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A New Synthetic Route to $Mg_2Na_2NiH_6$ Where a $[NiH_4]$ Complex Is for the First Time Stabilized by Alkali Metal Counterions

Karim Kadir* and Dag Noréus

Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University,
S-106 91 Stockholm, Sweden

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$Mg_2Na_2NiH_6$ was synthesized by reacting NaH and Mg_2NiH_4 at 310 °C under hydrogen pressure. The novel structure type was refined from neutron-diffraction data in the orthorhombic space group *Pnma* (No. 62), with unit cell dimensions of $a = 11.428(2)$, $b = 8.442(2)$, and $c = 5.4165(9)$ Å and a unit cell volume = 523 Å^3 ($Z = 4$). The structure can be described by $(Mg_2H_2)^{2+}$ layers intersected by $(Na_2NiH_4)^{2-}$ layers. The $[NiH_4]^{4-}$ complex is approximately tetrahedral, indicating formal zerovalent nickel. This is the first example of a solid-state hydride where a $[NiH_4]^{4-}$ complex is directly stabilized by alkali metal ions instead of the more polarizing Mg^{2+} ions. A rather long nickel–hydrogen bond distance of 1.65 Å indicates a weaker Ni–H bond as a result of the weaker support from the less polarizing alkali metal counterions.

Introduction

With the use of a new synthetic technique for metal hydrides, a quaternary $Mg_2Na_2NiH_6$ hydride was discovered. It has a structure related to but also interestingly different from Mg_2NiH_4. Both hydrides have high hydrogen contents, 3.8 and 3.6 wt %, respectively, making them candidates for hydrogen storage. Both contain 18 electrons, within $[NiH_4]$ complexes, and with formal zerovalent nickel. This implies unusual and interesting structural and bonding properties. In Mg_2NiH_4, the rather weak Ni−H bond in the $[NiH_4]$ complex is strengthened by the support from strongly polarizing Mg^{2+} ions. This makes Mg_2NiH_4 too stable with respect to hydrogen release for most practical applications. In $Mg_2Na_2NiH_6$, the $[NiH_4]$ complex is surrounded by less polarizing Na^+ ions, which results in weaker Ni−H bonds as will be described below.

Mg_2NiH_4 became a target for many studies since its discovery by Reilly and Wiswall in 1968.[1] Mg_2NiH_4 is at first sight an unlikely compound. The structure is built by close-to-tetrahedral $[NiH_4]$ complexes counterbalanced by magnesium ions. The central nickel atom is in a formal zerovalent d^{10} oxidation state surrounded by four hydride ligands. Such low oxidation states usually require good electron-accepting ligands, for example, carbonyl, cyanide, or phosphine groups, where suitable ligand orbitals help to relieve the high electron density on the central atom. This is conventionally referred to as electron “back-donation”. In homoleptic complexes with hydrogen as the ligand this is not directly possible. In solid-state hydrides, however, the easily deformable electron density of the very polarizable hydride ion H^- offers a mechanism for relief of the high electron density indirectly by transferring it to the counterions in the solid-state lattice. In the related hydrides of Li_2PdH_2 and Na_2PdH_2, this leads to metallic conductivity when a small number of electrons is transferred to the alkali metal matrix, from the linear 14 electron $[PdH_2]$ complex with formal zerovalent d^{10} palladium.[2,3]

As the lattice is directly involved in the stabilization mechanism, it implies that lattice defects such as disorder and impurities may have profound effects on stability as well as the electric properties. Mg_2NiH_4 is a semiconductor with a not too wide band gap of 1.7 eV similar to that of silicon. Doping from impurities or nonstoichiometry can give it metal-like electric conductivity, and we have reported that this conductivity is connected to the presence of a stacking fault in the lattice and described how it can be switched on and off by manipulating the density of stacking faults.[4] The nickel−hydrogen bond in the $[NiH_4]$ complex is rather weak, and theoretical calculations of the electron structure show

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* To whom correspondence should be addressed. E-mail: karim@struc.su.se. Tel: +46 8 16 23 83. Fax: +46 8 15 21 87.

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that the complex needs support from the small and strongly polarizing Mg^{2+} counterions for stability.[5,6] Similarly, all of the transition metal hydrido complexes of the first row transition metals have mainly been synthesized with Mg^{2+} counterions either alone or in combination with other counterions. There are now a number of these as shown by the examples of $Mg_3CrH_{\sim6}$, $Mg_3MnH_{\sim6}$, Mg_3MnH_7, Mg_2FeH_6, Mg_2CoH_5, $CaMgNiH_4$, $SrMgNiH_4$, $YbMgNiH_4$, and $LaMg_2NiH_7$.[7−12] Of all of these complexes, only $[FeH_6]^{4-}$ has been synthesized without Mg^{2+} counterions, but then only with low yield in incomplete reactions (i.e., in Ca_2FeH_6 and Sr_2FeH_6 with a not too electron-dense d^6 configuration).[13] We also tried to make the corresponding hydrides with alkali metal counterions by reacting powders of all the first row transition metals with the alkali metals of Li, Na, and K or corresponding binary hydrides at temperatures and hydrogen pressures of up to 600 °C and 150 bar. In no case could we obtain a reaction. On the other hand, transition metal hydrido complexes of the second and third row transition metals, which are held together by stronger bonds, have been synthesized in large numbers with counterions of most of the alkali earth as well as alkali metals group. This shows that magnesium is especially important for stabilizing first row transition metal hydrido complexes, but in this paper we report the first quaternary hydride of this type, where an alkali metal is directly involved in the stabilization of a $[NiH_4]$ complex as its closest neighbor. It is also supported by Mg^{2+} ions but at a significantly longer distance from the complex. This hydride could not be synthesized directly from the elements but was made by first creating Mg_2NiH_4, which was subsequently reacted with NaH.

Experimental Section

The starting sodium metal ingot, with 99.95% purity, was obtained from Aldrich. The Mg_2Ni alloy ingot was obtained from Ergenics, USA (as their HYSTOR-301 Alloy). This alloy contains about 10 wt % extra magnesium to prevent the formation of the non-hydrogen absorbing $MgNi_2$ phase during casting. NaH/D and Mg_2NiH_4/D_4 were synthesized by reaction with H_2 and D_2 gases forming fine powders. The extra Mg in the Mg_2Ni alloy formed MgH_2/D_2. The X-ray powder diffraction patterns for the MgH_2/D_2, NaH/D, and Mg_2NiH_4/D_4 produced were consistent with data in the JCPDS tables. To protect the material from air or moisture, all storing and handling was done in a glovebox under continuously purified argon gas.

As nickel powder could not be made to react with Na or NaH, the quaternary hydride was made in a two-step reaction. First, the fine powders of Mg_2NiH_4 and NaH were mixed in a 1:1 molar ratio by grinding them together in a mortar. This mixture (∼2 g) was compacted in a tablet press at 3 kbar and sintered in a tube furnace at 300−315 °C in hydrogen of 50 bar for about 20 h. After cooling, the tablets were crushed and a small amount was removed for X-ray analysis. To obtain a fairly “single-phased” sample, the tablet had to be repressed again for two or three subsequent sintering periods. Additional starting material was added until we reached a molar ratio of 1:2 for Mg_2NiH_4 to NaH, whereby an olive-green powder was obtained. Several attempts were made in this iterative search before the optimum preparative conditions could be found. A typical successful synthesis started with a 1:2 molar mixture of Mg_2NiH_4 to NaH, which was compacted and sintered as described above. Regrinding, recompacting, and resintering were more essential than the length of the sintering period. During this period, we were able to add the balancing amounts of NaH and Ni powders. With each such cycle the amount of impurity phases was reduced. As this consumed a lot of deuterium, we stopped after three sintering periods for the larger sample used in the diffraction experiment.

X-ray and Neutron Powder Diffraction Data Collection and Structure Refinements. X-ray diffraction photographs were obtained from a subtraction-geometry Guinier-Hägg focusing camera, using strictly monochromatized Cu Kα_1 radiation. A single-coated X-ray film (CEA Reflex 15) was used in all the work. The films were evaluated by means of a computer-controlled single-beam microdensitometer designed for the scanning analysis of X-ray powder photographs.[14] The θ scale was calibrated by means of the internal (silicon) standard technique, using a parabolic correction curve. To localize the hydrogen atoms in the new hydrides we prepared a $Mg_2Na_2NiD_6$ sample for neutron diffraction. The diffraction patterns were recorded at room temperature at the R2 reactor in Studsvik, Sweden, using a cylindrical vanadium sample holder (diam = 5 mm) and a neutron wavelength of 1.47 Å.

With the use of the TREOR program[15] and the least-squares refinements program PIRUM,[16] the final X-ray powder pattern of $Mg_2Na_2NiH_6$ could be indexed on the basis of an orthorhombic structure with unit cell dimensions of $a = 11.428(2)$, $b = 8.442(2)$, and $c = 5.4165(9)$ Å and unit cell volume of 523 Å^3. The deuteride, $Mg_2Na_2NiD_6$, has unit cell dimensions of $a = 11.403(2)$, $b = 8.411(3)$, and $c = 5.405(2)$ Å and a unit cell volume of 518 Å^3. Metal deuterides often have smaller unit cell dimensions than those of the corresponding hydrides due to unharmonicity in the hydrogen vibrations. Several syntheses of both the hydride and the deuteride were made to verify that the difference in unit cell volume was not due to differences in hydrogen content. All syntheses, however, gave the same unit cell dimensions as given above, indicating that the compound had a preference for formation with full stoiciometry.

Systematic absences were consistent with space group *Pnma* (No. 62).[17] The positions of the heavy atoms were found by direct methods (SHELXS[18]), and subsequent Rietveld refinements RIET94[19,20] and FULLPROF[21] based on X-ray and neutron powder

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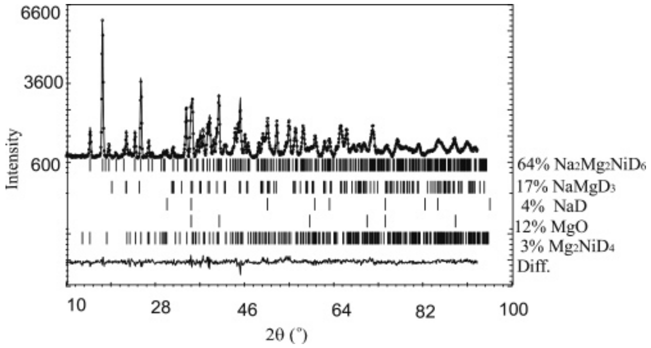

Figure 1. Rietveld-fitted profile and difference plot for $Mg_2Na_2NiD_6$. The neutron-diffraction data is obtained at room temperature with a wavelength = 1.47 Å. Tick marks and refined weight percentage are (top) for $Mg_2Na_2NiD_6$ and (below) for the impurity phases of $NaMgD_3$, NaD, MgO, and Mg_2NiD_4, respectively.

Table 1. Atomic Parameters from Rietveld-Fitted Neutron Powder Diffraction Data for $Mg_2Na_2NiD_6$ (Space Group *Pnma*; $Z = 4$)

atom	site	x	y	z	B_{iso}	Occ
Ni	4c	−0.001(3)	$^1/_4$	0.942(6)	2.3(8)	1
Mg	8d	0.270(3)	0.013(4)	0.863(7)	0.6(8)	1
Na1	4c	0.402(8)	$^1/_4$	0.030(2)	2.3(3)	1
Na2	4c	0.165(7)	$^1/_4$	0.573(2)	0.2(2)	1
D1	4c	0.099(4)	$^1/_4$	0.160(8)	4.1(2)	1
D2	8d	0.022(3)	0.102(3)	0.747(6)	1.9(8)	1
D3	4c	−0.141(4)	$^1/_4$	0.025(9)	2.6(1)	1
D4	8d	−0.135(3)	−0.016(5)	0.933(7)	4.5(1)	1

Table 2. Shortest Interatomic Distances (Å) and Angles (deg) Found in $Mg_2Na_2NiD_6$ in the NiD_4 Complex[a]

Ni−D1 = 1.65(2)	D1−Ni−D2 = 110.6(2)
2× Ni−D2 = 1.66(1)	D2−Ni−D2 = 96.0(2)
Ni−D3 = 1.64(2)	D1−Ni−D3 = 118.0(3)
	D2−Ni−D3 = 110.0(2)
Mg−D4 = 1.90(2)	Na1−D2 = 2.40(3)
Mg−D4 = 1.94(2)	Na1−D3 = 2.47(4)
Mg−D3 = 2.73(2)	Na2−D1 = 2.36(3)
D1−D4 = 2.06(2)	Na2−D2 = 2.23(2)
	Na2−D3 = 2.27(3)
Ni−Na1 = 2.80(4)	Mg−Na1 = 2.64(3)
Ni−Na2 = 2.75(3)	Mg−Na2 = 2.59(2)
Na1−Na2 = 3.07(4)	Mg−Mg = 2.75(1)

[a] Estimated standard deviations in parentheses.

patterns of $Na_2Mg_2NiD_6$ gave the atomic coordinates listed in Table 1. The final Rietveld *R* values were Bragg $R = 7.3$, $R_F = 4.6$, $R_P = 5.5$, and $R_{WP} = 7.05\%$ (cf. Figure 1). The interatomic distances are given in Table 2.

Results and Discussion

The structure of $Mg_2Na_2NiD_6$, as depicted in Figure 2 can be described by $(Mg_2D_2)^{2+}$ layers intersected by $(Na_2NiD_4)^{2-}$ layers. The $[NiD_4]^{4-}$ complex is approximately tetrahedral, indicating a formal zerovalent oxidation state for the central nickel atom. It is, however, slightly more distorted in $Mg_2Na_2NiD_6$ than in Mg_2NiD_4. The average Ni−D distance in $Mg_2Na_2NiD_6$ is 1.65 Å. This is significantly longer than the average distance of 1.54 Å in the corresponding complex in Mg_2NiD_4, indicating a weaker bond. In Mg_2NiD_4 the small polarizing Mg^{2+} ions compress the complex.[5] In $Mg_2Na_2NiD_6$ the Mg−D distance to the hydrogen atoms in the complex is a long >2.7 Å compared with 1.9−2.1 Å in Mg_2NiD_4. A short Mg−D comparable to that in MgD_2 is only found within the $(Mg_2D_2)^{2+}$ layers. On the other hand, the Na−D distances in the $(Na_2NiD_4)^{2-}$ layers are short, indicating considerable electron overlap and covalent bonding contribution to the complex. The Na−D distances are significantly shorter compared with NaD (2.45 Å), whose bonding we earlier described with a substantial covalent character as compared to the ionic and isostructural NaCl.[22,3]

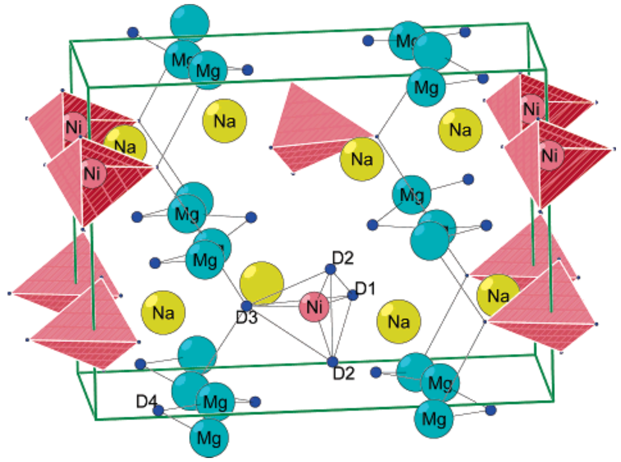

Figure 2. The structure of $Mg_2Na_2NiD_6$ viewed along the *c*-axis. The unit cell axes are marked with green lines. Ni atoms and NiH_4 tetrahedra are red. The hydrogen atoms (small, blue) are connected to the closest Ni and Mg atoms. The structure can be visualized as $(Mg_2H_2)^{2+}$ layers intersected by $(Na_2NiH_4)^{2-}$ layers.

This means that Na^+ has overtaken the role of Mg^{2+} as a stabilizer for the NiH_4 complex and could open the possibility of the synthesis of Na_4NiH_4 or even Li_4NiH_4 with possibly better hydrogen storage properties. Unfortunately, so far we have failed to do this. It could be due to some kinetic restriction necessitating the presence of Mg for formation of the NiH_4 complex or that the $(Na_2NiD_4)^{2-}$ layers still need the support from the $(Mg_2D_2)^{2+}$ layers for stability. In this respect, it is interesting to note that the unusually short D−D distance (2.06 Å) between the hydrogen atoms in the $(Na_2NiD_4)^{2-}$ and $(Mg_2D_2)^{2+}$ layers is shorter than the minimum distance of 2.1 Å stipulated by the "Switendick criterion".[23,24] This indicates a fairly strong interaction between the layers mediated by the hydrogen atoms. We hope to elucidate this phenomenon by synthesizing and characterizing additional quaternary hydrides of this kind.

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Supporting Information Available: Observed, calculated, 2θ, d-values, and intensities for $Na_2Mg_2NiH_6$ using Guinier-Hägg X-ray diffraction Cu Kα_1 radiation and with Si as the internal standard at 293 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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