Complex hydrides, such as NaAlH₄, are reversible hydrogen stores operating only at elevated temperatures, even in the presence of catalysts. Chemical hydrides, such as NH₂BH₄ (AB), release a number of by-products upon thermolysis and are often non-reversible. Here we show that ball milling of NaAlH₄-4AB mixture or heating it to ~70 °C produces the first Al-based amidoborane Na[Al(NH₂BH₄)]₄ and 4.5 wt% of pure hydrogen. The structure was solved from synchrotron X-ray powder diffraction and confirmed through DFT and spectroscopic studies, contains previously unknown tetrahedral [Al(NH₂BH₄)]⁺ anions, where NH₂BH₄⁻ ligands are coordinated to Al via N atoms. Upon heating, this complex yields in two steps 9 wt% of hydrogen with traces of ammonia, NaBH₄, and amorphous products.

The structure of Na[Al(NH₂BH₄)]₄ (space group P-1, a = 9.4352(2), b = 7.7198(1), c = 7.6252(1) Å; α = 97.211(1), β = 109.223(2), γ = 89.728(2)°, Rₚ = 5.7 %) is the second amidoborane with a triclinic structure, after the bimetallic Na[Li(NH₂BH₄)]₄. The central Al atom adopts tetrahedral coordination exclusively via nitrogen atoms from four NH₂BH₄⁻, making it a new member of Al complex hydrides with tetrahedral coordination, after alanates AlH₄⁻, complex amides [Al(NH₂)₄]⁺ and borohydrides [Al(BH₄)₄]⁻. The structure consists of [Al(NH₂BH₄)]⁺ anions and Na⁺ cations, the latter are being octahedrally coordinated by six BH₄⁻ groups, similar to Na⁺ in Na₂[Mg(NH₂BH₄)] [12]. The Na(NH₂BH₄)₆ octahedra are linked via edges into infinite zig-zag chains. The dehydrogenation of the complex is partially reversible: ~27% of the released hydrogen can be reabsorbed at 250 °C and 150 bar of hydrogen. Hydrogen reabsorption does not regenerate NaAlH₄ or Na[Al(NH₂BH₄)]₄, but occurs between amorphous products and intermediates of the dehydrogenation. Further study of the Al-B-N-H products may open a way to a new family of reversible hydrogen storage materials. The combination of complex and chemical hydrides is made possible thanks to the lower stability of Al-H bonds compared to B-H and due to the strong Lewis acidity of the complex-forming Al⁺. This system opens a way to a series of aluminium tetraamidoboranes with improved hydrogen storage properties such as hydrogen storage density, hydrogen purity and the reversibility.


Keywords: X-ray powder diffraction, complex hydrides, hydrogen storage