**Supporting Information**

*Infrared spectroscopy*

IR spectrum for hexa-aqua dodecahydro *closo*-dodecaborate of nickel shown in Figure SI1 is typical for isolated $B_{12}H_{12}^{2-}$ anions and water molecules [1, 2]. One can observe the absorption of B-H cage at 1063 $cm^{-1}$ and B-H stretching absorption around 2470 $cm^{-1}$. The absorptions characteristic of water are observed at 1605 $cm^{-1}$ for bending mode and around 3500 $cm^{-1}$ for stretching mode.

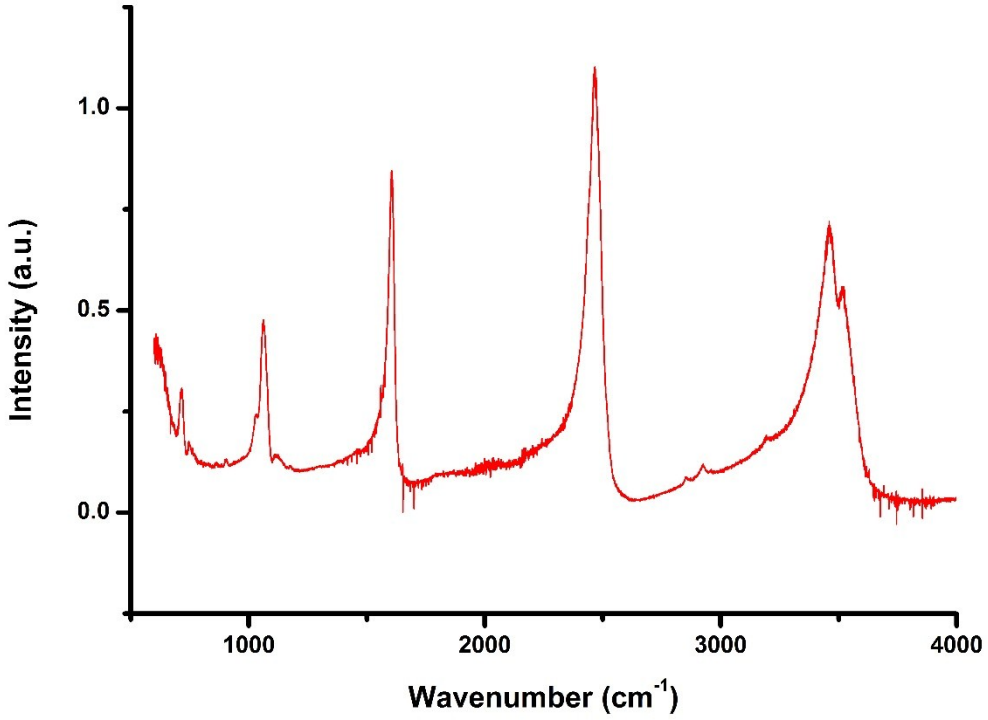


**Figure SI1.** IR spectra of *tri*-$Ni(H_2O)_6B_{12}H_{12}$ at room temperature.

[1] Muetterties E.L., Balthis J.H., Chia Y.T., Knoth W.H., Miller H.C., *Inorg. Chem*., **1964**, 3, 444-451.

[2] Max J.J., Chapados C., *Journal of chemical physics*, **2009**, 131, 184505.

*Rietveld plots*

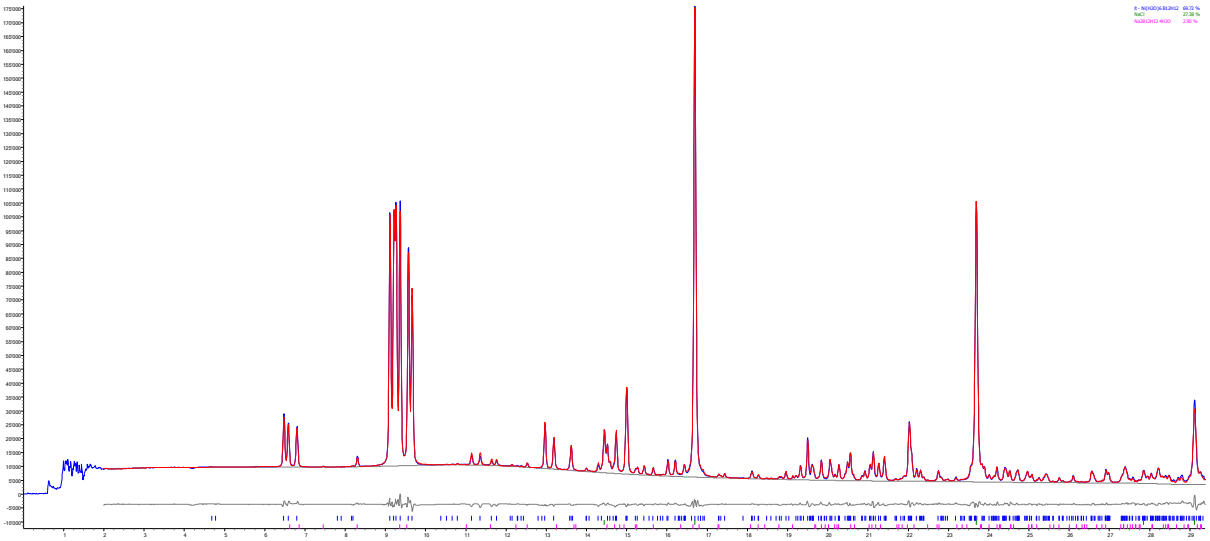

**Figure SI2.** Rietveld plot for refinement of *tri*-$Ni(H_2O)_6B_{12}H_{12}$ at T = 30 °C. SNBL, λ = 0.8187 Å, $\chi^2$ = 4489, $R_{wp}$ (bgr. corrected) = 0.05, $R_{Bragg}$ = 0.01.

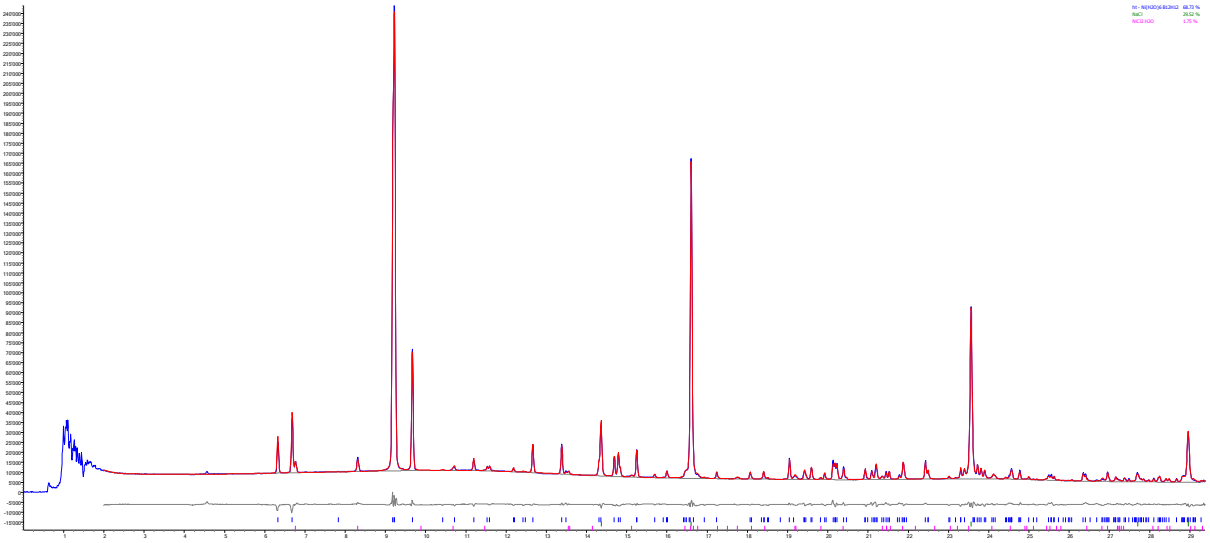

**Figure SI3.** Rietveld plot for refinement of $m_2$-$Ni(H_2O)_6B_{12}H_{12}$ at T = 182 °C. SNBL, λ = 0.8187 Å, $\chi^2$ = 5625, $R_{wp}$ (bgr. corrected) = 0.07, $R_{Bragg}$ = 0.02.

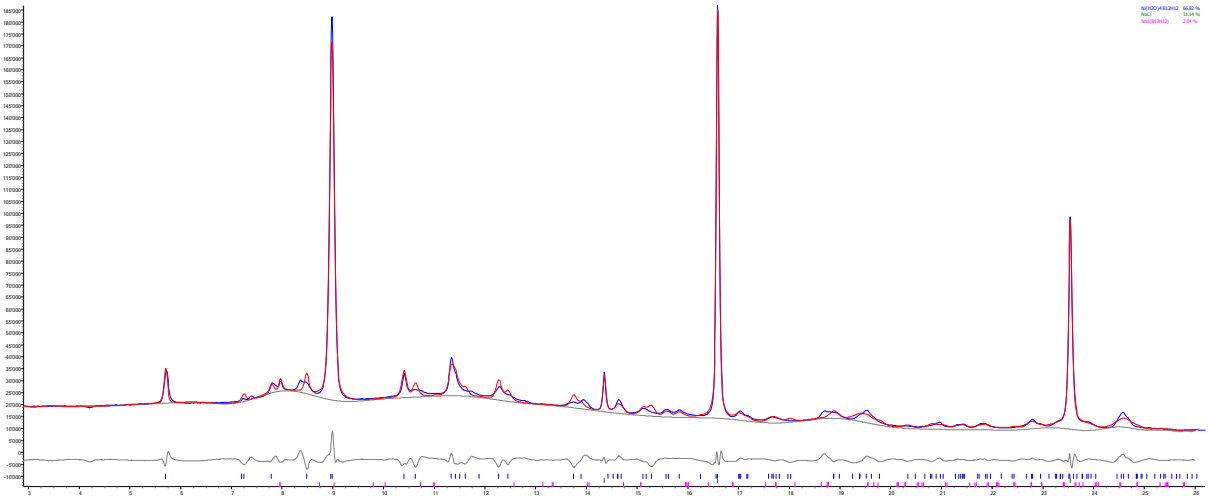

**Figure SI4.** Rietveld plot for refinement of *m*-$Ni(H_2O)_4B_{12}H_{12}$ at T = 200 °C. SNBL, λ = 0.8187 Å, $\chi^2$ = 24964, $R_{wp}$ (bgr. corrected) = 0.13, $R_{Bragg}$ = 0.03.

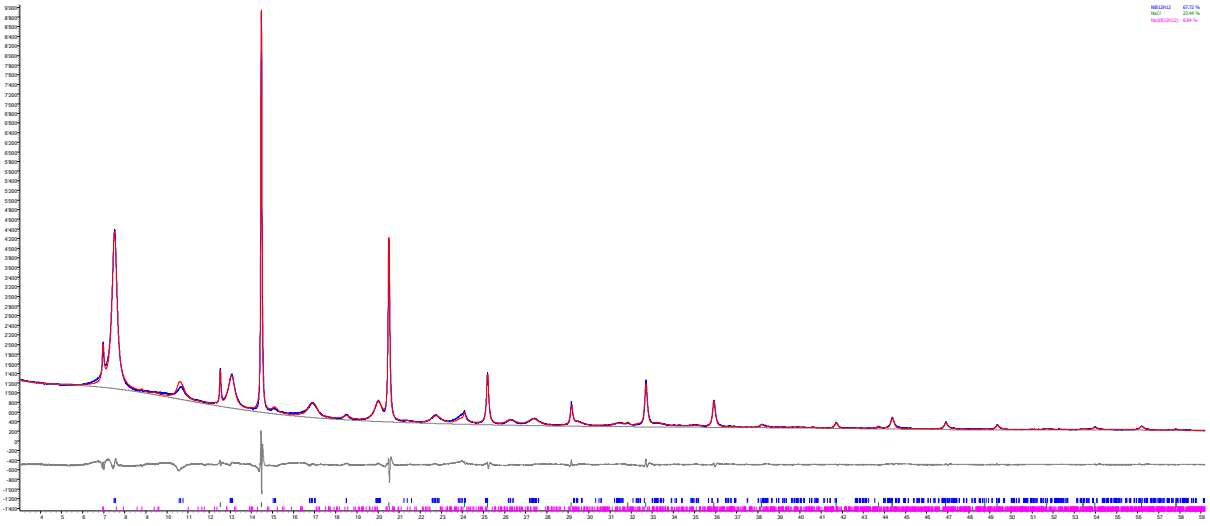

**Figure SI5.** Rietveld plot for refinement of *m*-$NiB_{12}H_{12}$ at T = 20 °C. SLS, λ = 0.7097 Å, $\chi^2$ = 21, $R_{wp}$ (bgr. corrected) = 0.12, $R_{Bragg}$ = 0.01.

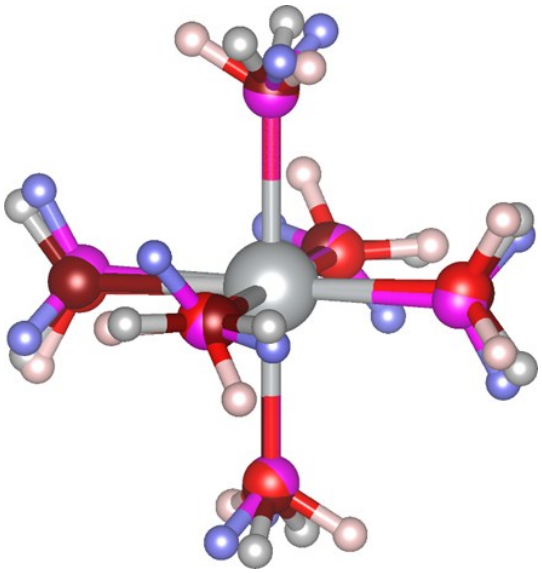

**Figure SI6**. Superposition of $Ni(H_2O)_6^{2+}$ complex extracted from *tri*-$Ni(H_2O)_6(B_{12}H_{12})$ (pink, light blue) and *m*$_2$-$Ni(H_2O)_6(B_{12}H_{12})$ (red, light pink). The gas phase molecule is shown for comparison in brown (oxygen) and grey (hydrogen). The nickel atom as large grey sphere.

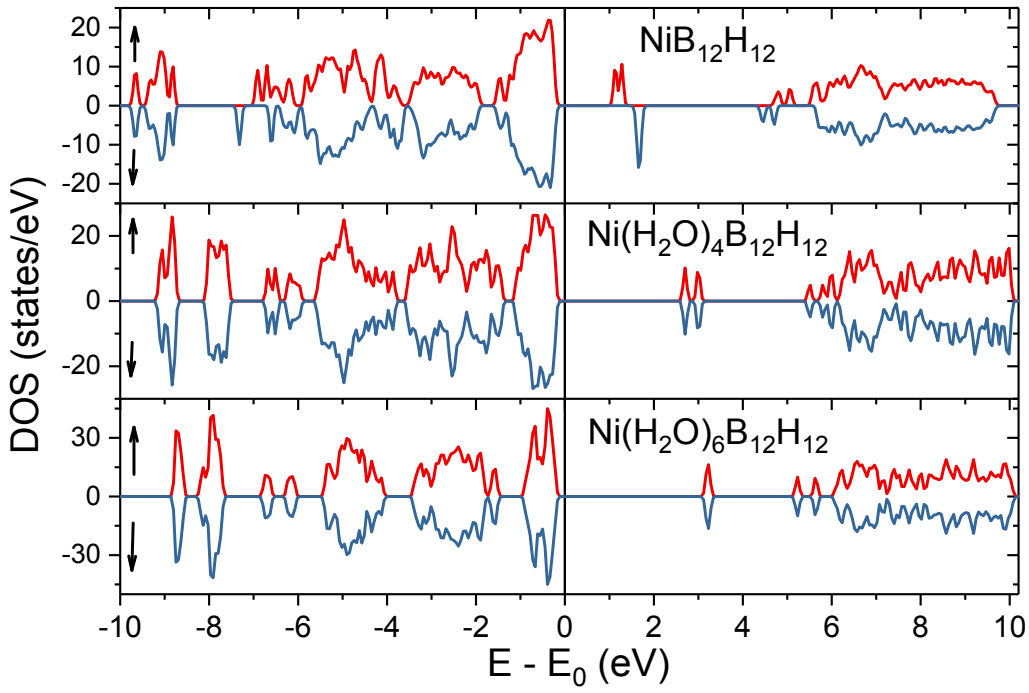


**Figure SI7**. Electronic density of states for Ni-*closo*-borates. All systems are insulating, and the gap states related to *d*-shell of Ni are present. For the octahedrally coordinated cation in *tri*-$Ni(H_2O)_6B_{12}H_{12}$ the $e_g$ states are located 3.05 eV above the Fermi level; quasi-square planar coordination in *m*-$Ni(H_2O)_4B_{12}H_{12}$ splitting of $d_{x2-y2}$ and $d_{z2}$ are 2.55 eV above Fermi level. For anhydrous compound more complex structure of the empty gap states located 1.32 eV above Fermi level are present. The position of these gap states depends on Hubbard on-site repulsion U.

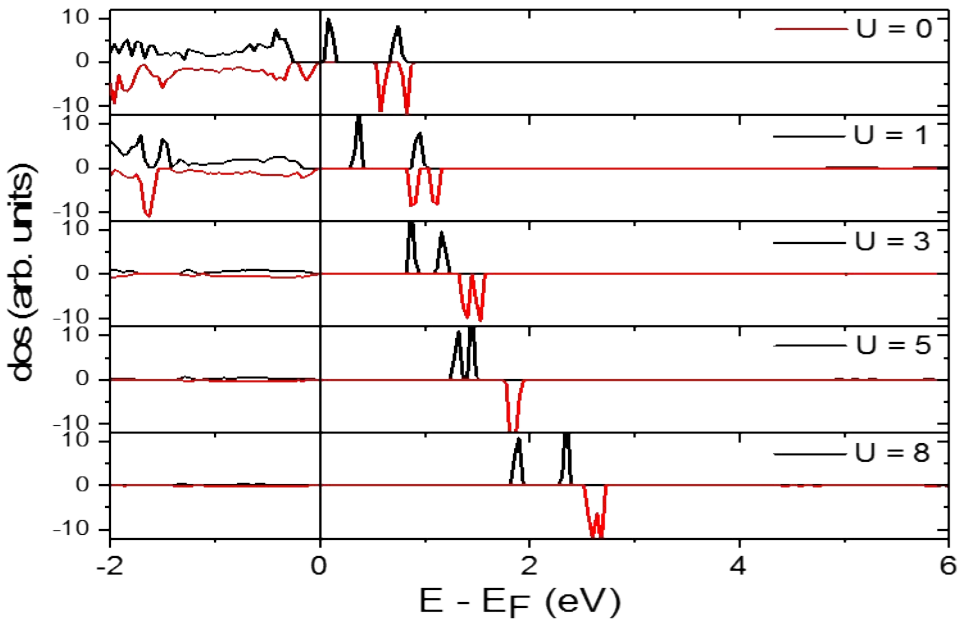


**Figure SI8**. The density of states for nickel *d*-states calculated for anhydrous $NiB_{12}H_{12}$ using various Hubbard on-site repulsion U in eV. The position and splitting of the gap states depends strongly on the strength of U.