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Synthesis and structure determination of complex zinc hydrides
Part 4: Trirubidium and tricaesium tetrahydridozincate(II) hydride, Rb_3ZnH_5 and Cs_3ZnH_5

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Abstract

Rb_3ZnH_5, Cs_3ZnH_5 and their deuterides have been prepared by reacting stoichiometric mixtures of the binary alkali hydrides (deuterides) and zinc metal powder at 650 K under 80 bar hydrogen (deuterium) pressure, and characterized by X-ray and neutron powder diffraction at room temperature. The compounds crystallize with the Cs_3CoCl_5 structure type, space group $I4/mcm$, $Z=4$, and contain tetrahedral $[ZnD_4]^{2-}$ complexes with Zn–D bond distances of 1.659(2) Å (Rb) and 1.704(3) Å (Cs), and octahedrally coordinated hydride anions with M–D average distances of 2.91 Å (Rb) and 3.05 Å (Cs). The displacement amplitudes of hydrogen indicate the onset of orientational disorder of the tetrahedral complexes. The compounds decompose at 630 K (Rb) and 625 K (Cs) in hydrogen at ambient pressure. Their hydrogen storage efficiencies are of 45.5 (Rb) and 39.7 g H_2 l^{-1} (Cs), and 1.53 (Rb) and 1.1 wt% (Cs).

Keywords: Ternary zinc hydrides; Neutron powder diffraction; Hydride complex

1. Introduction

In the previous parts of this series we have reported the synthesis, crystal structure and thermal stability of orthorhombic K_2ZnH_4 [1] and its analogues M_2ZnH_4 (M=Rb, Cs) [2], and of tetragonal K_3ZnH_5 [3]. While the orthorhombic hydrides contain tetrahedral zinc–hydrogen complexes $[ZnH_4]^{2-}$ only, the tetragonal hydride contains both $[ZnH_4]^{2-}$ complexes and H^- anions bonded to K only. All compounds decompose at temperatures around 600 K. Here we present the synthesis, the crystal structure and the thermal stability of the caesium and rubidium analogues of K_3ZnH_5.

2. Experimental

2.1. Synthesis

Rb_3ZnH_5 and Cs_3ZnH_5, and their deuterides were synthesized by reacting the binary alkali hydrides (deuterides) with zinc powder (5N Ventron, 200 mesh) in a 3:1 molar ratio at 650 K under a hydrogen (deuterium) atmosphere (purity: H_2 6N, D_2 2N8) of 80 bar pressure during four days. The samples were colourless, extremely sensitive to air and moisture, and pyrophoric.

2.2. X-ray diffraction

Powder patterns were collected at room temperature with a Philips PW 1820 (Bragg–Brentano geometry, Cu Kα radiation) using a sealed sample holder in order to prevent decomposition of the sample. The patterns were indexed on a body centered tetragonal cell with refined lattice parameters as given in Table 1. A preliminary structure refinement confirmed the Cs_3CoCl_5 type cation

Table 1
Cell parameters

	a (Å)	*c* (Å)	*V* (Å^3)
Rb_3ZnH_5	7.9476(2)	11.6520(6)	735.99(5)
Rb_3ZnD_5	7.9404(2)	11.6293(7)	733.23(6)
Cs_3ZnH_5	8.3130(4)	12.1986(6)	842.99(9)
Cs_3ZnD_5	8.3052(3)	12.1875(5)	840.65(7)

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Table 2
Refinement results on neutron powder diffraction data

Atom	Site	x/a	y/b	z/c	U_{iso} ($\times 10^2$ Å^2)
Rb_3ZnD_5					
Rb1	8h	0.6826(2)	0.1826(2)	0	2.21(9)
Rb2	4a	0	0	1/4	2.99(13)
Zn1	4b	0	1/2	1/4	1.86(8)
D1	16l	0.1196(2)	0.6196(2)	0.1662(2)	5.07(5)
D2	4c	0	0	0	2.81(9)
$R_{Bragg}=9.7\%$, $R_p=4.9\%$, $R_{WP}=5.8\%$, $S=1.7$ for 119 reflections					
Cs_3ZnD_5					
Cs1	8h	0.6815(3)	0.1815(3)	0	1.77(9)
Cs2	4a	0	0	1/4	2.53(13)
Zn1	4b	0	1/2	1/4	1.58(8)
D1	16l	0.1157(2)	0.6157(2)	0.1693(3)	4.69(5)
D2	4c	0	0	0	3.11(9)
$R_{Bragg}=9.2\%$, $R_p=4.8\%$, $R_{WP}=5.6\%$, $S=1.2$ for 134 reflections.					

$T=295$ K; e.s.d. in parentheses; space group *I4/mcm* (No. 140), $Z=4$; form of temperature factor: $T=\exp[-8\pi^2 U_{iso}(\sin^2\theta/\lambda^2)]$.

model as found for the potassium analogue K_3ZnH_5 [3]. Attempts to measure diffraction patterns for the members of the M_3ZnH_5 series (M=K, Rb, Cs) at high temperature (up to 580 K, sealed quartz capillaries, Huber Guinier camera 631-632) and low temperature (down to 10 K, Huber diffractometer G645) were only partially successful. While the K compound gave useful data, the Rb compound reacted with the capillary and the Cs compound showed too great absorption.

2.3. Neutron diffraction

Powder patterns were collected at room temperature on D1A at the Institut Laue–Langevin in Grenoble (cylindrical vanadium container of 6 mm inner diameter, $\lambda=1.909$ Å; 2Θ range 6–156°; 2Θ step 0.05°). The deuterium positions of K_3ZnD_5 were taken as starting parameters for a Rietveld refinement. The programme DBWS 9006PC [4] was used and the scattering lengths as tabulated in Ref. [5] were used. The following 21 parameters were refined during the last cycles: one zeropoint, four background parameters, two scale factors, three profile parameters, one mixing parameter, two lattice parameters, three positional parameters and five isotropic temperature factors. As the site occupancies did not differ significantly from unity they were fixed together with the structure parameters for the impurity phases. The refinement results are summarized in Table 2, and the intensity difference plots are represented in Fig. 1. A list of interatomic distances is given in Table 3.

2.4. Thermal stability

The thermal stability for all members of the M_3ZnH_5 series (M=K, Rb, Cs) was determined by thermogravimetry (TG) in the temperature range between 300 K and 720 K by using the equipment described previously [1]. The heating rate was 1 K min^{-1} and the atmosphere was hydrogen at ambient pressure. The TG plots (not shown) were similar to those observed for the M_2ZnH_4

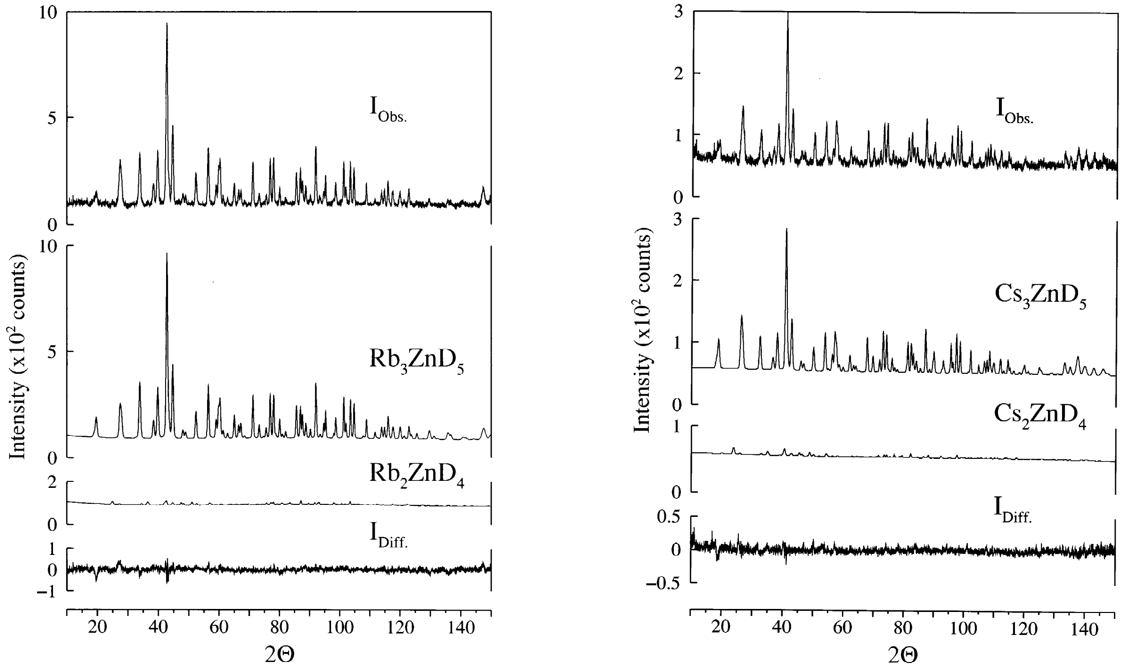

Fig. 1. Observed, calculated and difference neutron diffraction patterns of (a) Rb_3ZnD_5 and (b) Cs_3ZnD_5.

Table 3
Selected interatomic distances (Å) and angles (°), (e.s.d. in parentheses)

Rb_3ZnD_5					
Zn	D1	1.659(2) 4x	D1	Zn	1.659(2)
	D1ZnD1	110.2(1)		D1	2.686(2)
		108.1(1)		D1	2.722(3) 2x
				Rb1	2.944(2)
Rb1	D2	2.908(2) 2x		Rb1	3.122(2)2x
	D1	2.944(2) 2x		Rb2	3.313(1) 2x
	D1	3.122(2) 4x			
	Zn	3.558(1) 2x	D2	Rb2	2.907(1) 2x
				Rb2	2.908(2) 4x
Rb2	D2	2.907(1) 2x			
	D1	3.313(2) 8x			
Cs_3ZnD_5					
Zn	D1	1.704(3) 4x	D1	Zn	1.704(3)
	D1ZnD1	111.1(1)		D1	2.727(2)
		106.3(1)		D1	2.811(4) 2x
				Cs1	3.122(3)
Cs1	D2	3.045(3) 2x		Cs1	3.241(3)2x
	D1	3.122(3) 2x		Cs2	3.484(2) 2x
	D1	3.241(3) 4x			
	Zn	3.719(1) 2x	D2	Cs1	3.045(3) 4x
				Cs2	3.047(1) 2x
Cs2	D2	3.047(1) 2x			
	D1	3.484(2) 8x			

series (see Fig. 2 in Ref. [2]) except that the onset decomposition temperatures were shifted to somewhat different values: 620 (K), 630 (Rb) and 625 K (Cs).

3. Results and discussion

Rb_3ZnD_5 and Cs_3ZnD_5 can be classified as complex hydrides which are isostructural with their potassium analogue K_3ZnD_5 (for a structural drawing see Fig. 2 in Ref. [3]). They contain two types of deuterium atoms, one (D1) forming tetrahedral $[ZnD_4]^{2-}$ complexes with Zn–D bond distances of 1.659(2) Å (Rb) and 1.704(3) Å (Cs), and the other (D2) being octahedrally coordinated by alkali atoms with M–D average bond distances of 2.91 Å (Rb) and 3.05 Å (Cs). As expected, these distances are longer than the corresponding ones in the potassium compound: Zn–D=1.655 Å, K–D=2.78 Å [3]. Interestingly, the displacement amplitudes of D1 are anomalously high compared to those of D2 (see Table 2). This suggests that the $[ZnH_4]^{2-}$ groups are relatively mobile at room temperature and could become rotationally disordered at high temperature. This possibility is corroborated by the observed temperature dependencies of the cell parameters. As shown in Fig. 2, the tetragonal lattice of K_3ZnH_5 expands very anisotropically and tends to become cubic at high temperature. This behavior is consistent with a gradual onset of rotational disorder of the $[ZnH_4]^{2-}$ groups. An order–disorder transition of this type was recently observed for the isostructural fluorosulfate $K_3[SO_4]F$ [6] in which the SO_4^{2-} groups are directionally ordered in the tetragonal room temperature modification (a_t, c_t), and presumably disordered in the cubic high temperature modification ($a_c = c_t/2 = a_t\sqrt{2}$). The fact that such a transition was not observed in the present hydrides could be due to their decomposition below the transition temperature.

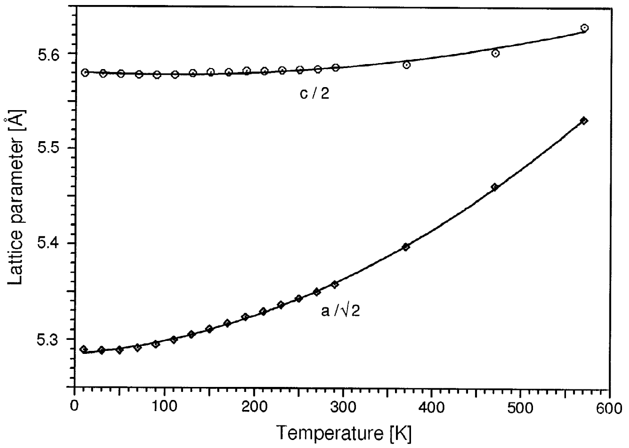

Fig. 2. Cell parameters of tetragonal K_3ZnD_5 as a function of temperature.

The atomic volume of hydrogen was recently calculated and discussed for various metal hydride structures [7]. Similar calculations for the present series reveal the following results. Firstly, the values for the M_3ZnH_5 (K: 9.3, Rb: 9.6, Cs: 9.5 cm^3 mol^{-1}) and M_2ZnH_4 series (K: 8.9, Rb: 9.2, Cs: 9.2 cm^3 mol^{-1}) are much smaller than those of the binary series of MH hydrides (K: 12.2, Rb: 13.0, Cs: 13.7 cm^3 mol^{-1} [7]). This expected trend correlates with the smaller space requirement of hydrogen in covalently bonded systems compared to saltlike systems. Secondly, the values within each series increase as one goes from light to heavy members. This trend is also expected and can be interpreted as a result of matrix effects, although the very small difference between the Rb and Cs members is surprising in view of the large difference between binary RbH and CsH. This suggests that the atomic volume of hydrogen is not only influenced by the electronic state of hydrogen and some matrix effects, but also by the thermal behavior of the hydrogen atoms or complexes. Thirdly, the values for the M_3ZnH_5 series are generally bigger than those in the structurally related M_2ZnH_4 series. This is presumably due to the presence of saltlike hydrogen in the former series and its absence in the latter series. However, an estimation of the atomic hydrogen volumes of the M_3ZnH_5 series in terms of weighted sums of the corresponding volumes of the M_2ZnH_4 and MH series gives values which exceed the observed ones by up to 6.3%. This shows that the concept of additivity of atomic hydrogen volumes is questionable even in closely related structures, and that an “average” value for the atomic hydrogen volume does not allow one to discuss bonding or other properties of hydrides containing electronically different types of hydrogen.

The thermal stabilities of the M_3ZnH_5 series (decomposition temperatures at ambient pressure: 620–630 K) do not differ much from those of the M_2ZnH_4 series (decomposition temperatures: 580–645 K). Whether or not the decomposition of the M_3ZnH_5 series occur via binary MH and intermetallic MZn_{13} as in the M_2ZnH_4 series, or directly into the elements remains an open question. Finally the hydrogen storage efficiencies are 45.5 (Rb) and 39.7 (Cs) g H_2 l^{-1}, and 1.53 (Rb) and 1.06 wt% (Cs).

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