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Karim Kadir* and Dag Noréus: A New Synthetic Route to $Mg_2Na_2NiH_6$ Where a $[NiH_4]$ Complex Is for the First Time Stabilized by Alkali Metal Counterions

Pages 2220−2223. Prompted by a report in the Swiss Society for Crystallography Newsletter SKG/SSCr No. 75 by Orlova and Yvon suggesting a transposition of the atoms to better describe the structure,[1] the structure was reinvestigated. A better fitting of the Rietveld refinement can be made if the magnesium atom position was interchanged with the deuterium position in the Mg−D layer outside of the complex between the $Na[NiD_4]$ layer (cf. Figure 1 and Tables 1 and 2). The R_F and R_B values were reduced from 4.6 and 7.3 to 3.0 and 5.0, respectively. This slight improvement of the earlier reported fit is attributed to the small difference in the neutron scattering length between magnesium and deuterium. The differences in the refined atomic parameters were marginal, but the $[NiD_4]$ complex in Figure 1 is now surrounded by both sodium and magnesium counterions instead of only sodium counterions. This means that the title compound is still the first where a $[NiH_4]$ complex is synthesized with alkali metal counterions but now has additional support from polarizing magnesium ions, underlining the importance of magnesium for supporting nickel hydrido complexes in the solid state.[2,3] In the $[NiH_4]$ complex, it is mainly the s and d electrons that are bonding active,[3,4] but the 3d electrons are not as good for bonding with hydrogen compared to the more diffuse 4d or 5d electron orbitals with which many hydrido complexes have been found with less polarizing counterions. There is therefore still no nickel hydrido complex without the support of magnesium. In Figure 1, the shortening of the D−D distances within the complex, from D1−D3 (2.67 Å) over D1−D2 and D2−D3 (2.56 Å) to D2−D2 (2.45 Å), is

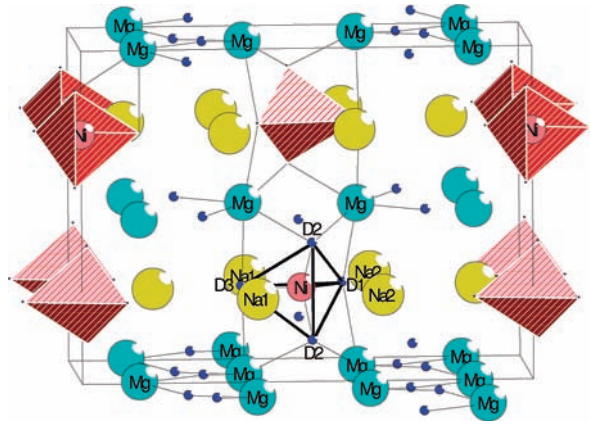

Figure 1. Crystal structure of $Mg_2Na_2NiD_6$.

Table 1. Crystallographic Parameters for $Mg_2Na_2NiD_6$ in Space Group *Pnma* (62), $Z = 4$[a]

atom positions						
atom	site	*x*	*y*	*z*	B_{iso}	Occ
Ni	4c	0.0013(6)	0.25	0.9451(1)	1.44(1)	1
Mg	8d	−0.1271(6)	−0.007(1)	0.9437(2)	2.71(2)	1
Na1	4c	0.3909(2)	0.25	0.0386(4)	3.33(4)	1
Na2	4c	0.1716(1)	0.25	0.5673(3)	2.67(4)	1
D1	4c	0.0979(1)	0.25	0.1453(2)	4.63(3)	1
D2	8d	0.0202(6)	0.1043(8)	0.7644(1)	3.02(2)	1
D3	4c	−0.1300(8)	0.25	0.0350(2)	2.71(2)	1
D4	8d	0.2743(6)	0.0132(9)	0.8557(1)	3.58(2)	1

[a] $R_B = 4.95\%$, $R_F = 2.97\%$, $R_P = 3.6\%$, and $R_{WP} = 4.62\%$. The structure was refined from neutron powder diffraction data by using the Rietveld refinement program (*RIET94*[5,6] and *FULLPROF*[7]). (estimated standard deviations from the refinements are in parentheses).

Table 2. Shortest Interatomic Distances in Ångströms Found in $Mg_2Na_2NiD_6$ and Angles in the NiD_4 Complex (Estimated Standard Deviations in Parentheses)

Distances (Å) in $Mg_2Na_2NiD_6$			
Ni−D1	1.55(1)	Mg−D1	2.13(1)
Ni−2D2	1.58(1)	Mg−D2	2.15(1)
Ni−D3	1.58(1)	Mg−D2	2.16(1)
		Mg−D3	2.22(1)
Ni−2Mg	2.57(1)	Mg−D4	2.00(1)
Ni−2Mg	2.61(1)	Mg−D4	1.98(1)
Ni−Na1	3.06(2)		
Ni−Na1	2.90(2)	Mg−Mg	2.96(1)
Ni−Na2	2.81(2)	Mg−Na1	3.39(2)
		Mg−Na2	3.38(2)
Na1−D1	2.91(2)	Na2−D1	2.43(2)
Na1−D2	2.52(2)	Na2−2D2	2.37(2)
Na1−D3	2.32(2)	Na2−D3	2.33(2)
Na1−2D4	2.59(1)	Na2−D4	2.57(1)
Na1−Na2	3.25(3)	Na2−2D4	2.79(1)
D1−2D2	2.56(1)	D2−D2	2.45(1)
D1−D3	2.67(1)	D2−D3	2.56(1)
D1−D4	2.88(1)	D2−D4	2.98(1)
		D2−D4	3.04(1)
D3−2D4	2.82(1)	D4−2D4	2.768(3)
D3−D4	3.10(1)		
Angles (deg) in the NiD_4 Complex			
D1−Ni−D2	109.7(2)	D1−Ni−D3	117.5(2)
D2−Ni−D2	101.6(3)	D3−Ni−D2	108.6(6)

possibly explained by a compression from magnesium that creates an internal pressure by striving to reduce the hydrogen coordination number.[3] The Mg−D distances involving the complexes are around 2.2 Å, and the Mg−D distance to the interstitial D is 2.0 Å, similar to that in MgH_2.

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