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High pressure synthesis and structure of Na_2PdH_4

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Abstract

The ternary sodium palladium hydride Na_2PdH_4 and its analogous deuteride were prepared via the reaction of sodium hydride (deuteride) with palladium sponge at 770 K and 1800 bar hydrogen (deuterium) pressure. Its structure was determined from X-ray diffraction studies of powder samples in the temperature range 9 to 600 K and an elastic neutron diffraction experiment on the deuterium compound at room temperature. The atomic arrangement in Na_2PdH_4 contains isolated square-planar $[PdH_4]^{2-}$ groups and is isotypic with that of Na_2PtH_4 (space group *I4/mmm*, $Z = 2$).

Keywords: Metal hydride; High pressure synthesis; Neutron diffraction; Crystal structure; Palladium

1. Introduction

Previous investigations of the sodium–palladium–hydrogen system led to the preparation of the compounds Na_2PdH_2 [1] and $NaPd_3H_2$ [2]. Their crystal structures have been completely solved by a combination of X-ray and elastic neutron diffraction experiments. Whereas the structure of Na_2PdH_2 contains linear $[PdH_2]^{2-}$ dumbbells in which Pd has an oxidation state of zero, the atomic arrangement in the compound $NaPd_3H_2$ can be described in terms of an intermetallic phase into which hydrogen is incorporated. Varying the experimental conditions such that hydrogen pressures up to 200 bar were applied, did not produce any new hydride. The first metal hydride containing Pd in the oxidation state of +2 has been synthesized by the partial exchange of Pt by Pd in the mixed crystals of the composition $Na_2Pt_xPd_{1-x}H_4$ [3]. In the field of ternary palladium hydrides containing the heavier alkali metals potassium, rubidium and caesium, only salt-like compounds were found [4–9]. Here, in addition to the linear $[PdH_2]^{2-}$ dumbbells, planar $[PdH_4]^{2-}$ squares with Pd in oxidation state +2 have been observed in the structures of these compounds.

The observation that higher oxidation states of the transition metal (i.e. platinum) can be stabilized by high hydrogen pressures resulting in compounds containing platinum in oxidation state +4 [10–12] prompted us to reinvestigate whether ternary sodium palladium hydrides, containing palladium in oxidation state +2, could now be prepared.

In this paper we report the high pressure synthesis of the new ternary sodium palladium hydride, Na_2PdH_4.

2. Synthesis

The compound Na_2PdH_4 was synthesized by the reaction of sodium hydride, a detailed synthesis of which has been previously given [13], with palladium sponge (Johnson Matthey, specified purity 99.9%) in a respective 2:1 molar ratio at 770 K for 12 h under a hydrogen (Linde, specified purity 99.9995%) pressure in the range 1800 to 2500 bar. Recently we succeeded in the construction of a high pressure apparatus, in which hydrogen pressures up to 4 kbar are now accessible for the synthesis of ternary hydrides [10]. The preparation of the deuterium compound was carried out analogously. The reaction products are grey microcrystalline powders which are very sensitive to moisture and air.

3. Structure determination and discussion

The reaction products were characterised by X-ray

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Table 1
Na_2PdX_4 and Na_2PtX_4 [3,14] with X = H or D: comparison of the lattice constants (Å) from X-ray diffraction experiments (Guinier-Simon camera, Cu $K\alpha_1$ radiation)

	Na_2PdX_4		Na_2PtX_4	
	295 K	9 K	295 K	610 K
Space group	*I4/mmm*	*I4/mmm*	*I4/mmm*	*Fm3m*
X = H	a = 5.344(1)		a = 5.254(1)	a = 7.298(1)
	c = 6.625(1)		c = 6.782(1)	
X = D	a = 5.336(1)	a = 5.296(1)	a = 5.255(1)	
	c = 6.616(1)	c = 6.552(1)	c = 6.751(1)	

Table 2
Na_2PdD_4; structural parameters obtained from an elastic neutron diffraction experiment on TAS 1 at room temperature (space group: *I4/mmm*; $Z = 2$)

	Na_2PdD_4
Number of reflections	19
2θ regions (deg)	3–100.4
Angular step $\Delta 2\theta$ (deg)	0.1
Wavelength (Å)	2.0141
a (Å)	5.338(1)
c (Å)	6.614(2)
Pd in (2a) 0 0 0	
B_{iso} (Å^2)	0.1(4)
Na in (4d) 0 $\frac{1}{2}$ $\frac{1}{4}$	
B_{iso} (Å^2)	1.3(4)
D in (8h) x x 0	x = 0.2128(9)
B_{iso} (Å^2)	2.7(2)
R_{Bragg}	0.096

powder diffraction (Cu $K\alpha_1$ radiation) studies at room temperature. The data analysis indicated a tetragonal, body-centred unit cell, in which the palladium and sodium atoms form an atomic arrangement analogous to that found in Na_2PtH_4 [14]. Since Na_2PtH_4 undergoes a reversible phase transition to a cubic face-centred cell at 570 K as a consequence of the mobility of the hydrogen atoms [13], additional X-ray diffraction experiments were carried out in the temperature range from 9 to 600 K. However, the measurements gave no indication of a structural change in Na_2PdH_4 before the decomposition into Na_2PdH_2 occurred. A comparison of the lattice constants is given in Table 1.

Elastic neutron diffraction experiments on the deuterium compound were carried out at room temperature using the triple axis spectrometer TAS 1 at the reactor DR 3 at the Risø National Laboratory,

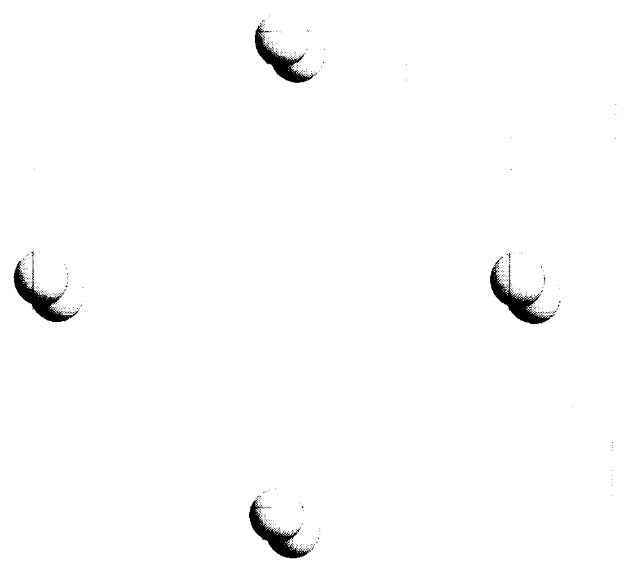

Fig. 1. Crystal structure of the room temperature modification of the palladium hydride Na_2PdD_4 viewed approximately along [001]. The $[PdD_4]^{2-}$ squares at $z = 0$ and 1/2 respectively and the sodium ions at $z = 1/4$ and 3/4 are depicted.

Table 3
Selected interatomic distances (Å) in the ternary metal deuterides Na_2PdD_4 and Na_2PtD_4 [14] at room temperature

	Na_2PdD_4	Na_2PtD_4	
Pd–D	1.606(3) 4×	Pt–D	1.639(4) 4×
D–D	2.272(9) 2×	D–D	2.318(8) 2×
Na–D	2.525(3) 8×	Na–D	2.519(3) 8×
Pd–Pd	5.018(1) 8×	Pt–Pt	5.020(1) 8×
Pd–Na	3.140(1) 8×	Pt–Na	3.123(1) 8×

Roskilde, Denmark in order to determine the positions of the deuterium atoms. The sample of Na_2PdD_4 was loaded into a cylindrical aluminium can (internal diameter 10 mm; length 40 mm; wall thickness 0.05 mm) under argon before sealing with a Viton ring. The analysis of the data, using the DBWS 9006 program [15], confirmed that the structure of Na_2PdD_4 is isotypic with that of Na_2PtD_4 [14] at room temperature. The characteristic structural units are square planar $[PdD_4]^{2-}$ groups, which are arranged in an ordered manner. The results of the final refinement are shown in Table 2. The crystal structure is depicted in Fig. 1. A comparison of the bond distances in both ternary sodium deuterides is given in Table 3.

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