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Al₆H₁₈: A baby crystal of γ -AlH₃B. Kiran,^{1,a)} Anil K. Kandalam,^{2,a)} Jing Xu,³ Y. H. Ding,^{3,a)} M. Sierka,⁴ K. H. Bowen,⁵ and H. Schnöckel⁶¹*Department of Chemistry, McNeese State University, Lake Charles, Louisiana 70609, USA*²*Department of Physics, West Chester University, West Chester, Pennsylvania 19383, USA*³*State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Republic of China*⁴*Institut für Materialwissenschaft und Werkstofftechnologie, Friedrich-Schiller-Universität Jena, Löbdergraben 32, D-07743 Jena, Germany*⁵*Departments of Chemistry and Material Sciences, Johns Hopkins University, Baltimore, Maryland 21218, USA*⁶*Institute of Inorganic Chemistry and Center for Functional Nanostructures (CFN), Karlsruhe Institute of Technology (KIT), 76128 Karlsruhe, Germany*

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Using global-minima search methods based on the density functional theory calculations of (AlH₃)_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 AlH₃ 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 Al₆H₁₈ cluster, with its hexa-coordination of the Al atoms, resembles the unit-cell of γ -AlH₃, thus Al₆H₁₈ is designated as the “baby crystal.” The fragmentation energies of the (AlH₃)_n ($n = 2-8$) along with the dimerization energies for even n clusters indicate an enhanced stability of the Al₆H₁₈ 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. [<http://dx.doi.org/10.1063/1.4754506>]

Although solid AlH₃ has been known for over 60 years,¹ only recently polymeric aluminum hydride or alane (AlH₃) has attracted considerable attention as a potential hydrogen storage material due to its high volumetric (148 kgH₂/m³) and gravimetric (10.1 wt. %) hydrogen capacity.^{2,3} AlH₃ is a metastable solid at room temperature known to exist at least in seven polymorphs⁴⁻⁷ (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 (AlH₆) and differs only in the way these octahedra are connected together. Since, the bulk AlH₃ is a polymeric solid, the entire solid can be constructed from monomeric AlH₃ units. This raises an interesting question: At what cluster size, n , do the aluminum atoms in (AlH₃)_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 (AlH₃)_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_nH_m systems which include boron analogues,¹¹ Jellium hydrides,^{12,13} and also (Al_nH_{3n+1})⁻ ($n = 3-8$).¹⁴ A few experimental and compu-

tational studies¹⁵⁻²³ on neutral and anionic (AlH₃)_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 (AlH₃)_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 γ -AlH₃, 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 γ -AlH₃.

The lowest and other higher energy isomers of (AlH₃)_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_nH_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

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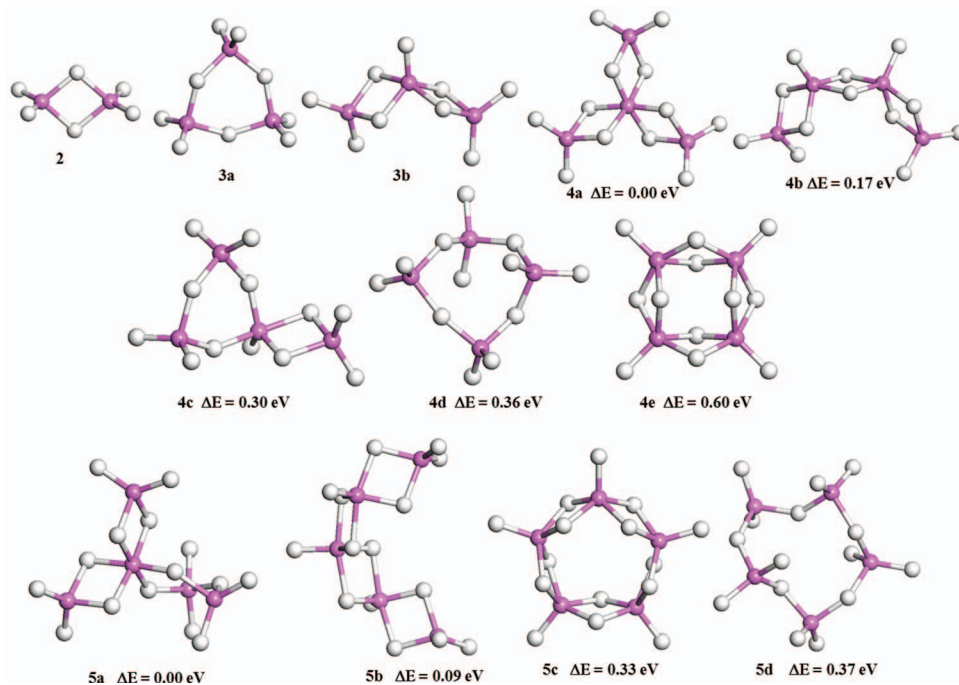


FIG. 1. The lowest energy structure, the helical, and the ring structures of $(\text{AlH}_3)_n$ ($n = 1-5$) clusters. The relative energies (ΔE) calculated at the PW91/DNP level are also shown.

checked with CCSD(T) with augmented CC-pVTZ basis set using GAUSSIAN03 program.²⁹

The lowest and other higher energy isomers of $(\text{AlH}_3)_n$ ($n = 2-8$) are given in Figures 1 and 2. For Al_2H_6 , as anticipated, the lowest energy structure, **2a**, is an analog of diborane and Ga_2H_6 [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.⁸ In the case of Al_3H_9 , 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

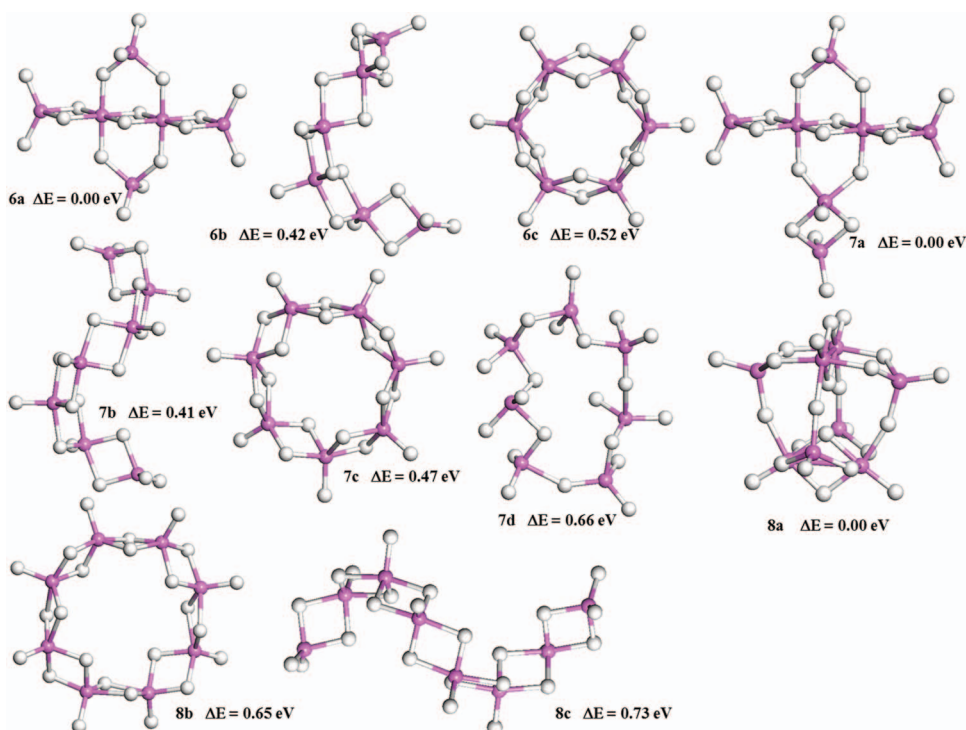


FIG. 2. The lowest energy structure, the helical, and the ring structures of $(\text{AlH}_3)_n$ ($n = 6-8$) clusters. The relative energies (ΔE) calculated at the PW91/DNP level are also shown.

tetrahedral AlH_4 units attached to the central AlH . In structure **3b**, the coordination around central Al atom is five. In the earlier study,¹⁶ Kawamura *et al.* considered the ring (**3a**) structure as a template for higher alanes ($(\text{AlH}_3)_n$ ($n = 4-7$)), while in a recent study²³ 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 AlH_3 units increases both of these structural motifs do not correlate to the most stable geometry. The addition of fourth AlH_3 unit to Al_3H_9 can be achieved in four different ways; (i) by extending the Al_3H_9 ring (**3a**) to the next higher order ring structure Al_4H_{12} , **4d**. (ii) by adding an AlH_3 on the **3a** ring resulting in a penta-coordinated Al atom (**4c**). (iii) a linear extension of Al_3H_9 (**3b**) unit resulting in two penta-coordinated Al atoms, **4b**. Finally, the additional AlH_3 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 AlH_4 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 Al_4H_{12} appear to have been derived from Al_3H_9 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 lowest 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 Al_4H_{12} . The lowest energy structure of Al_5H_{15} , **5a**, is an extension of **4a**, with the additional AlH_3 attaching to one of the peripheral tetra-coordinated Al. The helical structure of Al_5H_{15} , **5b** is found to be 0.09 eV higher in energy, while the ring structures of Al_5H_{15} 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 Al_6H_{18} cannot be constructed by a simple addition of one or two AlH_3 units to the lowest energy structures of either Al_5H_{15} or Al_4H_{12} . As shown in Figure 2, the lowest energy isomer of Al_6H_{18} , **6a**, contains two hexa-coordinated di-hydrogen bridged Al atoms, surrounded by four tetrahedral AlH_4 units. Interestingly, the next three higher energy isomers, **6a'**–**a'''** (see supplementary material³¹) consist of at least one hexa-coordinated Al atom, but differing only in the arrangement of the tetrahedral AlH_4 units. The helical structure of Al_6H_{18} , **6b**, and the ring structure, **6c**, are significantly higher in energy ($\Delta E = 0.4-0.6$ eV) than **6a**, indicating the strong preference for the hexa-coordinated Al over penta- or tetra-coordination. Significantly, the coordination around the central $\text{Al}(\text{HH})\text{Al}$ unit is identical to the coordination of corresponding Al atoms in $\gamma\text{-AlH}_3$. A comparison, highlighting the similarity in the coordination sphere around Al atoms in both **6a** and $\gamma\text{-AlH}_3$, is shown in Figure 3. Since a bulk-like coordination in polymeric- AlH_3 is observed for the first time in Al_6H_{18} , following the definition of baby-crystal,³² one can

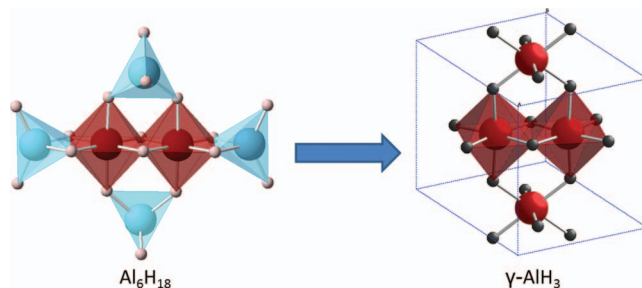


FIG. 3. The structural similarities between Al_6H_{18} cluster and the unit cell of $\gamma\text{-AlH}_3$.

classify Al_6H_{18} as the baby-crystal of $\gamma\text{-AlH}_3$. In addition, the structure **6a** resembles those of the oxygen bridged transition-metal-based chelated complexes, signifying the robustness of structural arrangement.³³

The lowest energy isomers **7a** (Fig. 2) and **7a'**, **7a''** (see supplementary material³¹) of the next higher alane, Al_7H_{21} , preserve the Al_6H_8 skeleton by attaching the AlH_3 moiety to one of the peripheral AlH_4 units. Neither the helical nor the ring structures (**7b**–**7d**) are energetically competitive with the isomers containing hexa-coordinated Al. In the case of Al_8H_{24} , the general expectation is that the additional AlH_3 on Al_7H_{21} would coordinate with one of the peripheral AlH_4 units, keeping the existing Al_6H_8 framework intact. However, the most stable structure, **8a**, of Al_8H_{24} is a cage structure, with four hexa-coordinated Al atoms with similar bonding features as in Al_6H_8 cluster, **6a** and the remaining four tetrahedral aluminum atoms are connecting them to form 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 Al_6H_8 framework, **8a''** and **8a'''** (see supplementary material³¹), are 0.22 and 0.28 eV higher in energy, respectively. Not surprisingly, both the ring (**8b**) and the helical structures (**8c**) of Al_8H_{24} 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 Al_7H_{21} and Al_8H_{24} reveal the robustness of the hexaAl–(H)₂–hexaAl core unit, which is first observed in Al_6H_{18} . Furthermore, the preference for various low energy hexa-coordinated isomers indirectly supports the existence of numerous polymorphs of AlH_3 solid.

The thermodynamic stabilities of the $(\text{AlH}_3)_n$ clusters have been analyzed using the following fragmentation equations and the results from the first two equations are graphed in the supplementary material³¹

$$\text{BE}/n = -\{[E(\text{AlH}_3)_n]/n - E(\text{AlH}_3)\}, \quad (1)$$

$$\Delta E_n = -\{E(\text{AlH}_3)_n - E(\text{AlH}_3)_{n-1} - E(\text{AlH}_3)\}, \quad (2)$$

$$\Delta \varepsilon_n = -\{E(\text{AlH}_3)_n - 2E(\text{AlH}_3)_n/2\}, \text{ where } n \text{ is even.} \quad (3)$$

Equation (1) corresponds to the binding energy per AlH_3 unit. Following this equation, the calculated BE/n values of $(\text{AlH}_3)_n$ 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 AlH_3 unit of $(\text{AlH}_3)_n$ cluster remained nearly constant around 1 eV for any given n , while the BE/n for the γ - AlH_3 is calculated to be 1.49 eV. Owing to the presence of lower coordinated Al atoms on the surface, the $(\text{AlH}_3)_n$ clusters under current study, cannot reach the bulk limit. Equation (2) represents the relative stability of $(\text{AlH}_3)_n$ cluster against fragmentation into an AlH_3 unit and $(\text{AlH}_3)_{n-1}$ cluster. The fragmentation energies, ΔE_n of $(\text{AlH}_3)_n$ ($n = 2$ –8) clusters, obtained using Eq. (2) are: $\Delta E_2 = 1.65$ eV, $\Delta E_3 = 1.07$ eV, $\Delta E_4 = 1.24$ eV, $\Delta E_5 = 0.99$ eV, $\Delta E_6 = 1.39$ eV, $\Delta E_7 = 1.07$ eV, and $\Delta E_8 = 1.29$ 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 Al_2H_6 , the highest fragmentation energy appears at $n = 6$, indicating that Al_6H_{18} is highly stable relative to its neighboring clusters, Al_5H_{15} and Al_7H_{21} . This coincides with the fact that the appearance of the bulk-like coordination occurs at $n = 6$. Furthermore, the dimerization energies of $(\text{AlH}_3)_n$ for even n , calculated using Eq. (3), for Al_4H_{12} (**4a**, 0.66 eV), Al_6H_{18} (**6a**, 0.91 eV), and Al_8H_{24} (**8a**, 0.79 eV), also shows the enhanced stabilization of Al_6H_{18} .

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 $(\text{AlH}_3)_n$ 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 - AlH_3 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 $(\text{AlH}_3)_n$, 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 Al_5H_{15} , the lowest energy isomer, **5a**, has six $2c-2e$ and seven $3c-3e$ 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 sp^λ hybridization of the Al atoms in Al–H and Al–H–Al bonds. To do this, we will focus on two stoichiometries, Al_4H_{12} (**4a** and **4b**) where the preference for hexa-coordination of Al has been first manifested and the baby-crystal Al_6H_{18} (**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 sp^3 hybridization in its bonding, whereas the terminal tetra-coordinated Al atom rehybridizes as $sp^{1.7}$ and $sp^{6.7}$ 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 rule³⁴ 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 $sp^{2.9}$ to $sp^{4.0}$. Not surprisingly, this phenomenon holds well for all cluster sizes and results in stabilizing the hexa-coordination. For example, in Al_6H_{18} , **6a**, the average hybridization of the hexa-coordinated Al atom ($sp^{3.1}$) is closer to the ideal value than the tetra-coordinated Al atoms ($sp^{1.6}$ (radial) and $sp^{6.8}$ (bridge)). Note that in γ - AlH_3 , all Al atoms have the ideal (sp^3) hybridization. Therefore, according to the hybridization analysis the stability of the various coordination modes are $6 > 5 > 4$. On the other hand, considerable charge separation between aluminum and hydrogen leading to the increased ionic ($\text{Al}^{\delta+}$ and $\text{H}^{\delta-}$) description of the bonding also contributes to the stabilization of hexa-coordination. The increased stabilization of hexa-coordination is also reflected in the energy ordering of the isomers. For a given stoichiometry, isomers with higher number of hexa-coordinated Al atoms are strongly preferred. For example, in Al_6H_{18} , structure **6a'** (see supplementary material³¹) with only one hexa-coordinated Al is 0.25 eV higher in energy than **6a**, which has two such Al atoms. This preference continues for higher alanes as well. In Al_8H_{24} , structures **8a**, **8a'**, and **8a''** have 4, 3, and 2 hexa-coordinated Al atoms, respectively, and their stabilities also decrease accordingly (**8a** (0.00), **8a'** (0.12), and **8a''** (0.22) eV).

In conclusion, we have shown the evolution of hexa-coordination and the formation of baby-crystal of $(\text{AlH}_3)_n$ oligomers. In contrast to the previous studies, our calculations show that in $(\text{AlH}_3)_n$ ($n \geq 4$) 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, Al_6H_{18} can be classified as a “baby-crystal” of γ - AlH_3 .

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