pattern from another novel material (**3**), which is different from that of $KZn(BH_4)Cl_2$ and **2** (Supporting Information, Figure S3). The powder diffraction pattern of **3** differs from the one reported for the previously suggested $K_2Zn_3(BH_4)_8$ composition,[22] which has not been observed in this study. The samples milled at different $KBH_4/ZnCl_2$ ratios have also been investigated by ^{11}B MAS NMR spectroscopy, which reveals two boron-containing phases: KBH_4 [$\delta_{iso}(^{11}B) = -37.8$ ppm], and **3** [$\delta_{iso}(^{11}B) = -42.0$ ppm]. The shift towards lower frequency for **3** suggests that the BH_4^- ions are coordinated by Zn^{2+} ions. However, we have so far not been successful in solving the structure of **3**. Compound **3** appears to decompose in two steps between 120 and 350 °C, which is significantly lower than for KBH_4. This indicates that **3** may be another new zinc-based borohydride.

Conclusions

The first mixed-anion and mixed-cation borohydride, $KZn(BH_4)Cl_2$, has been synthesized and characterized along with two other new zinc-based borohydrides. The significant structural diversity of homoleptic (homoligand) complex anions, such as $[Sc(BH_4)_4]^-$, $[Zn_2(BH_4)_5]^-$, and $[Zn(BH_4)_3]_n^{n-}$, recently found in the mixed alkali and d-block metal borohydrides,[5,6,8,10] is complemented now by the first heteroleptic complex anion $[Zn(BH_4)Cl_2]^-$. Various modifications of the coordination sphere for the transition element is an additional factor enabling adjustment of the stability of similar heteroleptic structures. Thus, the addition of metal halides to borohydrides may open a route for the design and preparation of new hydrogen storage materials, potentially with improved thermodynamic and kinetic properties for hydrogen release and uptake.

Experimental Section

The samples were prepared from KBH_4 and $ZnCl_2$ mixed in the molar ratios 1:1, 2:1, 3:1 and 4:1. All samples were ball-milled under argon for 120 min by using a sample/ball ratio of approximately 1:35. The chemicals used were KBH_4 (≥90%, Aldrich) and $ZnCl_2$ (≥98%, Aldrich). All handling and manipulation of the chemicals were performed in an argon-filled glove box with a circulation purifier, $p(O_2, H_2O) < 0.1$ ppm.

All samples were initially investigated by powder X-ray diffraction with a Stoe diffractometer and a curved position sensitive detector [Ge(111) monochromator, Cu-$K_{\alpha 1}$, $\lambda = 1.54060$ Å and 0.4 mm glass capillaries sealed with glue used as sample holders]. Subsequently, synchrotron radiation powder X-ray diffraction (SR-PXD) data were collected at beamline BM01A at the European Synchrotron Radiation Facility, Grenoble, France by using an MAR345 detector, a calibrated wavelength of $\lambda = 0.701135$ Å and 0.5 mm glass capillaries as sample holders. The 2D SR-PXD data were integrated into 1D powder patterns. Diffraction peaks were indexed by Dicvol[23] in a primitive monoclinic cell. The structure was solved in the space group $P2_1$ by global optimization in direct space with the program FOX,[24] varying positions of one Zn^{2+}, one K^+, two Cl^- and one BH_4^- ion and using antibump restraints of 1.6–2.1 Å. Examination of the resulting structure by Platon[25] revealed higher crystallographic symmetry, e.g. space group $P2_1/m$. The final refinement was performed by the Rietveld method in $P2_1/m$ with the program Fullprof.[26] The background was described by linear interpolation between selected points. Because all atoms occupy special positions on the mirror plane, the refinement involved only few refined parameters. At room temperature the unit cell parameters are $a = 7.6257(9)$, $b = 5.7375(6)$, $c = 6.8786(9)$ Å, $\beta = 97.794(15)°$, $Z = 2$. The highest-quality data set was recorded at 82 °C, for which the refined structure is reported. The agreement factors are: R_{wp} (not corrected for background) = 6.60%, R_p (corrected for background) = 16.8%, R_{Bragg} = 11.2%.

Raman spectroscopic study was performed using a Renishaw InVia Reflex, using a 488 nm excitation laser, with a power of about 2 mW on the sample. An Instec HCS621V cell was used for inert sample transfer and measurement.

Solid-state ^{11}B MAS NMR spectra were recorded with Varian Unity-INOVA-300 (7.05 T) and -400 (9.39 T) spectrometers by using homebuilt X-[^1H] double-resonance MAS NMR probes for 5 mm o.d. rotors. The NMR experiments were performed at ambient temperatures by using air-tight end-capped zirconia rotors packed with the sample in an argon-filled glove box. The ^{11}B isotropic chemical shifts are in ppm relative to neat $F_3B{\cdot}O(CH_2CH_3)_2$. Simulations of the MAS NMR spectra were performed by using the STARS software package.[20]

Simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed, and the decomposition temperatures were measured as the onset temperatures observed by DSC [heating rate 10 °C/min, room temp. to 500 °C, helium flow: 50 mL/min (protective flow: 25 mL/min), corundum crucibles].

Supporting Information (see footnote on the first page of this article): Experimental details, crystallographic information, Raman spectrum, details on the thermal expansion of **1**, TGA/DSC curve and XRD pattern for the compound **3**.

Acknowledgments

The authors are grateful to the Swiss-Norwegian Beam Lines for the provision of in-house beam time. We are also grateful to Dr. Hans Hagemann, Department of Physical Chemistry, University of Geneva, for helpful discussions. We thank the Danish Council for Strategic Research via Centre for Energy Materials, CEM for funding, the Danish Natural Science Research Councils for funding to the Instrument Centre for Solid-State NMR Spectroscopy and DanScatt.

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Received: February 2, 2010