Synthesis and structure determination of complex zinc hydrides Part 2. Tripotassiumtetrahydridozincate(II) hydride, K₃[ZnH₄]H

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Abstract

K_3ZnH_5 and its deuteride were prepared by reacting stoichiometric amounts of KH (KD) and Zn metal at 650 K and 80 bar hydrogen (deuterium) pressure and characterized by X-ray and neutron powder diffraction. It crystallizes with the tetragonal Cs_3CoCl_5 structure type, space group $I4/mcm$ (No. 140), $Z=4$, cell parameters $a=7.5982(3)$, $c=11.1929(5)$ Å (hydride) and $a=7.5819(4)$, $c=11.1671(5)$ Å (deuteride), and contains tetrahedral $[ZnH_4]^{2-}$ anions with Zn–H bond distances of 1.655(2) Å and H–Zn–H bond angles of 107.15(9)° and 110.64(6)°, octahedrally coordinated hydrogen anions with K–H bond distances of 2.776(2) and 2.792(1) Å, and two sorts of potassium cations. K_3ZnD_5 decomposes at 620(10) K to KD and Zn.

Keywords: Deuterides; Potassium; Zinc hydrides

1. Introduction

The existence of a potassium–zinc hydride of composition K_3ZnH_5 has been conjectured [1] but not confirmed experimentally. During the synthesis of dipotassium tetrahydridozincate, K_2ZnH_4, by solid state reaction (see previous paper of this series [2]), we have found evidence for the formation of such a compound. Here we report on its successful synthesis and crystal structure.

2. Experimental details

2.1. Synthesis

Crystalline K_3ZnH_5 and its deuteride were obtained by reacting KH (KD) with Zn powder (5N Ventron, −200 mesh) in a 3:1 molar ratio at 650 K and a hydrogen (6N) or deuterium (2N8) pressure of 80 bar for 4 days. The colourless powders were extremely sensitive to moisture and air and had to be handled in a glove-box under purified argon. Binary KH (KD) was prepared by reacting potassium (Alfa 98%) at 750

K and 100 bar pressure for 10 days in Ni crucibles coated with Mo foil.

2.2. Thermal stability

The thermal decomposition of K_3ZnD_5 was measured in 1 bar deuterium in the temperature range from 300 to 725 K with equipment described in Ref. [2].

2.3. X-Ray diffraction

X-Ray powder diffraction data were collected at room temperature as described previously [2]. The pattern was indexed on a b.c.t. cell with refined lattice parameters $a=7.5982(3)$, $c=11.1929(5)$ Å (hydride) and $a=7.5819(4)$, $c=11.1671(5)$ Å (deuteride). A preliminary structure refinement by taking the cation positions of Cs_3CoCl_5 [3] as starting parameters converged at $R_{wp}=4.8\%$, $R_B=8.7\%$ and $S=2.2$ for the hydride and $R_{wp}=4.3\%$, $R_B=8.0\%$ and $S=2.1$ for the deuteride. Small amounts of K_2ZnD_4 and KD impurity phases were found in the deuteride sample.

2.4. Neutron diffraction

Neutron diffraction data were collected at room temperature on the powder diffractometer DMC [4]

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of the reactor SAPHIR at the Paul Scherrer Institute in Villigen as described before [2]. The transmission factor was measured ($\mu r = 0.065$) and the data corrected accordingly. For the refinement of the deuterium positions the chlorine positions of Cs_3CoCl_5 were taken as starting parameters (programme DBWS-9006PC [5]; scattering lengths (fm) $b_{Zn} = 3.67$, $b_K = 5.68$, $b_D = 6.671$ [6]). All site occupation factors refined to values close to unity and thus were fixed together with the parameters for the impurity phases. The following 22 parameters were allowed to vary during the last refinement cycles: zero point (one), background (six), scale (one), profile (three), mixing (one), cell (two), positional (three) and isotropic displacement (five). Results and standardized [7] atomic coordinates are listed in Table 1 and bond distances and bond angles in Table 2. The diffraction patterns are shown in Fig. 1 and structural drawings in Figs. 2 and 3. No indication of a symmetry lowering from body centred to primitive as described for the structurally related hydrides Cs_3MgH_5 and Rb_3MgH_5 [8] was found.

Table 1
Refinement results on neutron powder diffraction data for K_3ZnD_5 ($T = 295$ K; estimated standard deviations in parentheses)

Atom	Site	x/a	y/b	z/c	U_{iso} ($\times 10^{-2}$ Å^2)
K1	$8h$	0.6829(3)	0.1829(3)	0	1.46(9)
K2	$4a$	0	0	$\frac{1}{4}$	2.15(13)
Zn1	$4b$	0	$\frac{1}{2}$	$\frac{1}{4}$	1.57(8)
D1	$16l$	0.1242(1)	0.6242(1)	0.1619(2)	4.27(5)
D2	$4c$	0	0	0	2.19(9)

Space group $I4/mcm$ (No. 140).
Cell parameters $a = 7.5819(4)$, $c = 11.1671(5)$ Å, $V = 641.94(7)$ Å^3, $Z = 4$.
$R_{Bragg} = 4.2\%$, $R_p = 2.2\%$, $R_{wp} = 2.9\%$, $S = 2.1$ for 132 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_3ZnD_5 (estimated standard deviations in parentheses)

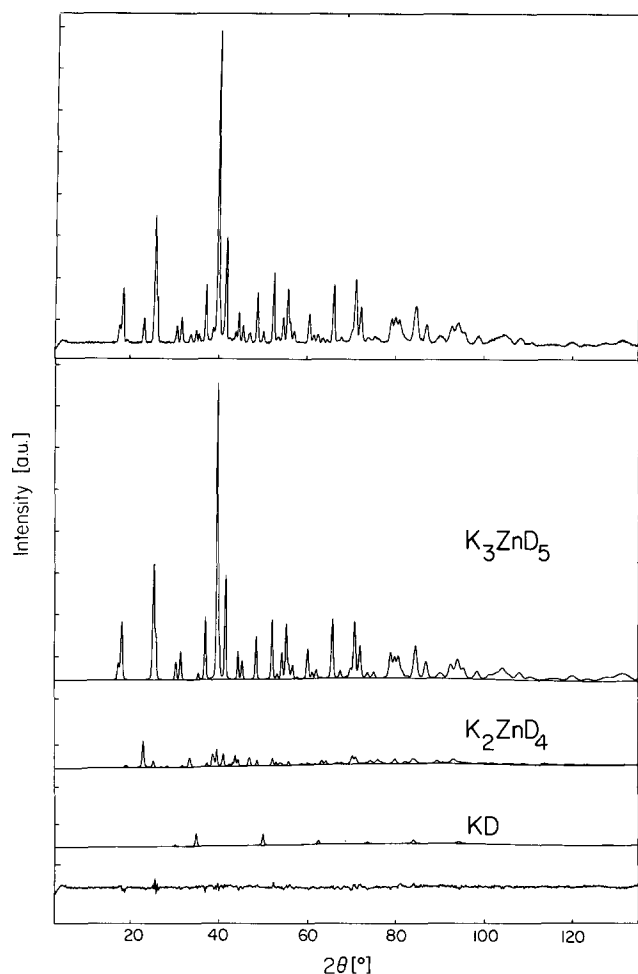| Zn–D1	1.655(2) 4×	D1–Zn	1.655(2)
K1	3.412(1) 4×	D1	2.663(1)
K2	3.791(1) 4×	D1	2.722(2) 2×
		K1	2.748(2)
		K1	2.982(2) 2×
		K2	3.158(1) 2×
K1–D1	2.748(2) 2×		
D2	2.776(2) 2×	D2–K1	2.776(2) 4×
D1	2.982(2) 4×	K2	2.792(1) 2×
Zn	3.412(1) 2×	D1	3.504(1) 8×
K2–D2	2.792(1) 2×	D1–Zn–D1	110.64(6)
D1	3.158(1) 8×		107.15(9)
Zn	3.791(1) 4×		

Fig. 1. Observed (top), calculated (middle) and difference (bottom) neutron powder patterns of K_3ZnD_5 containing K_2ZnD_4 and KD impurity phases ($\lambda = 1.7031$ Å, maximum count 3.3×10^4).

3. Results and discussion

K_3ZnD_5 is the second structurally characterized deuteride in the potassium–zinc–deuterium system. Like $K_2[ZnD_4]$ it contains nearly regular tetrahedral 18-electron $[Zn^{II}D_4]^{2-}$ complexes with metal–deuterium (D1) bond distances of 1.655 Å ($K_2[ZnD_4]$, 1.632–1.665 Å) and D–Zn–D bond angles of 110.64(6)° and 107.15(9)° ($K_2[ZnD_4]$, 108.0(2)° – 112.7(4)°). Unlike $K_2[ZnD_4]$, however, it also contains deuteride anions (D2) that are exclusively bonded to potassium. They fill octahedral holes and have K–D bond distances of 2.776(2) and 2.792(1) Å.

The $[ZnD_4]^{2-}$ tetrahedra in K_3ZnD_5 (point symmetry $-42m$) are surrounded by two sorts of potassium cations in an eightfold configuration (Fig. 3). One of them (K1) connects the $[ZnD_4]^{2-}$ tetrahedra to quasi-two-dimensional structural slabs of composition $\{K[ZnD_4]\}^-$ that run parallel to the ab plane. The other (K2) connects the deuteride anions (D2) to quasi-two-dimensional sheets of composition $\{K_2D\}^+$ that separate the $\{K[ZnD_4]\}^-$ slabs along [001]. These structural
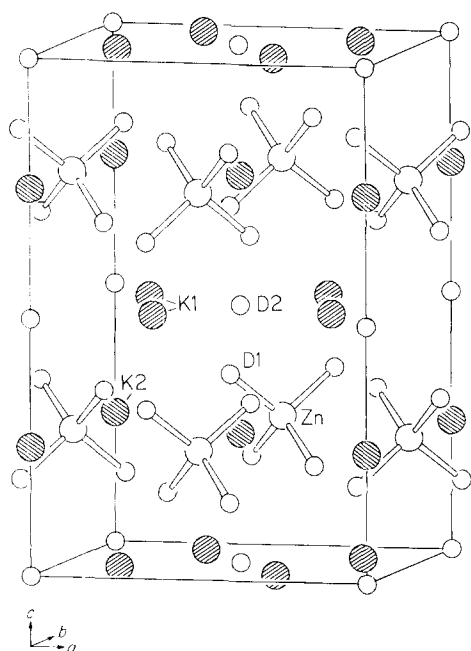
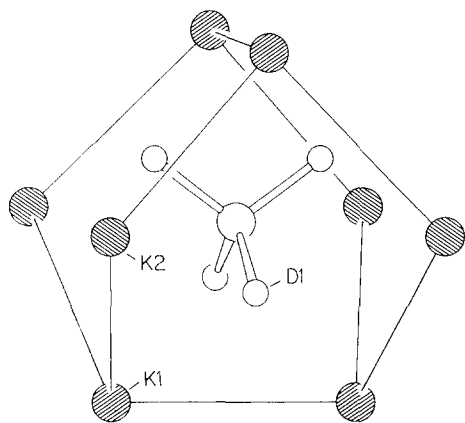Fig. 2. Projection of the structure of tetragonal K_3ZnD_5 approximately along b.

Fig. 3. Potassium environment of the $[ZnD_4]^{2-}$ complex in K_3ZnD_5 (view approximately perpendicular to the fourfold axis).

features and the observed bond distances and bond angles are consistent with the formulation of K_3ZnD_5 as a tetrahydrodozincate(II) hydride with limiting ionic formula $3K^+ [ZnD_4]^{2-} D^-$. The shortest D–D distance is 2.663(1) Å. In the structures of Rb_3MgH_5 and Cs_3MgH_5 [8] the symmetry is lowered to $P4/ncc$. Because the hydrogen positions in these compounds have not been determined, comparison with K_3ZnH_5 is not possible.

In 1 bar D_2 K_3ZnD_5 decomposes in the temperature range from 620(10) to 720(5) K and is slightly more stable than K_2ZnD_4 (580 K). The decomposition occurs in two steps: in the first to KD, Zn and D_2; in the second step KD disintegrates to K metal and D_2. The desorption enthalpy was not determined. The hydrogen concentration is 2.68 wt.%, corresponding to 56 gH_2 l^{-1} or 3.34×10^{22} H atoms cm^{-3}.

Acknowledgments

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