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Synthesis and structure determination of complex zinc hydrides Part 1: Dipotassiumtetrahydridozincate(II): $K_2[ZnH_4]$

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Abstract

K_2ZnH_4 and its deuteride were prepared by a solid state reaction between stoichiometric amounts of KH (KD) and Zn metal powders at 650 K and 80 bar hydrogen (deuterium) pressure, and characterized by X-ray and neutron powder diffraction. They crystallize with the orthorhombic β-K_2SO_4 structure type, space group $Pnma$ (No. 62), $Z = 4$, cell parameters $a = 7.7601(5)$, $b = 5.8636(4)$, $c = 10.2832(7)$ Å (hydride); $a = 7.7579(4)$, $b = 5.8631(3)$, $c = 10.2813(5)$ Å (deuteride). Zinc is tetrahedrally coordinated by deuterium with bond distances in the range of 1.632(4) to 1.665(4) Å and bond angles in the range 108.0° to 112.7°. K_2ZnD_4 decomposes in 1 bar D_2 at 580(10) K to KD and Zn.

Keywords: Zinc hydrides; Solid state reactions; Deuterium

1. Introduction

Complex metal hydrides based on alkali metals and group 1B or 2B elements have been synthesized so far only by wet chemistry methods, and none of them have been structurally characterized. In the system potassium–zinc–hydrogen, for example, three crystalline compounds have been reported: K_2ZnH_4, prepared by a reaction of KH with $Zn(sec-C_4H_9)_2$ [1], KZn_2H_5, obtained by reacting $KZn(CH_3)_2H$ or $KZn_2(CH_3)_4H$ with AlH_3 in THF [2], and $KZnH_3$, prepared by a reaction of $KZn(CH_3)_2H$ with $LiAlH_4$ in THF [2].

Partial structure information has been given only for K_2ZnH_4 for which infrared spectroscopy and X-ray powder diffraction data were considered [1] to be consistent with a tetragonal K_2NiF_4 type atom arrangement. Zinc in this arrangement would be octahedrally coordinated by bridging hydrogen ligands.

In the first paper of this series we report on the synthesis of $K_2[ZnH_4]$ by a solid state reaction. A full structure analysis by neutron diffraction shows that it crystallizes with the orthorhombic β-K_2SO_4 structure type in which zinc is tetrahedrally coordinated by terminal hydrogen ligands.

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2. Experimental details

2.1. Synthesis

In view of the extreme sensitivity of the samples to moisture and air, all manipulations were performed in an argon filled glove box. Colourless crystalline products were obtained by reacting KH (KD) with Zn powder (5N Ventron, − 200 mesh) in a 2:1 molar ratio at 650 K under 80 bar hydrogen (6N) or deuterium (2N8) pressure for four days. Higher temperatures favoured the irreversible formation of the intermetallic compound KZn_{13} [3]. Potassium hydride (deuteride) was prepared by reacting potassium (Alfa 98%) at 750 K and 100 bar pressure for 10 days in Ni crucibles coated with Mo foil.

No evidence for the previously reported [2] hydrides KZn_2H_5 and $KZnH_3$ was found. Attempts to prepare these compounds by solid state reaction between KH and Zn in the ratios 1:2 and 1:1 respectively, always gave mixtures of K_2ZnH_4 and KZn_{13}.

2.2 Thermal stability

The thermal stability of K_2ZnD_4 was determined on a SARTORIUS M25D-P high-pressure high-temper-

Table 1

Refinement results on neutron powder diffraction data for K_2ZnD_4 ($T=295$ K; estimated standard deviations in parentheses)

Atom	Site	x/a	y/b	z/c	U_{iso} $(\times 10^{-2}$ Å$^2)$
K1	4c	0.1618(7)	1/4	0.4079(8)	1.43(12)
K2	4c	0.4873(8)	1/4	0.6918(5)	0.61(12)
Zn1	4c	0.2352(4)	1/4	0.0807(5)	0.81(7)
D1	8d	0.3110(4)	0.0182(6)	0.1547(3)	3.58(7)
D2	4c	0.0251(4)	1/4	0.0885(5)	3.92(10)
D3	4c	0.8080(7)	1/4	0.5707(5)	3.42(12)

Space group *Pnma* (No. 62). Cell parameters $a=7.7579(4)$, $b=5.8631(3)$, $c=10.2813(5)$ Å, $V=467.65(5)$ Å^3, $Z=4$. $R_{Bragg}=4.2\%$, $R_p=2.2\%$, $R_{wp}=2.9\%$, $S=2.1$ for 347 reflections. Form of temperature factor: $T=\exp[-8\pi^2 U_{iso}(\sin^2\theta/\lambda^2)]$.

Table 2

Selected interatomic distances (Å) and angles (°) in K_2ZnD_4 (estimated standard deviations in parentheses)

Zn	D2	1.632(4)	K2	D2	2.897(7)
	D3	1.656(7)		D2	3.120(3) 2×
	D1	1.665(4) 2×		Zn	3.399(7)
	D1–Zn–D1	109.5(3)		Zn	3.589(4) 2×
	D1–Zn–D2	109.3(2) 2×		Zn	4.324(5) 2×
	D1–Zn–D3	108.0(2) 2×		Zn	4.451(7)
	D2–Zn–D3	112.7(4)			
	K1	3.312(6)	D1	Zn	1.665(4)
	K2	3.399(7)		D3	2.687(6)
	K1	3.412(9)		D2	2.689(4)
	K1	3.520(5) 2×		D1	2.718(5)
	K2	3.589(4) 2×		K2	2.723(6)
	K2	4.324(5) 2×		K2	2.823(6)
	K1	4.450(6)		K1	2.993(8)
	K2	4.451(7)		K1	3.110(8)
K1	D2	2.818(6)	D2	Zn	1.632(4)
	D3	2.950(1) 2×		D1	2.689(4) 2×
	D1	2.993(8) 2×		D3	2.740(7)
	D1	3.110(6) 2×		K1	2.818(6)
	D1	3.156(8) 2×		K2	2.897(7)
	D3	3.215(8)		K2	3.120(3) 2×
	D2	3.451(9)			
	Zn	3.312(6)	D3	Zn	1.656(7)
	Zn	3.412(9)		D1	2.687(6) 2×
	Zn	3.520(5) 2×		D2	2.738(7)
				K2	2.783(8)
K2	D1	2.723(6) 2×		K2	2.810(8)
	D3	2.782(8)		K1	2.949(1) 2×
	D3	2.810(8)		K1	3.215(8)
	D1	2.823(6) 2×			

Fig. 1. Observed (top), calculated (middle) and difference (bottom) neutron powder patterns of K_2ZnD_4, containing K_3ZnD_5 and KZn_{13} impurity phases ($\lambda=1.7031$ Å, max. count: 3.2×10^4).

Fig. 2. Projection of the structure of orthorhombic K_2ZnD_4 approximately along the *b*-axis. Filled circles K.

ature microbalance equipped with an IGAS pressure control and data acquisition system (HIDEN ANALYTICAL, England). The sample was heated under a constant pressure of 1 bar deuterium with a rate of 1 K min^{-1} up to 725 K and the decrease of weight was measured as a function of temperature.

2.3. X-ray diffraction

X-ray powder diffraction data were collected at room temperature (Philips PW 1820, Bragg-Brentano ge-
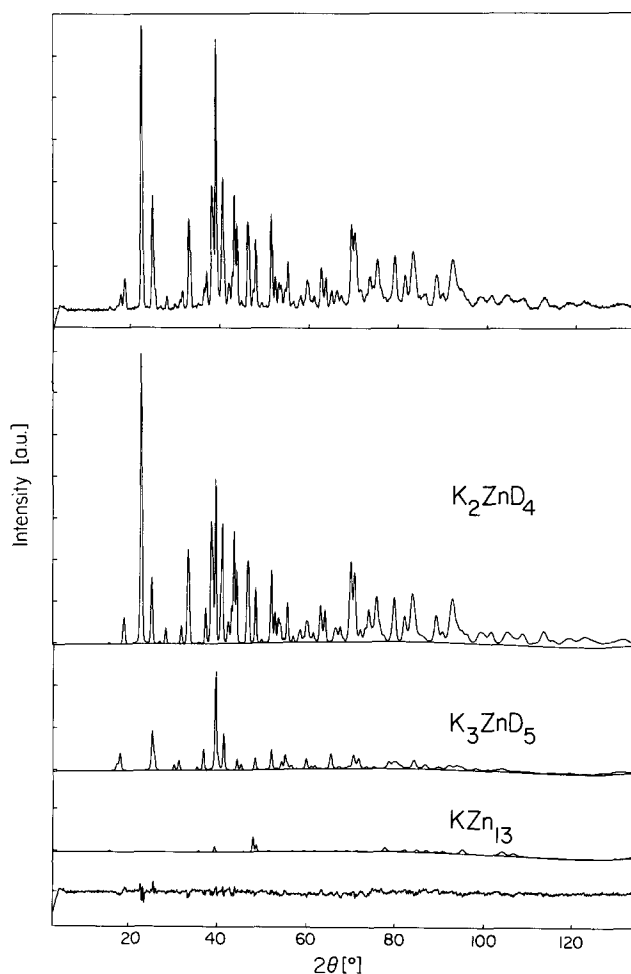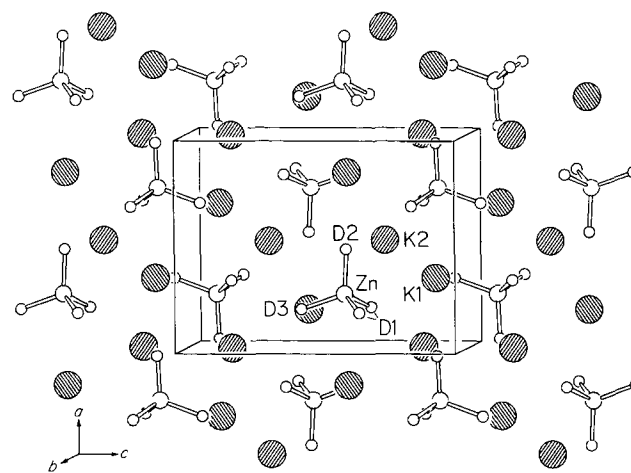
ometry, Cu Kα radiation) by using a special sample holder to prevent decomposition of the sample as a result of oxidation in air. The pattern was indexed on an orthorhombic cell with refined parameters
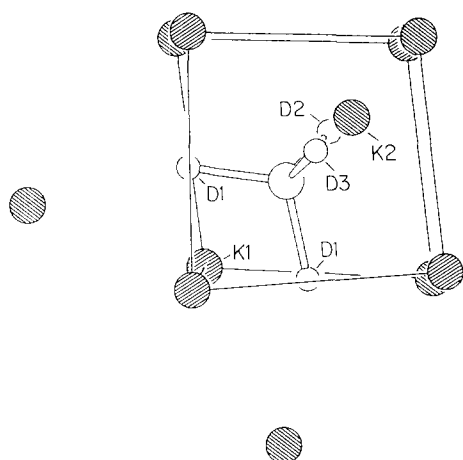
Fig. 3. Potassium environment (3.3–4.6 Å) of the ZnD_4^{2-} complex.

$a = 7.7601(5)$, $b = 5.8636(4)$, $c = 10.2832(7)$ Å (hydride) and $a = 7.7579(4)$, $b = 5.8631(3)$, $c = 10.2813(5)$ Å (deuteride). A preliminary structure refinement on the deuteride sample by taking the cation positions of β-K_2SO_4 [4] as a starting model converged at $R_{wp} = 3.6\%$, $R_B = 10.5\%$ and $S = 1.99$. Small amounts of intermetallic KZn_{13} and a new complex hydride of composition K_3ZnH_5 were found [5]. During irradiation by X-rays the colour of the sample changed from white to yellow.

2.4. Neutron diffraction

Neutron diffraction data were collected at room temperature on the powder diffractometer DMC [6] of the reactor SAPHIR at the Paul Scherrer Institute in Villigen, Switzerland (cylindrical vanadium container of 9 mm inner diameter, Ge(311), $\lambda = 1.7031$ Å; 2θ range 3–135°; 2θ step 0.1°; sample weight 3.5 g; high intensity mode). The transmission factor was measured ($\mu r = 0.08$) and the data corrected accordingly. For the refinement of the deuterium positions the oxygen positions of β-K_2SO_4 were taken as starting parameters (program DBWS 9006PC [7], scattering lengths (fm): $b_{Zn} = 3.67$, $b_K = 5.68$, $b_D = 6.671$ [8]). All site occupation factors refined to values close to 100% and thus were fixed at unity. During the last refinement cycles, the parameters of the impurity phases were also fixed, leaving the following 34 refineable parameters: one zeropoint; six background parameters; one scale factor; three profile parameters; one mixing parameter; three lattice parameters; 13 positional parameters and six isotropic displacement parameters. Refinement results and standardized [9] atomic coordinates are given in Table 1, and bond distances and bond angles in Table 2. Profile plots are shown in Fig. 1 and structural drawings are shown in Figs. 2 and 3.

3. Results and discussion

K_2ZnD_4 crystallizes with the orthorhombic β-K_2SO_4 structure-type (Fig. 2), in contrast to the corresponding fluoride K_2ZnF_4 which adopts the tetragonal K_2NiF_4 structure type [10]. Zinc in the deuteride is tetrahedrally coordinated by deuterium with bond distances in the range 1.632(4) to 1.665(4) Å (average 1.655 Å), and bond angles (108.0(2)°–112.7(4)°) that differ only a little from the ideal value of 109.5°. The ZnD_4 unit (point symmetry m) is surrounded by 11 potassium cations at distances in the range [Zn–K] = 3.312(6)–4.451(7) Å forming an approximately tricapped cubic configuration (Fig. 3). The two potassium sites are coordinated by 11 (K1) and 9 (K2) deuterium atoms at distances in the ranges 2.818(6)–3.451(9) Å and 2.723(6)–3.120(3) Å, respectively. The shortest D–D distance is 2.687(6) Å.

The structural features of the deuteride are consistent with its formulation as a complex tetradeuteridozincate(II), $K_2[ZnD_4]$. In the twofold negatively charged complex $[Zn^{II}D_4]^{2-}$, Zn is presumably sp^3 hybridized and fulfills the 18-electron rule in analogy to the isoelectronic fourfold negatively charged tetrahedral $[Ni^0D_4]^{4-}$ complex in Mg_2NiD_4 [11].

Structurally related hydrides, in which zinc is substituted by alkaline earths such as magnesium, are known to exist. Cs_2MgH_4 and Rb_2MgH_4, which contain relatively large alkali cations, presumably crystallize with the β-K_2SO_4 structure type [12], whereas K_2MgH_4 which contains a smaller alkali cation was reported to crystallize with the K_2NiF_4 structure type [13]. Their bonding, however, cannot be discussed because their hydrogen positions have not yet been confirmed by diffraction methods.

K_2ZnD_4 is relatively unstable. Under a pressure of 1 bar D_2 the decomposition starts slowly at a temperature of 580(10) K and is complete at 720 K. It occurs in a two step reaction: In the first step decomposition to KD, Zn metal and D_2 takes place, the second step consists in the decomposition of KD to K metal and D_2. The literature value for the decomposition temperature for KD is 676 K [14]. The desorption enthalpy has not been determined. K_2ZnH_4 with a hydrogen/metal ratio of 1.33 shows a hydrogen concentration of 2.73 wt.% corresponding to 57 gH_2 l^{-1} or 3.42×10^{22} H atoms cm^{-3}.

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