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Hydrogen positions in magnesium borohydride ammoniates

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Solid state hydrogen materials have been investigated intensively during the last decade as a result of their high hydrogen content [1]. This is attractive, because hydrogen is a promising energy carrier in a future society based on renewable energy. However, hydrogen is typically bonded too strongly by covalent/metallic/ionic bonds in the major part of the known solid state hydrogen storage materials. This gives rise to high operating temperature for hydrogen release and uptake.

Recently, dihydrogen bonds between partly negative hydrogen from for example BH_4^- and partly positive hydrogen atoms from for example NH_3 have shown promising properties. Unlike the classical hydrogen bonds, the dihydrogen bonds can react in the solid state via elimination of hydrogen by exchanging the weak $\text{H}\delta^+\cdots\text{H}\delta^+\cdots\text{H}\delta^+\cdots\text{H}\delta^+$ interactions for strong covalent bonds, and thus may open new routes to rational design of structures and hydrogen release reaction mechanisms. Among the most classical systems containing dihydrogen bonds are the amide-hydride system, $\text{LiNH}_2\text{-LiH}$ [2] and ammonia borane, NH_3BH_3 [3].

Metal borohydride ammoniates, $\text{M}(\text{BH}_4)_m\cdots n\text{NH}_3$, is a newer class, which has been studied for hydrogen storage purposes since 2009. From powder X-ray diffraction, Soloveichik et al. solved the crystal structures of two new magnesium borohydride ammoniates, namely $\text{Mg}(\text{BH}_4)_2\cdots 6\text{NH}_3$ and $\text{Mg}(\text{BH}_4)_2\cdots 2\text{NH}_3$ [4]. In $\text{Mg}(\text{BH}_4)_2\cdots 6\text{NH}_3$, Mg^{2+} is octahedrally coordinated by NH_3 , while the BH_4^- groups act as counter ions. On the other hand, Mg^{2+} is tetrahedrally coordinated by two NH_3 and two BH_4^- groups in $\text{Mg}(\text{BH}_4)_2\cdots 2\text{NH}_3$, and the structure is built of layers mediated by dihydrogen bonds. Whereas $\text{Mg}(\text{BH}_4)_2\cdots 6\text{NH}_3$ releases NH_3 (not suitable for hydrogen storage applications), mainly hydrogen is released from $\text{Mg}(\text{BH}_4)_2\cdots 2\text{NH}_3$ which may reflect the importance of the dihydrogen bond.

A range of new metal borohydride ammoniates with desirable hydrogen storage properties have been synthesized since 2009 [5,6]. However, the crystal structures are all solved from X-ray diffraction, which does not sufficiently determine the hydrogen positions. Indeed, these positions and the dihydrogen interaction are of high interest, since they play a crucial role tuning the compounds given rise to hydrogen release rather than ammonia release. Therefore, we would to investigate metal borohydride ammoniates by neutron diffraction for the first time; i.e. to accurately determine the hydrogen positions for $\text{Mg}(\text{BH}_4)_2\cdots 2\text{ND}_3$ and

Mg(11BD4)2•??6ND3 in order to better understand the dihydrogen interaction. The PUS instrument at the JEEP II infrastructure should be well-suited for this task. Samples with deuterium and 11-B are prepared due to the high cross sections for incoherent neutron scattering and neutron absorption for natural hydrogen and natural boron, respectively.

References

1. S. I. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel, and C. M. Jensen, *Chem. Rev.*, 2007, 107, 4111•??4132.
2. P. Chen, Z. Xiong, J. Luo, J. Lin, and K. L. Tan, *Nature*, 2002, 420, 302•??304.
3. W. T. Klooster, T. F. Koetzle, P. E. M. Siegbahn, T. B. Richardson, and R. H. Crabtree, *J Am Chem Soc*, 1999, 121, 6337•??6343.
4. G. Soloveichik, J.-H. Her, P. W. Stephens, Y. Gao, J. Rijssenbeek, M. Andrus, and J.-C. Zhao, *Inorg Chem*, 2008, 47, 4290•??4298.
5. Y. Guo, H. Wu, W. Zhou, and X. Yu, *J. Am. Chem. Soc.*, 2011, 133, 4690•??4693.
6. Y. Guo, X. Yu, W. Sun, D. Sun, and W. Yang, *Angew Chem Int Ed*, 2011, 50, 1087•??1091.