MS41-O5 The crystal structure and decomposition properties of the first Al-based amidoborane from *in situ* x-ray powder diffraction

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Complex hydrides, such as $NaAlH_4$, are reversible hydrogen stores operating only at elevated temperatures, even in the presence of catalysts. Chemical hydrides, such as NH_3BH_3 (AB), release a number of by-products upon thermolysis and are often non-reversible. Here we show that ball milling of $NaAlH_4$–4AB mixture or heating it to ~70 °C produces the first Al-based amidoborane $Na[Al(NH_2BH_3)_4]$ 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 $[Al(NH_2BH_3)_4]^-$ anions, where $NH_2BH_3^-$ ligands are coordinated to Al via N atoms. Upon heating, this complex yields in two steps 9 wt% of hydrogen with traces of ammonia, $NaBH_4$, and amorphous products.

The structure of $Na[Al(NH_2BH_3)_4]$ (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)°, R_F = 5.7 %) is the second amidoborane with a triclinic structure, after the bimetallic $Na[Li(NH_2BH_3)_2]$.[1] The central Al atom adopts tetrahedral coordination exclusively via nitrogen atoms from four $NH_2BH_3^-$, making it a new member of Al complex hydrides with tetrahedral coordination, after alanates AlH_4^-, complex amides $[Al(NH_2)_4]^-$ and borohydrides $[Al(BH_4)_4]^-$. The structure consists of $[Al(NH_2BH_3)_4]^-$ anions and Na^+ cations, the latter are being octahedrally coordinated by six BH_3 groups, similar to Na^+ in $Na_2[Mg(NH_2BH_3)_4]$.[2] The $Na(NH_2BH_3)_6$ 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 $NaAlH_4$ or $Na[Al(NH_2BH_3)_4]$, 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^{3+}. 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.

1. K. J. Fijalkowski, R. V. Genova, Y. Filinchuk et al. *Dalton Trans.* **2011**, *40*, 4407-4413.

2. H. Wu, W. Zhou, F. E. Pinkerton et al. *Chem. Commun.* **2011**, *47*, 4102-4204.

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