Development and Characterization of Reactive Hydro-*closo*-Borates with $[B_nH_n]^{2-}$ Anions (n = 10 and 12): From New Crystal Motifs to High-Energy Materials

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Hydro-*closo*-borates have been well studied for over six decades, during which various salts and organic derivatives could be synthesized and characterized [1]. Meanwhile, there is a growing emphasis on transitioning towards carbon-neutral energy sources. Boron, alongside carbon, aluminum and hydrogen, is capable of releasing significant energy amounts upon oxidation. Hydrogen exhibits the highest energy density among these elements, but the energy density of boron surpasses that one of carbon (H: 120 kJ/g, B: 58 kJ/g, C: 33 kJ/g).

Our research aimed to synthesize new types of solid energy carriers, focusing on hydro-*closo*-borates. Despite the extensive research, investigations into the energetic aspects of these hydro-*closo*-borates remained limited [2]. *Closo*-dodecaborate anions, particularly when saltified with metal cations like K^+, Rb^+ and Cs^+, exhibit remarkable stability. While the thermal decomposition of these salts is typically endothermic, the incorporation of energetic cations such as ammonium, hydrazinium and guanidinium activates hydro-*closo*-borates for chemical energy storage and hydrogen release. Oxoanions like nitrate and perchlorate were introduced to enhance the hydroborate activation and mitigate oxygen presence, resulting in higher energy release even under inert-gas atmosphere (N_2 or Ar).

We introduced the new energetic salts with hydrazinium [3] and guanidinium [4], and explored more complex compounds like *anti*-perovskites and entirely novel crystal-structure motifs. The synthesized energetic *anti*-perovskite compounds A_3BC, categorized by high energy content, feature hexagonal arrangements in two series: one with higher thermal stability ($Cs_3X[B_{12}H_{12}]$, $X^- = [NO_3]^-$, $[ClO_3]^-$, $[ClO_4]^-$) [5] and another one with reduced thermal stability, substituting cesium with hydrazinium ($(N_2H_5)_3X[B_{12}H_{12}] \cdot H_2O$, $X^- = [NO_3]^-$, $[ClO_4]^-$) [6]. Additionally, a new hexagonal channel motif for the composition A_4B_2C was developed with the synthesis of compounds like $(N_2H_5)_4X_2[B_{12}H_{12}]$ ($X^- = Cl^-$, Br^-), where hydrazinium cations and halide anions form hexagonal channels accommodating the anionic boron clusters (Figure 1). One of the reasons for their stability are dihydrogen bonds ($N^{\delta-}$–$H^{\delta+}\cdots H^{\delta-}$–$B^{\delta+}$), which result from the interaction between the negatively polarized hydrogen atoms at the boron-cluster anions $[B_{12}H_{12}]^{2-}$ and the positively polarized hydrogen atoms at the hydrogen-containing cations, such as ammonium $(NH_4)^+$, hydrazinium $(N_2H_5)^+$ or guanidinium $(CN_3H_6)^+$. But these are also paving the way for hydrogen evolution after thermal activation.

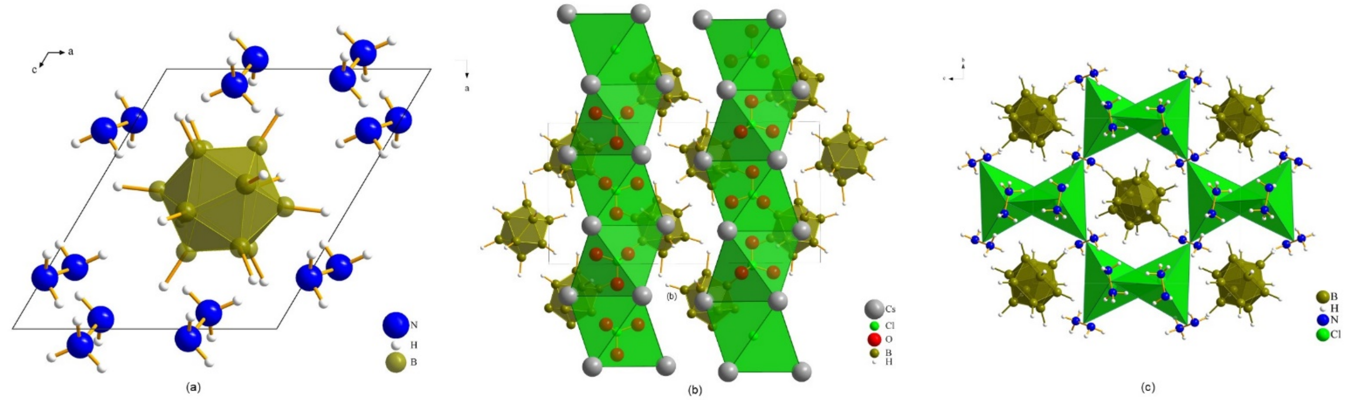

Figure 1. Crystal structures of $(N_2H_5)_2[B_{12}H_{12}] \cdot 2\ N_2H_4$ (a, *left*), $Cs_3[ClO_4][B_{12}H_{12}]$ (b, *mid*), $(N_2H_5)_4Cl_2[B_{12}H_{12}]$ (c, *right*).

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