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Crystal Structure of $Na_2Mg_2NiH_6$ Revisited

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The crystal structure of $Na_2Mg_2NiH_6$ as published by Kadir and Noréus (*Inorg. Chem.* **2007**, *46*, 2220−2223) is revised. While the reported space group symmetry and cell parameters are correct, the Mg and hydride positions need to be interchanged. Consequently, the tetrahedral $[NiH_4]^{4-}$ complexes are stabilized by both Na^+ and Mg^{2+} ions and not by Na^+ ions only, as was stated by the authors. The metal−hydrogen bond distances of the revised structure model differ by up to 0.6 Å from those reported and are more in line with those usually observed in these sorts of hydrides. An overview of the known cation configurations around solid-state $[NiH_4]^{4-}$ complexes is given.

Recently, a new nickel-based complex metal hydride of composition $Na_2Mg_2NiH_6$ has been reported by Kadir and Noréus.[1] Its structure was determined from X-ray diffraction (XRD) and neutron powder diffraction (NPD) data collected on a multiphase deuteride sample and described as an intersection of $(Mg_2H_2)^{2+}$ and $(Na_2NiH_4)^{2-}$ layers. A novel and particularly striking feature of this structure was the cation coordination of the tetrahedral $[NiH_4]^{4-}$ complex that consisted of five close Na^+ ions arranged in a pentagonal, nearly planar configuration (Ni−Na = 2.75−3.07 Å) and of four much more distant Mg^{2+} ions (Ni−Mg = 3.68−3.71 Å; see Figure 2 of ref 1). This feature prompted the authors to claim that $Na_2Mg_2NiH_6$ provides the first example for the stabilization of $[NiH_4]^{4-}$ hydrido complexes by alkali-metal counterions.

Apart from this unusual cation configuration, a closer look at the reported structure revealed other puzzling features. First, the $(Mg_2H_2)^{2+}$ layers actually consist of quasi-infinite −Mg−H−Mg−H− zigzag chains that are separated from each other by Na^+ ions at conspicuously short metal−metal distances (Na−Mg = 2.66 Å) and unusually long metal−hydrogen distances (Na−H ∼ 3.3 Å), thus leaving the Na cations and H anions in energetically unfavorable environments. This contrasts with most other known complex metal hydrides in which the metal cations are well separated from each other and the hydride anions (i.e., those outside the transition-metal complexes) have higher coordination numbers (mostly 4-fold tetrahedral; for a recent review, see ref 2). Second, the Mg−H bond distances involving the hydrogen atoms in the complex are rather long (shortest Mg−H = 2.72 Å) and not in line with those usually observed in complex transition-metal hydrides such as, for example, Mg_2NiD_4 (Mg−D = 1.97−2.25 Å).[3] Finally, theoretical XRD patterns as calculated from the atomic coordinates reported in ref 1 showed significant discrepancies with respect to the XRD patterns provided in ref 1 and those measured by us on a sample that had been prepared independently before. In view of these inconsistencies and the novelty of the bonding feature claimed, we decided to look more closely into the structure of this compound. For this purpose, we prepared a new hydride sample in accordance with the conditions of the synthesis reported in ref 1 and performed an ab initio structure analysis on newly collected XRD and NPD data. Here we present the results of our analysis.

A sample of nominal composition $Na_2Mg_2NiH_6$ was prepared in a two-step procedure according to the reaction $Mg_2NiH_4 + 2NaH \rightarrow Na_2Mg_2NiH_6$. The starting hydride Mg_2NiH_4 was synthesized from the intermetallic compound Mg_2Ni by hydrogenation at 200 °C as described in ref 3, while NaH was purchased from Alfa (99.9%). A 1:2 mixture of Mg_2NiH_4 and NaH was ground to a fine powder in an agate mortar, compacted to pellets, put into a steel crucible, and sintered in an autoclave at 300−315 °C in 50 bar of hydrogen for about 24 h. After cooling, the tablets were crushed and a small amount was removed for X-ray analysis. This procedure was repeated until the abundance of the main phase was judged to be satisfactory. All samples were handled in an argon-filled glovebox. The final reaction product had an intense dark-olive-green color and was sensitive to air. It was characterized by XRD at room temperature on a Bragg−Brentano diffractometer. The refined cell parameters [a = 11.4297(3) Å, b = 8.4430(2) Å, c = 5.4197(1) Å, V = 523.01(2) Å^3] were consistent with, but more precise than, those reported previously for the hydride [a = 11.428(2) Å, b = 8.442(2) Å, c = 5.4165(9) Å, V = 523 Å^3].[1] The systematic extinctions confirmed space group *Pnma*. Four metal sites were found by the program *FOX*,[4] one Mg site in general position 8d, and one Ni site and two Na

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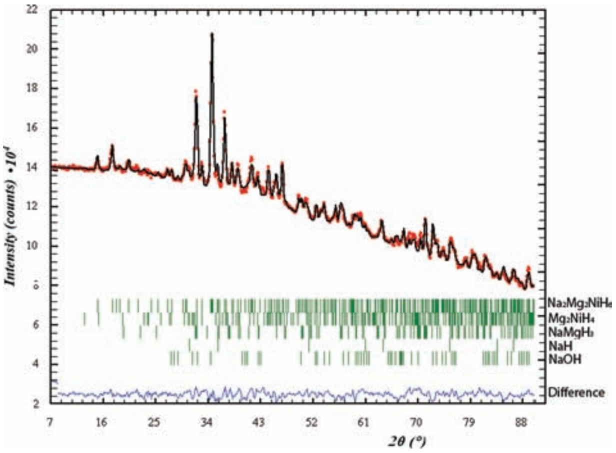

Figure 1. Observed (points) and calculated (line) NPD patterns for a hydride sample containing $Na_2Mg_2NiH_6$ (69 wt %), Mg_2NiH_4 (4 wt %), $NaMgH_3$ (10 wt %), NaH (3 wt %), and NaOH (14 wt %). Vertical bars indicate the positions of the Bragg peaks; the difference pattern is represented at the bottom; λ = 1.494 Å; T = 293 K; HRPT at SINQ (PSI, Villigen, Switzerland), high-intensity mode, 2θ range 5−164°, step size 0.1°, sample mass 5 g, the vanadium container having a 9 mm diameter; data collection time ~ 16 h; data were corrected for absorption.

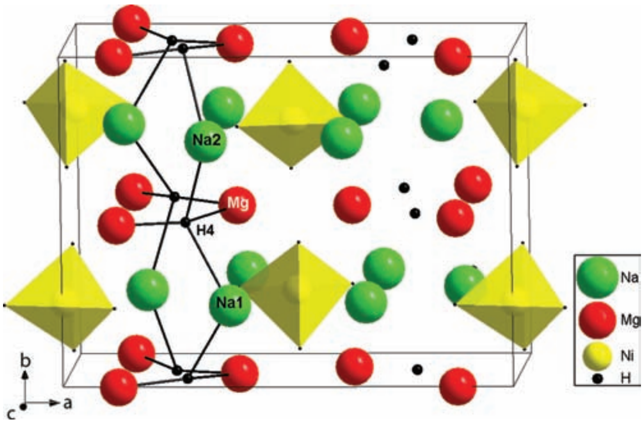

Figure 2. Revised structure of orthorhombic $Na_2Mg_2NiH_6$.

Table 1. Neutron Structure Refinement Results^b on Hydride $Na_2Mg_2NiH_6$

atom	site	x	y	z	B_{iso}	occupancy
Ni	4c	0.0051(8)	$^1/_4$	0.942(1)	1.10(2)	1
Mg	8d	0.3704(7)	−0.003(2)	0.556(2)	3.0(2)	1
Na1	4c	0.392(2)	$^1/_4$	0.074(5)	3.3(4)	1
Na2	4c	0.163(2)	$^1/_4$	0.562(4)	1.4(4)	1
H1	4c	0.109(4)	$^1/_4$	0.186(7)	10.4(9)	1
H2	8d	0.020(1)	0.104(2)	0.769(2)	1.4(3)	1
H3	4c	−0.123(2)	$^1/_4$	0.025(4)	3.1(5)	1
H4	8d	0.276(1)	0.995(2)	0.860(3)	3.9(5)	1

[a] *Pnma*, Z = 4, a = 11.433(1) Å, b = 8.4435(8) Å, c = 5.4180(7) Å, V = 523.0(1) Å^3; esd's in parentheses. [b] Refinement indices R_b = 6.8%, R_f = 5.5%, R_p = 14.1%, R_{wp} = 11.5%, χ^2 = 7.6. A total of 58 parameters were refined: 5 scale, 11 profile, 14 cell, and 29 atomic.

sites in special position 4c, and refined by the program *FULLPROF.2000*.[5] Interestingly, while the coordinates of Ni and Na were consistent with those reported, those of Mg differed markedly (see below). The abundance of the main phase in our sample (~69 wt % $Na_2Mg_2NiH_6$) was slightly higher than that in the previous study[1] (64 wt % $Na_2Mg_2NiD_6$).

The H positions were determined from NPD data collected on the same sample. Four such sites were identified and refined by *FULLPROF.2000*,[5] two in general position 8d (H2 and H4) and two in special position 4c (H1 and H3). One of the latter sites (H4) differed markedly from the D positions reported before (see below). An interchange between Na and Mg (difficult to distinguish by XRD data alone) led to an unsatisfactory fit between the observed and calculated data. The refined NPD pattern is presented in Figure 1, and the results are summarized in Table 1.

Interestingly, in spite of the relatively high background in our NPD patterns due to the incoherent scattering contribution of hydrogen, the precision of our data is superior to that of the deuteride data reported before, as can be seen from the estimated standard deviations (esd's) of the hydride that are lower by a factor of 3, on average, compared to those of the deuteride (Table S1 in the Supporting Information).

As expected, the new structure model for the hydride (called the "hydride model" from here on; Figure 2) differs considerably from that reported for the deuteride (called the "deuteride model" from here on; Figure 2 in ref 1). The biggest difference concerns the Mg position and one of the H positions. Specifically, a comparison between the atomic coordinates reveals that the Mg and H4 positions in the hydride model are close to the D4 and Mg positions, respectively, in the deuteride model; i.e., these positions appear to be interchanged (Figure S3 and Table S1 in the Supporting Information).

In order to rule out the possibility of polymorphism, various additional structure refinements and intensity simulations were performed. First, theoretical XRD patterns were calculated for both models and compared with the observed XRD patterns of our hydride sample. While the calculated patterns differed substantially for both models, only that of the hydride model fitted our observed pattern (Figure S2 in the Supporting Information). In order to quantify this misfit, the deuteride model was refined against our XRD profile, yielding agreement indices (R_b = 44%, R_f = 19%, R_p = 83%, χ^2 = 80) that were significantly worse than those obtained for the hydride model (R_b = 6%, R_f = 6%, R_p = 22%, χ^2 = 3). Second, integrated XRD intensities were calculated for both models and compared with the observed data as reported in ref 1 and with our data. Again, our hydride model fit both data sets better than the deuteride model (Table S2 in the Supporting Information), thus leaving little doubt about the correctness of this model.

Not surprisingly, the quasi-interchange between a cation (Mg^{2+}) and an anion (H^-) site has profound consequences on the crystal chemistry. As can be seen on Figure 2, the revised structure model of $Na_2Mg_2NiH_6$ can be described as a stacking of $(NaMgH_2)^+$ and $(NaMgNiH_4)^-$ slabs rather than an intersection of $(Mg_2H_2)^{2+}$ and $(Na_2NiH_4)^{2-}$ layers (see also Figure S3 in the Supporting Information). Consequently, the $[NiH_4]^{4-}$ complexes in $Na_2Mg_2NiH_6$ are no longer coordinated by Na^+ ions only in a quasi-planar configuration but by both Mg^{2+} and Na^+ ions in a three-dimensional configuration.

Clearly, the latter configuration is more favorable from an energetic point of view and more in line with the configurations observed in other complex metal hydrides containing tetrahedral $[NiH_4]^{4-}$ complexes. As shown in Figure 3, these

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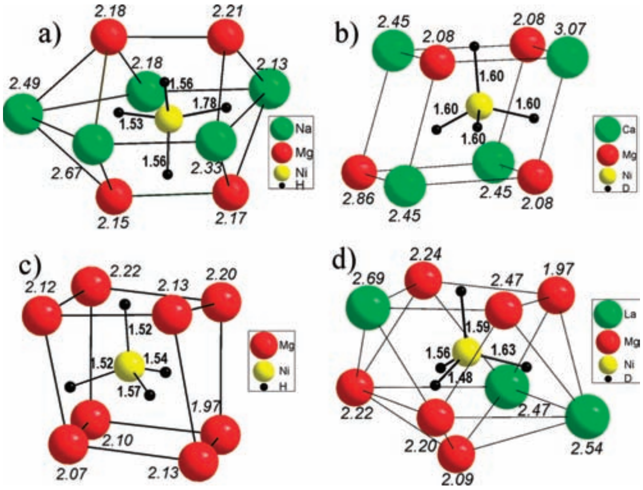

Figure 3. Cation environments of tetrahedral $[NiH_4]^{4-}$ complexes in (a) $Na_2Mg_2NiH_6$ (present work), as compared to (b) $CaMgNiD_4$ (ref 6), (c) Mg_2NiD_4 (ref 3), and (d) $LaMg_2NiD_7$ (ref 7). Bold: Ni−H (D) bond lengths (Å). Italics: shortest distances between cations and hydrogen ligands of the complex; esd's are generally 0.02 Å.

configurations display a variety of geometries, ranging from slightly distorted cubic (8Mg) in Mg_2NiD_4[3] (Figure 3c) to strongly distorted cubic (4Mg + 4M) in $MMgNiD_4$ (M = Ca, Sr, Eu, Yb)[6] (Figure 3b), and irregular 9-fold (6Mg + 3La) in $LaMg_2NiD_7$[7] (Figure 3d). As to the cation configuration around the hydrogen anion (H4), it is clearly 4-fold (2Mg, Na1, and Na2; see Figure 2 and Table S3 in the Supporting Information) and not 2-fold (2Mg) as reported.

Likewise, the metal−metal distances of the revised structure (Mg−Ni = 2.60 Å instead of 3.68 Å in ref 1; Mg−Na = 3.20 Å instead of 2.66 Å) are more in line with those usually observed in complex metal hydrides such as Mg_2NiD_4, $CaMgNiD_4$, and $LaMg_2NiD_7$ (see Tables 2 and S3 in the Supporting Information) and in saline metal hydrides such as $NaMgH_3$ (Mg−Na = 3.24 Å).[8] This is particularly true for the metal−hydrogen distances relevant for stabilization of the $[NiH_4]^{4-}$ complex. While the Ni−H bond distances within the complex are similar for both models, albeit of greater precision in the present study (Table S1 in the Supporting Information), the closest Mg−H distances involving the H atoms of the complex in the present model are ~0.6 Å shorter (Mg−H = 2.15 Å instead of 2.72 Å in the reported model) and more in line with those usually observed in complex transition-metal hydrides such as Mg_2NiD_4 (Mg−D = 1.97 Å). Finally, the H−H contact distances in the hydride model are within the usually accepted limits (shortest H−H = 2.47 Å) but longer than those in the deuteride model (shortest D−D = 2.07 Å).

Table 2. Selected Interatomic Distances (Å) in Hydrides Containing $[NiH_4]^{4-}$ Complexes; Mg−H Distances Refer to H Atoms of the Complex

		compound				
		$Na_2Mg_2NiH_6$ (present work)	Na_2Mg_2-NiD_6[1]	Mg_2-NiH_4[3]	CaMg-NiH_4[6]	$LaMg_2$-NiH_7[7]
Mg−H	max	2.21	2.72	2.25	2.86	2.25
	min	1.97	2.72	1.97	2.08	1.82
	ave	2.11	2.72	2.03	2.29	2.03
Ni−H	max	1.78	1.67	1.57	1.60	1.63
	min	1.56	1.64	1.52	1.60	1.49
	ave	1.61	1.66	1.54	1.60	1.58
Mg−Ni		2.60	3.68	2.65	2.53	2.59
Na−Mg		3.20	2.66			
H−H	min	2.47	2.07	2.43	2.59	2.12

In conclusion, the structure model of $Na_2Mg_2NiH_6$ presented in this work not only is more precise and better reproduces the XRD diffraction intensities than the deuteride model reported previously but also presents more attractive crystal chemistry features. While both models have the same space group and similar axial cell ratios, the Mg and hydride sites in the deuteride model need to be interchanged.

A likely reason for the mix-up in the previous work is the relatively low quality of the deuteride sample investigated combined with the small scattering contrast between Mg and D for thermal neutrons (5.375 fm for Mg versus 6.671 fm for D)[9] compared to the stronger contrast between Mg and H in the present study (−3.739 fm for H).[9] A major consequence of these findings is that the bonding features as discussed in ref 1 are not pertinent; i.e., a $[NiH_4]^{4-}$ complex exclusively stabilized by Na^+ ions still waits to be discovered.

During the reviewing procedure of the present paper, a correction by the authors of ref 1 has been submitted to, and has appeared in *Inorg. Chem.* **2009**, *48* (7), 3288−3289, and confirms the revised structure of the present paper.

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Supporting Information Available: Comparison between structure models, observed and calculated XRD and NPD patterns, experimental and calculated XRD patterns, a listing of observed and calculated powder diffraction intensities, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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