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Al$_6$H$_{18}$: A baby crystal of $\gamma$-AlH$_3$

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Using global-minima search methods based on the density functional theory calculations of (AlH$_3$)$_n$ ($n = 1–8$) clusters, we show that the growth pattern of alanes for $n \geq 4$ is dominated by structures containing hexa-coordinated Al atoms. This is in contrast to the earlier studies where either linear or ring structures of AlH$_3$ were predicted to be the preferred structures in which the Al atoms can have a maximum of five-fold coordination. Our calculations also reveal that the Al$_6$H$_{18}$ cluster, with its hexa-coordination of the Al atoms, resembles the unit-cell of $\gamma$-AlH$_3$, thus Al$_6$H$_{18}$ is designated as the “baby crystal.” The fragmentation energies of the (AlH$_3$)$_n$ ($n = 2–8$) along with the dimerization energies for even $n$ clusters indicate an enhanced stability of the Al$_6$H$_{18}$ cluster. Both covalent (hybridization) and ionic (charge) contribution to the bonding are the driving factors in stabilizing the isomers containing hexa-coordinated Al atoms. © 2012 American Institute of Physics.

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Although solid AlH$_3$ has been known for over 60 years,$^1$ only recently polymeric aluminum hydride or alane (AlH$_3$)$_n$ has attracted considerable attention as a potential hydrogen storage material due to its high volumetric (148 kgH$_2$/m$^3$) and gravimetric (10.1 wt. %) hydrogen capacity.$^2,3$ AlH$_3$ is a metastable solid at room temperature known to exist at least in seven polymorphs$^4–7$ (alpha, alpha', beta, epsilon, gamma, and zeta). The common structural feature in all these polymorphs is that each aluminum atom is surrounded by six hydrogen atoms in an octahedral fashion (AlH$_6$) and differs only in the way these octahedra are connected together. Since, the bulk AlH$_3$ is a polymeric solid, the entire solid can be constructed from monomeric AlH$_3$ units. This raises an interesting question: At what cluster size, $n$, do the aluminum atoms in (AlH$_3$)$_n$ clusters adopt hexa-coordination and exhibit structural features similar to one of the polymorphs of the bulk? In order to answer this question, we carried out systematic investigation using the density functional theory (DFT) based unbiased global minima search methods (genetic algorithm) of (AlH$_3$)$_n$ ($n = 1–8$) clusters.

Compared to the boron hydrides experimental studies on aluminum hydrides are scarce.$^8–10$ Recently, Bowen’s group has identified several types of Al$_n$H$_m$ systems which include boron analogues,$^{11}$ Jellium hydrides,$^{12,13}$ and also (Al$_n$H$_{3n-1}$)$^-$ ($n = 3–8$).$^{14}$ A few experimental and computational studies$^{15–23}$ on neutral and anionic (AlH$_3$)$_n$ clusters have also been previously reported. Kawamura et al., identified the cyclic isomers, with single and double hydrogen bridged Al atoms, as the most stable arrangement for the neutral (AlH$_3$)$_n$ ($n = 3–7$) clusters.$^{16}$ On the other hand, recently Cui et al. have shown that one-dimensional helical structures are more stable than the cyclic isomers$^{23}$

In this Communication, we will demonstrate that neither the helical nor the cyclic templates form the basis for most stable structures for higher alanes. Instead, a new prototype based on the unit cell of $\gamma$-AlH$_3$, in which two Al atoms with hexa-coordination, forms a template for higher alanes, $n \geq 6$. This new template can be considered as a “baby crystal” for $\gamma$-AlH$_3$.

The lowest and other higher energy isomers of (AlH$_3$)$_n$ ($n = 2–8$) clusters were obtained using the unbiased systematic structure search based on genetic algorithm method.$^{24,25}$ In this procedure, all the structures generated either through initial population or cross breeding were fully optimized without any constraints using BP functional and def2-SV(P) basis set, employing TURBOMOLE.$^{26}$ The validity of this method had been tested with the known aluminum hydride structures. This method correctly identified global minima for all the known Al$_n$H$_m$ clusters.$^{11}$ The lowest energy structures were further re-optimized using the DMol3 program suite.$^{27}$ In this step, the PW91 functional form,$^{28}$ along with the DNP basis set were employed. All the structures and the relative energies discussed in the following are based on the DMol3 calculations. On selective clusters the DFT energies were
The lowest and other higher energy isomers of (AlH₃)ₙ (n = 2–8) are given in Figures 1 and 2. For Al₂H₆, as anticipated, the lowest energy structure, 2a, is an analog of diborane and Ga₂H₆ [Ref. 30], the di-hydrogen-bridged isomer connecting two tetrahedral Al atoms. The molecular structure of dialane, which has been generated in solid Ar, has been firmly established by the IR studies in solid-hydrogen matrix by Andrews and co-workers. In the case of Al₃H₉, the two lowest energy isomers are isoenergetic. Structure 3a, is a ring structure with three Al–H–Al bridges and six Al–H terminal bonds. The second isomer, 3b, which is marginally higher in energy (0.01 eV), is a linear extension of dialane, in which two...
tetrahedral AlH₄ units attached to the central AlH. In structure 3b, the coordination around central Al atom is five. In the earlier study, Kawamura et al. considered the ring (3a) structure as a template for higher alanes ((AlH₃)ₙ (n = 4–7)), while in a recent study by Cui and co-workers, the helical extension of the linear (3b) structure was shown to be lower in energy than the ring structure. However, as the number of AlH₃ units increases both of these structural motifs do not correlate to the most stable geometry. The addition of fourth AlH₃ unit to Al₆H₁₈ can be achieved in four different ways; (i) by extending the Al₁₃H₉ ring (3a) to the next higher order ring structure Al₄H₁₂, 4d. (ii) by adding an AlH³ on the 3a ring resulting in a penta-coordinated Al atom (4c). (iii) a linear extension of Al₁₃H₉ (3b) unit resulting in two penta-coordinated Al atoms, 4b. Finally, the additional AlH₃ unit can be attached to the central Al–H unit in 3b resulting in the formation of hexa-coordinated central Al atom surrounded by the three AlH₄ units, isomer 4a. Contrary to the previous studies, our calculations show that the structure 4a, with hexa-coordinated Al atom at the center is energetically most preferred. The linear structure (4b) and the ring structures (4c and 4d) are 0.17, 0.30, and 0.36 eV higher in energy, respectively. Even though the lowest energy isomers of Al₄H₁₂ appear to have been derived from Al₁₃H₉ isomers, it should be emphasized that the search for the most stable structures has been carried independently for each stoichiometry by the unbiased global minima search method (genetic algorithm). To verify whether the structure containing hexa-coordinated Al is the most preferred geometry, we have carried out ab initio calculations of the two energy isomers at the CCSD(T)/aug-cc-pVTZ level. The energy difference between 4a and 4b is 0.17 eV confirming that 4a is indeed the lowest energy structure of Al₄H₁₂. The lowest energy structure of Al₁₃H₁₅, 5a, is an extension of 4a, with the additional AlH₃ attaching to one of the peripheral tetra-coordinated Al. The helical structure of Al₁₃H₁₅, 5b is found to be 0.09 eV higher in energy, while the ring structures of Al₁₃H₁₅ with single- and double-hydrogen bridged isomers, 5c and 5d are 0.33 and 0.37 eV, respectively.

In a significant departure from the lower alanes, the most stable structure of Al₆H₁₈ cannot be constructed by a simple addition of one or two AlH₃ units to the lowest energy structures of either Al₁₃H₁₅ or Al₄H₁₂. As shown in Figure 2, the lowest energy isomer of Al₆H₁₈, 6a, contains two hexa-coordinated di-hydrogen bridged Al atoms, surrounded by four tetrahedral AlH₄ units. Interestingly, the next three higher energy isomers, 6a′-a″″ (see supplementary material) consist of at least one hexa-coordinated Al atom, but differing only in the arrangement of the tetrahedral AlH₄ units. The helical structure of Al₆H₁₈, 6b, and the ring structure, 6c, are significantly higher in energy (ΔE = 0.4–0.6 eV) than 6a, indicating the strong preference for the hexa-coordinated Al over penta- or tetra-coordination. Significantly, the coordination around the central Al(HH)Al unit is identical to the coordination of corresponding Al atoms in γ-AlH₃. A comparison, highlighting the similarity in the coordination sphere around Al atoms in both 6a and γ-AlH₃, is shown in Figure 3. Since a bulk-like coordination in polymeric-AlH₃ is observed for the first time in Al₆H₁₈, following the definition of baby-crystal, one can classify Al₆H₁₈ as the baby-crystal of γ-AlH₃. In addition, the structure 6a resembles those of the oxygen bridged transition-metal-based chelated complexes, signifying the robustness of structural arrangement.

The lowest energy isomers 7a (Fig. 2) and 7a′, 7a″ (see supplementary material) of the next higher alane, Al₁₇H₂₁, preserve the Al₁₃H₉ skeleton by attaching the AlH₃ moiety to one of the peripheral AlH₄ units. Neither the helical nor the ring structures (7b–7d) are energetically competitive with the isomers containing hexa-coordinated Al. In the case of Al₂₃H₂₄, the general expectation is that the additional AlH₃ on Al₁₇H₂₁ would coordinate with one of the peripheral AlH₄ units, keeping the existing Al₁₃H₉ framework intact. However, the most stable structure, 8a, of Al₂₃H₂₄ is a cage structure, with four hexa-coordinated Al atoms with similar bonding features as in Al₁₃H₉ cluster, 6a and the remaining four tetrahedral aluminum atoms are connecting them to from the cage. In this unusual cage structure, the H–H non-bonding distance is 1.89 Å. On the other hand, the structures based on Al₁₃H₉ framework, 8a′ and 8a″″ (see supplementary material), are 0.22 and 0.28 eV higher in energy, respectively. Not surprisingly, both the ring (8b) and the helical structures (8c) of Al₂₃H₂₄ are significantly higher in energy. It should be noted that while the difference between various hexa-coordinated isomers for any given cluster is rather small (0.1–0.3 eV), these isomers are significantly lower in energy than the corresponding ring and helical isomers, indicating the preference for hexa-coordination. Note that this trend is independent of the theoretical method used. In addition, the low energy isomers of Al₁₇H₂₃ and Al₁₇H₂₄ reveal the robustness of the hexaAl-(H)₂-hexAl core unit, which is first observed in Al₁₃H₁₈. Furthermore, the preference for various low energy hexa-coordinated isomers indirectly supports the existence of numerous polymorphs of AlH₃ solid.

The thermodynamic stabilities of the (AlH₃)ₙ clusters have been analyzed using the following fragmentation equations and the results from the first two equations are graphed in the supplementary material:

\[ \Delta E/n = -\{E(AlH₃)ₙ/n - E(AlH₃)\}, \]
\[ \Delta E_n = -\{E(AlH₃)ₙ - E(AlH₃)ₙ₋₁ - E(AlH₃)\}, \]
\[ \Delta ε_n = -\{E(AlH₃)ₙ - 2E(AlH₃)ₙ/2\}, \text{ where } n \text{ is even.} \]
Equation (1) corresponds to the binding energy per AlH₃ unit. Following this equation, the calculated BE/n values of (AlH₃)ₙ are 0.82 eV (n = 2), 0.90 eV (n = 3), 0.99 eV (n = 4 and 5), 1.06 eV (n = 6 and 7), and 1.09 eV (n = 8). Thus, the binding energy per AlH₃ unit of (AlH₃)ₙ cluster remained nearly constant around 1 eV for any given n, while the BE/n for the γ-AlH₃ is calculated to be 1.49 eV. Owing to the presence of lower coordinated Al atoms on the surface, the (AlH₃)ₙ clusters under current study, cannot reach the bulk limit. Equation (2) represents the relative stability of (AlH₃)ₙ cluster against fragmentation into an AlH₃ unit and (AlH₃)ₙ₋₁ cluster. The fragmentation energies, ΔEₙ of (AlH₃)ₙ (n = 2–8 clusters), obtained using Eq. (2) are: ΔE₂ = 1.65 eV, ΔE₃ = 1.07 eV, ΔE₄ = 1.24 eV, ΔE₅ = 0.99 eV, ΔE₆ = 1.39 eV, ΔE₇ = 1.07 eV, and ΔE₈ = 1.29 eV. Thus, we see that, the energies corresponding to the even n are significantly more stable than their neighboring odd n. This is due to the fact that in the case of even n, an additional hexa-coordinated Al atom appear, thereby providing additional stabilization over its immediate neighbors. In fact, apart from Al₂H₆, the highest fragmentation energy appears at n = 6, indicating that Al₆H₁₈ is highly stable relative to its neighboring clusters, Al₄H₁₅ and Al₇H₂₅. This coincides with the fact that the appearance of the bulk-like coordination occurs at n = 6. Furthermore, the dimerization energies of (AlH₃)ₙ for even n, calculated using Eq. (3), for Al₄H₁₂ (4a, 0.66 eV), Al₆H₁₈ (6a, 0.91 eV), and Al₈H₂₄ (8a, 0.79 eV), also shows the enhanced stabilization of Al₆H₁₈.

Natural bond orbital method has been used to understand the electronic structure of these alanes. This method searches for the best “Lewis structure” that can accurately describe the given wave function within the set bonding parameters. Since by definition, all alanes are electron deficient, inclusion of both 2c–2e and 3c–2e bonding features provide an improved description of the Lewis structure for any given alane. Accordingly, all the (AlH₃)ₙ clusters considered here have a common bonding pattern; each terminal (radial) Al–H is a 2c–2e bond and each Al–H–Al bridge can be described as a 3c–2e bond. This description not only describes the bonding for the global minima but is true for higher energy isomers as well. Since each Al and H atom in the bulk γ-AlH₃ is a part of Al–H–Al bridge, by extension, the entire crystal is made up of 3c–2e bonds. Therefore, it is conceivable to consider that in alanes (AlH₃)ₙ as n increases isomers with large number of 3c–2e bonds should be favored, which in turn implies the preference for hexa-coordination of Al. However, this is not the case. For example, consider Al₅H₁₅, the lowest energy isomer, 5a, has six 2c–2e and seven 3c–2e bonds. However, the structure 5c, with only five 2c–2e bonds but ten 3c–2e bonds, is in fact 0.33 eV higher in energy. Therefore, the increased preference for hexa-coordination in higher alanes is not related to the number of 3c–2e bonds. Next consider the nature of the sp⁶ hybridization of the Al atoms in Al–H and Al–H–Al bonds. To do this, we will focus on two stoichiometries, Al₄H₁₂ (4a and 4b) where the preference for hexa-coordination of Al has been first manifested and the baby-crystal Al₆H₁₈ (6a and 6b). Consider structures 4a and 4b, together they have aluminum atoms in all the three (tetra, penta, and hexa) coordination modes. In 4a, only the central Al atom forms ideal sp⁶ hybridization in its bonding, whereas the terminal tetra-coordinated Al atom rehybridizes as sp³ and sp⁶, towards 2c–2e and 3c–2e bonds. This rehybridization of the Al atom where hybrid orbitals with large p contribution are directed towards more electronegative atom H in 3c–2e bonds is in accordance with Bent’s rule but results in the reduced overlap with terminal hydrogen atoms. In 4b, the hybridization of a penta-coordinated Al in all its 3c–2e bonds varies from sp² to sp⁴. Not surprisingly, this phenomenon holds well for all cluster sizes and results in stabilizing the hexa-coordination. For example, in Al₆H₁₈, 6a, the average hybridization of the hexa-coordinated Al atom (sp³) is closer to the ideal value than the tetra-coordinated Al atoms (sp⁴). Thus, we see that, the energies corresponding to the even n are significantly more stable than their neighboring odd n. This is due to the fact that in the case of even n, an additional hexa-coordinated Al atom appear, thereby providing additional stabilization over its immediate neighbors. In fact, apart from Al₂H₆, the highest fragmentation energy appears at n = 6, indicating that Al₆H₁₈ is highly stable relative to its neighboring clusters, Al₄H₁₅ and Al₇H₂₅. This coincides with the fact that the appearance of the bulk-like coordination occurs at n = 6. Furthermore, the dimerization energies of (AlH₃)ₙ for even n, calculated using Eq. (3), for Al₄H₁₂ (4a, 0.66 eV), Al₆H₁₈ (6a, 0.91 eV), and Al₈H₂₄ (8a, 0.79 eV), also shows the enhanced stabilization of Al₆H₁₈.

In conclusion, we have shown the evolution of hexacoordination and the formation of baby-crystal of (AlH₃)ₙ oligomers. In contrast to the previous studies, our calculations show that in (AlH₃)ₙ (n ≥ 4) neither the helical nor the cyclic structure (with the maximum coordination for Al atom being five), is energetically favorable compared to the structures containing hexa-coordinated Al atoms. Based on the structural and energetic criteria, Al₆H₁₈ can be classified as a “baby-crystal” of γ-AlH₃.
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