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Aluminium complexes of B- and N-based hydrides: Synthesis, structures and hydrogen storage properties☆

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ARTICLE INFO

Article history:
Received 15 February 2016
Received in revised form
20 May 2016
Accepted 23 May 2016
Available online 11 June 2016

Keywords:
Aluminium
Complex hydrides
Crystal structure
New materials
Hydrogen storage

ABSTRACT

The storage of hydrogen in a solid state is one of the main challenges for stationary and mobile applications. Light metal hydrides have attracted significant attention as potential candidates for energy storage. Remarkably, Al-containing hydrides, namely AlH_3 and $M(AlH_4)_n$, are among the most fascinating classes of materials, able to cycle up to 5.5 wt% of hydrogen at moderate temperatures. This review covers the recent research on the families of Al-based complex hydrides involving other light elements such as B and N. They were classified according to the charge of the Al-based complexes, as anionic, molecular, cationic or "autoionized" where Al is centering both the cation and the anion. The factors influencing the stability and the hydrogen purity of the series of anionic aluminium amides $M[Al(NH_2)_4]_n$, borohydrides $M[Al(BH_4)_4]$ and amidoboranes $M[Al(NH_2BH_3)_4]$, as well as molecular $[Al(L)(BH_4)_3]$ (L = molecular ligands) and cation $[Al(NH_3)_6]^{3+}$-based complexes are discussed. In particular, the ability of the strong Lewis acid Al^{3+} to coordinate both the initial hydrogenated species as well as their dehydrogenation products makes it a good template for chemical transformations involving light chemical and complex hydrides.

Introduction

An increase in the consumption of non-renewable fossil fuels is producing not only a challenge of new sustainable energy carriers, but also leads to environmental pollution and climate changes induced by carbon dioxide CO_2. Thus the transition towards a new carbon-free and reliable energy system capable of substituting current and future energy demands is one of the greatest challenges of the 21st century. In line with these demands, hydrogen has an extreme potential as the cleanest energy carrier, see e.g. Ref. [1]. It can be produced from renewable energy sources by electrolytic water splitting from hybrid solar–hydrogen or other systems [2]. However, a major challenge in the future of the "hydrogen economy" is the development of efficient hydrogen storage systems, especially for mobile applications [3,4]. In particular, the efficient storage of pressurized and liquefied hydrogen has technical issues of high pressures (350–700 bar) and cryogenic temperatures (−253 °C) [4]. That is why in recent years much attention was paid to solid state hydrogen storage in a form of light metal complex and chemical hydrides, from which hydrogen can be released either by thermolysis or via hydrolysis [5–8].

☆ Dedicated to the 65 years anniversary of Professor Gérald Pourcelly.

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http://dx.doi.org/10.1016/j.ijhydene.2016.05.196

Mobile applications is one of the most important directions for the "hydrogen economy". According to the U.S. Department of energy, perspective systems for mobile applications require high hydrogen content which should be above 5.5 wt %, and a low gravimetric density of 40 g/L [9]. The second important detail is a low operational temperature (60–120 °C), suitable for proton-exchange membrane fuel cells PEMFC [10]. These requirements, together with reversibility, are limiting the number of possible solid state hydrogen storage systems. It is noteworthy that nowadays most of the advanced systems in terms of these limitations should contain light atoms (approximately with atomic number $Z \leq 13$). That is why Al-containing hydrides of AlH_3 [11,12] and alkali metal alanates of $M[AlH_4]_n$ [e.g. 13], which potentially contain up to 10.1 wt% of hydrogen and a metal which is highly abundant in nature, has attracted a great deal of attention. $NaAlH_4$ is the most intensively studied member of Al-based hydrides due to its high hydrogen capacity of 5.6 wt% and hydrogen release reversibility, when catalyzed by a small amount of a transition metal catalyst (e.g. 2–4 mol% Ti) [14–16]. This fascinating discovery was a breakthrough in solid state hydrogen storage since it exhibits approximately twice the reversible capacity of any of the conventional metal hydrides (e.g. $LaNi_5H_x$, $FeTi_2H_x$) [17]. Since that time, the systems of AlH_3 and $M[AlH_4]_n$ have been intensively investigated both in terms of their crystal structures [18] and hydrogen storage properties [13].

The interest in Al-containing complex hydrides and their reactive hydride composites (RHC) as perspective hydrogen storage systems remained high during last two decades. Indeed, in recent years, many new Al-based complex hydrides involving other light elements such as N and B have been characterized. In particular, the synthesis, crystal structures, thermal decomposition and hydrogen storage properties of hydridic $M[Al(NH_2)_4]_n$ ($M = Li^+$, Na^+, K^+, Rb^+, Cs^+, $n = 1$; $M = Ca^{2+}$, Mg^{2+}, Sr^{2+}, Ba^{2+}) [19,20] and $M[Al(BH_4)_4]$ ($M = Li^+$, Na^+, K^+, NH_4^+, Rb^+, Cs^+) have been presented recently [21,22]. The other direction of perspective B,N-containing systems is making use of $N{-}H^{\delta+}\cdots H^{\delta-}{-}B$ dihydrogen bonds, which play an important role in molecular packing in crystals and in H_2 evolution [23]. In line with this criteria, several Al-based B- and N-containing hydrides, such as an anionic $Na[Al(NH_2BH_3)_4]$ [24], molecular $[Al(NH_3BH_3)(BH_4)_3]$ [25] and cation $[Al(NH_3)_6]^{3+}$ derivatives, namely $[Al(NH_3)_6][BH_4]_3$ [26], $[Al(NH_3)_6][Li_2(BH_4)_5]$ and $[Al(NH_3)_6][Li_2(BH_4)_5]\cdot 3NH_3BH_3$ have been investigated [27,28].

This review paper will give a short description of synthesis, crystal structure and hydrogen storage properties of aluminium complexes with B- and N-based hydrides. We will not cover the systems where only hydrogen atoms are surrounding the central Al atom, such as alanates and in alane, referring the reader to the existing recent reviews [11–13]. Here we focus on those compounds where Al^{3+} cation is coordinating to complex hydrides created by other light elements such as B and N. Borohydrides $M(BH_4)_n$, amides $M(NH_2)_n$ and amidoboranes $M(NH_2BH_3)_n$ themselves carry a significant amount of hydrogen, but their chemistry with alkali and alkali-earth metals is limited by the choice of metals [29–31]. Introducing another complex-forming elements allows tuning stability of bimetallic series, as illustrated for example by Zn- and Cd-based borohydrides [32,33]. Importantly, the complex-forming metal, possessing higher electronegativity, is determining the stability of the bimetallic hydride [34]. Aluminium stands in the bimetallic series on its own, given its high polarizing power defined by the exceptional charge-to-radius ratio, low weight, high natural abundance, and the fact that the chemistry of Al complexes with B- and N-based hydrides has been explored only recently. Being an excellent Lewis acid, Al^{3+} is capable of coordinating the initial B- and N-based complex hydrides and their dehydrogenation products, thus serving as a template (or a matrix) for potential reversible dehydrogenation. The activation of neutral molecules, namely ammonia and ammonia borane, also requires a highly polarizing cation and have attracted increasing interest [7].

The systems listed above will be divided into three main groups. The first contains Al-centered complex anions, namely $M[Al(NH_2)_4]_n$, $M[Al(BH_4)_4]$ and $M[Al(NH_2BH_3)_4]$. The second are the molecular complexes and the third are complexes containing Al within complex cations, as for example $[Al(NH_3)_6]^{3+}$. There are also recent examples of "autoionized" complexes, where Al forms complex cation and anion within the same compound. The presence of dihydrogen bonds will be considered along with the cation Al–N and Al–B complex hydrides.

Synthesis

Synthesis of anionic $M[Al(NH_2)_4]_n$ ($M = Li^+$, Na^+, K^+, Rb^+, Cs^+, n = 1; $M = Ca^{2+}$, Mg^{2+}, Sr^{2+}, Ba^{2+}, n = 2)

The synthesis of $M[Al(NH_2)_4]_n$ can be performed in different ways, using the metals or their hydrides in presence of NH_3. Most of the alkali metal aluminium amides can be obtained by the reaction of Al in solution of the metals in liquid NH_3 [35]:

$$M + Al + 4NH_3 \rightarrow M[Al(NH_2)_4] + 2H_2 \ (M = \text{alkali metal}) \quad (1)$$

$M[Al(NH_2)_4]$ can be also formed from the reaction of the corresponding $MAlH_4$ with NH_3 [36]:

$$MAlH_4 + 4NH_3 \rightarrow M[Al(NH_2)_4] + 4H_2 \ (M = \text{alkali metal}) \quad (2)$$

The formation of $M[Al(NH_2)_4]_n$ (M = alkali or alkali earth metal) is also observed in the mechanochemical reaction of alkali and alkali earth metal hydrides with Al under NH_3 gas [19,20]:

$$MH_n + nAl + 4nNH_3 \rightarrow M[Al(NH_2)_4]_n + 2.5nH_2 \quad (3)$$

The mechanochemical treatment of their hydrides under liquid NH_3 yields $M[Al(NH_2)_4]_n$ (M = alkali or alkali earth metal):

$$MH_n + nAlH_3 + 4nNH_3 \rightarrow M[Al(NH_2)_4]_n + 4nH_2 \quad (4)$$

$Ba[Al(NH_2)_4]_2$ is found to be quite unstable at ambient conditions without ammonia pressure [37]. Recently, low temperature a single crystal measurement has revealed the