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Materials and Methods

Fig. S1

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Unexpected Stability of Al_4H_6^- : A Borane Analog?

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Whereas boron has many hydrides, aluminum has been thought to exhibit relatively few. A combined anion photoelectron and density functional theory computational study of the Al_4H_6^- anion and its corresponding neutral, Al_4H_6 , showed that Al_4H_6 can be understood in terms of the Wade-Mingos rules for electron counting, suggesting that it may be a borane analog. The data support an Al_4H_6 structure with a distorted tetrahedral aluminum atom framework, four terminal Al-H bonds, and two sets of counter-positioned Al-H-Al bridging bonds. The large gap between the highest occupied and the lowest unoccupied molecular orbitals found for Al_4H_6 , together with its exceptionally high heat of combustion, further suggests that Al_4H_6 may be an important energetic material if it can be prepared in bulk.

Even though aluminum and boron are sister elements in the periodic table, aluminum forms only a few hydrides, whereas boron has many, known as the boranes. The known hydride chemistry of aluminum is limited to AlH_3 and Al_2H_6 , seen in cryogenic matrices (1, 2) and perhaps the gas phase (3); alane, $(\text{AlH}_3)_n$, a polymeric solid; AlH_4^- and its alkali metal salts, the alanates, such as LiAlH_4 (4); Al_13H^- formed in beams (5, 6); and dissociative chemisorption products of $\text{D}_2 + \text{Al}_n^-$ interactions in beams (7). Boron hydrides, in contrast, exhibit a broad diversity of stoichiometries, such as B_2H_6 , B_4H_{10} , B_5H_9 , B_6H_{10} , and $\text{B}_{10}\text{H}_{14}$ (8–11). Given the electronic similarity between aluminum and boron, the lack of a comparable aluminum hydride chemistry is puzzling. Are analogous aluminum hydrides simply unstable under all circumstances, or might there be pathways by which they can be formed and environments in which they are stable?

We explored these questions by rapidly vaporizing aluminum metal in the presence of an abundant, albeit momentary, concentration of

hydrogen atoms and the cooling environment of a fast helium gas expansion. These conditions were provided by a pulsed arc discharge source (PACIS) (5, 12). The value of the PACIS source for studying aluminum cluster anion and hydrogen interactions was first realized by Ganteför and co-workers, who used it in photoelectron studies of HA_{13}^- and similarly sized aluminum cluster anions, each with up to two hydrogen atoms attached (5). In our study, such a source provided a doorway into a much wider world of aluminum hydride cluster anions. In a PACIS source, a discharge is struck between an anode and a grounded, metallic sample cathode as helium gas from a pulsed valve flows through the discharge region (Fig. 1). When an extender tube is added to this arrangement, additional gases can be added downstream. In

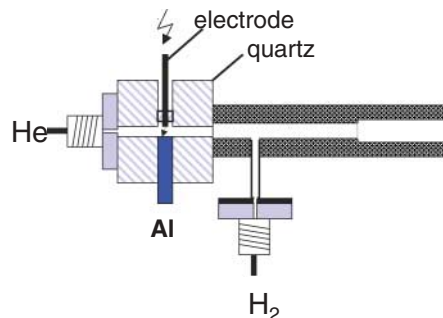


Fig. 1. Schematic diagram of a PACIS source.

our study, the sample electrode was aluminum, and hydrogen gas was back-filled before each discharge event. Upon initiation of the pulsed discharge, a plasma containing hydrogen atoms (the latter formed by the dissociation of H_2) expanded down the extender tube, cooling, clustering, and reacting along the way. The resulting anions were then subjected to extraction and mass analysis by a time-of-flight mass spectrometer. Their mass spectra revealed that between 1 and 10 hydrogen atoms had been attached to each aluminum cluster anion size. A typical experiment in which aluminum cluster anions, Al_n^- ($n = 3$ to 20), were generated thus revealed roughly 200 previously unobserved aluminum hydride anions. A por-

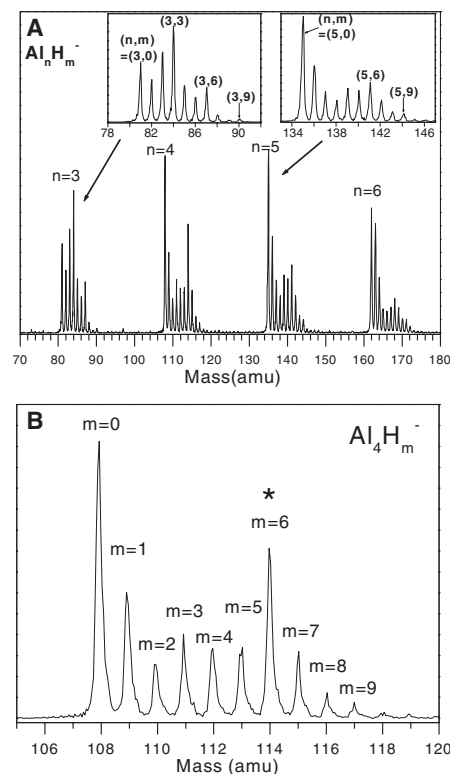


Fig. 2. (A) Mass spectrum showing the wide variety of Al_nH_m^- anions that are formed with the PACIS source. Insets show magnified views of selected portions of the mass spectrum, revealing individual Al_nH_m^- species. (B) A portion of the mass spectrum showing only the Al_4H_m^- series.

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tion of such a mass spectrum is presented in Fig. 2A.

Although we have results on many of these species, we chose to introduce this new family of aluminum hydrides by focusing on Al_4H_6^- and two similarly sized hydrides. Figure 2B, which highlights the Al_4H_m^- portion of the aluminum hydride anion mass spectrum, shows that Al_4H_6^- is a magic number species—i.e., a reproducibly intense mass peak relative to its neighbors. Most often, when a peak in a mass spectrum shows this behavior, the species represented by that peak is unusually stable. However, in the case of the anion, Al_4H_6^- , we saw no plausible reason for such special stability.

The explanation for its enhanced intensity lies in the photoelectron spectrum of Al_4H_6^- . Anion photoelectron spectroscopy was conducted by crossing a mass-selected anion beam with a fixed-frequency photon beam and analyzing the energy of the resultant photodetached electrons. The energetics are governed by the energy-conserving relationship, $h\nu = EBE + EKE$, where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the electron kinetic energy. Al_4H_6^- anions were generated in a PACIS source as described above and mass-selected by a time-of-flight mass spectrometer. Their excess electrons were photodetached by 4.66-eV photons

from the fourth harmonic of a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser and then detected by a magnetic bottle electron energy analyzer (13).

The photoelectron spectrum of Al_4H_6^- (Fig. 3A) displays two main features, a largely singular peak at $EBE \approx 1.4$ and two or more closely spaced peaks at higher EBE values. All of these peaks arise as a result of photodetachment transitions from the ground electronic state of the Al_4H_6^- anion to the ground and excited electronic states of its corresponding neutral, Al_4H_6 . Because the peak at lower EBE is due to the ground (anion) to ground (neutral) electronic transition, it provides a measurement of the adiabatic electron affinity (EA_a) of neutral Al_4H_6 . The EA_a of Al_4H_6 was determined to be 1.25 ± 0.15 eV (where the error is the standard deviation). Also, the vertical detachment energy (VDE), which is the EBE value of the maxima in the lower- EBE peak, was found to be 1.35 ± 0.05 eV. It represents the maximum Franck-Condon overlap between the anion and its corresponding neutral at the structure of the anion. Of more interest, however, is the energy splitting between the lower peak and the first feature among the higher- EBE set of peaks. Within Koopmans' approximation, this value is the highest occupied molecular orbital–lowest unoccupied molecu-

lar orbital (HOMO-LUMO) gap of the anion's corresponding neutral—i.e., the HOMO-LUMO gap for Al_4H_6 . Thus, the HOMO-LUMO gap of neutral Al_4H_6 is 1.9 eV. This very large HOMO-LUMO gap implies unusual stability. The HOMO-LUMO gap of C_{60} , for instance, is ~ 1.7 eV (14). The high stability of neutral Al_4H_6 suggests that it is particularly abundant, leading to enhanced Al_4H_6^- anion formation. Thus, the high stability of neutral Al_4H_6 appears to be the reason for the magic number prominence of anionic Al_4H_6^- in the mass spectrum. The high HOMO-LUMO gap of Al_4H_6 is put into further context by examining the photoelectron spectra of the species immediately adjacent in size, Al_4H_5^- and Al_4H_7^- . Their photoelectron spectra are presented in Fig. 3, B and C, respectively. They each display much smaller HOMO-LUMO gaps than does Al_4H_6 (~ 0.4 and ~ 0 eV, respectively), showing that Al_4H_6 is indeed unusually stable in comparison with aluminum hydrides of similar stoichiometries.

Having found neutral Al_4H_6 to be a particularly stable species, we conducted electronic structure calculations to determine its structure and the nature of its bonding. These were done at the Density Functional Theory–Generalized Gradient Approximation level of theory using a PerdewWang91 exchange-correlation functional with triple zeta valence polarization basis sets (15, 16). Geometries were optimized without symmetry constraints. Figure 4 presents the lowest energy structure of Al_4H_6 found by means of those calculations. The next higher-energy structures of Al_4H_6^- and Al_4H_6 were 0.33 and 1.07 eV, respectively, above their respective lowest-energy structures. In the lowest-energy structure of Al_4H_6 , the aluminum atom framework is a distorted tetrahedron with a terminal hydrogen atom bonded to each aluminum atom and with each of two hydrogen atoms forming counterpositioned bridging bonds across two aluminum atoms. Thus, there are four terminal hydrogen atoms (four Al-H bonds) and two bridging hydrogen atoms. The slight distortion of the aluminum framework's tetrahedral symmetry is due to the presence of the two sets of bridging bonds. These same calculations also gave energetic results that are in excellent agreement with those determined from the photoelectron spectrum of Al_4H_6^- . In particular, the calculations

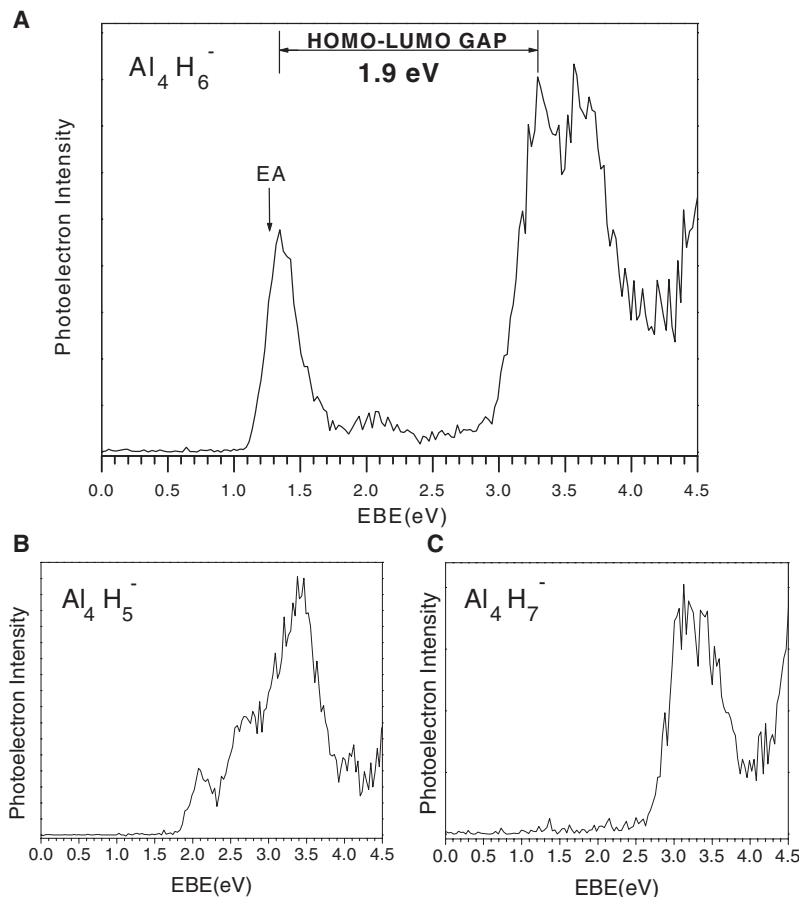


Fig. 3. The photoelectron spectra of (A) Al_4H_6^- , (B) Al_4H_5^- , and (C) Al_4H_7^- , all recorded with 4.66-eV photons.

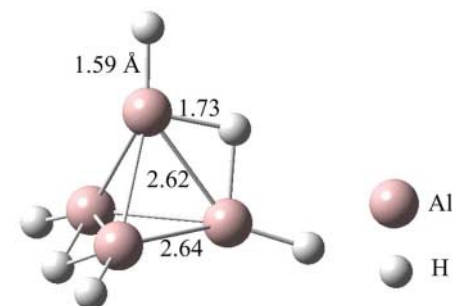


Fig. 4. The calculated structure of neutral Al_4H_6 , shown to be a distorted tetrahedron.

predicted a *VDE* value of 1.48 eV and an EA_4 value of 1.36 eV. The HOMO-LUMO gap was calculated using time-dependent density functional theory and was found to be 1.85 eV.

Because the structural features seen in Fig. 4 are reminiscent of those in boranes, it is natural to compare the structures of Al_4H_6 and B_4H_6 . Although B_4H_6 has not been observed experimentally, calculations have predicted that its structure is the same as that of Al_4H_6 (17). Moreover, $B_4H_2R_4$ derivatives of B_4H_6 have been synthesized, and they too display the same structure as that of Al_4H_6 (18). Thus, the similarity of the calculated structure of neutral Al_4H_6 to that of boranes led us to investigate whether the Wade-Mingos rules, originally established to relate borane geometries to their electronic structures, might also be applicable to the aluminum hydride species we observed. The best known form of the Wade-Mingos rules (10, 19–24) applies to closo-boranes of stoichiometry, $B_nH_n^{2-}$, which contain $(2n + 1)$ valence electron pairs. Of these, n pairs are required by the B-H terminal bonds, leaving $n + 1$ electron pairs for cage bonding. The Wade-Mingos ($n + 1$) rule states that a borane with $n + 1$ electron pairs for boron cage bonding will have a structure based on an n -vertex polyhedron, such as $B_6H_6^{2-}$, which is an octahedron. In addition to the boranes, Wade-Mingos rules have been successful in relating electronic structure to geometric structure in numerous other classes of cluster compounds.

In exploring the application of Wade-Mingos rules to Al_4H_6 , we treated it as $Al_4H_4^{2-}$, analogous to $B_nH_n^{2-}$, although formally Al_4H_6 should be written as $Al_4H_4^{2-} + 2H^+$ to account for all of the nuclei as well as the electrons. Treating Al_4H_6 as $Al_4H_4^{2-}$ is justified because the two bridging hydrogen atoms donate their two electrons to the aluminum skeletal cage. Thus, from an electron-counting perspective, Al_4H_6 can be viewed as $Al_4H_4 + 2e^-$ or $Al_4H_4^{2-}$. In the case of $Al_4H_4^{2-}$, there are 18 valence electrons. Eight of these are involved in forming four Al-H terminal bonds, leaving 10 electrons or five pairs for cage bonding. Because $n + 1 = 5$, n is equal to 4, which implies a tetrahedral structure. A strict application of Wade-Mingos concepts to the $n = 4$ case, however, would instead predict a Jahn-Teller distorted tetrahedral cage, given that the occupied molecular orbitals in tetrahedral symmetry are both degenerate and partially filled. Nevertheless, this symmetry-borne restriction is moot in the case of Al_4H_6 , because the presence of two bridging hydrogen atoms decreases its symmetry to D_{2d} . Specifically, the two sets of bridging bonds are each three-center, two-electron bonds in which the Al-Al linkage in each Al-H-Al bridge bond is virtual—i.e., the bridged hydrogen is an integral part of the closo- Al_4H_6 cage. Thus, with only minor caveats, the predicted structure is consistent with our calculated structure in Fig. 4, and although the Wade-Mingos rules were not developed for this particular case, they fit it relatively well. Thus, despite the differences

between the hydride chemistries of boron and aluminum, Al_4H_6 displays substantial bonding and structural similarities to the boranes and thus is analogous to them. There are also other interesting touchstones. For example, the bonding in Al_4H_6 would be considered by some to be an example of three-dimensional aromaticity (25), several other tetrahedral Al_4 structures have been observed among inorganic clusters in the solid state (26, 27), and before now, $Al_{12}R_{12}^{2-}$ (where R is a *t*-butyl group) was the only example of an aluminum cluster anion reported to adhere to the Wade-Mingos rules (28).

Furthermore, it now becomes clear why neither Al_4H_5 nor Al_4H_7 exhibit notable HOMO-LUMO gaps (Fig. 3, B and C). Both Al_4H_5 and Al_4H_7 have odd numbers of valence electrons (17 and 19, respectively), and the Wade-Mingos rules deal only with even numbers of electrons—i.e., with electron pairs. Thus, the large HOMO-LUMO gap of Al_4H_6 and the small HOMO-LUMO gaps of Al_4H_5 and Al_4H_7 are consistent with the Wade-Mingos rules.

Al_4H_6 is an impressive high-energy density molecule or cluster that may have application in propulsion. We calculated the heat of combustion of Al_4H_6 to the products, Al_2O_3 and water, to be 438 kcal/mol, ~2.6 times greater than that of methane. Moreover, given the thermodynamic driving force required to go all the way to alumina and water, it is unlikely that the combustion products of Al_4H_6 will stop at some intermediate species as boranes are known to do. Furthermore, the large HOMO-LUMO gap for Al_4H_6 implies that it may be relatively stable and perhaps can be synthesized in bulk quantities. If so, Al_4H_6 and related species could be important energetic materials.

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Divalent Metal Nanoparticles

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Nanoparticles can be used as the building blocks for materials such as supracrystals or ionic liquids. However, they lack the ability to bond along specific directions as atoms and molecules do. We report a simple method to place target molecules specifically at two diametrically opposed positions in the molecular coating of metal nanoparticles. The approach is based on the functionalization of the polar singularities that must form when a curved surface is coated with ordered monolayers, such as a phase-separated mixture of ligands. The molecules placed at these polar defects have been used as chemical handles to form nanoparticle chains that in turn can generate self-standing films.

Nanoparticles that consist of crystals of tens to thousands of atoms have been used as “artificial atoms” to form supracrystals that mimic ionic solids (1) or to form the

nanoscale equivalent of ionic liquids (2). Breaking the interaction symmetry in these isotropic and almost spherical materials is a major challenge. It is increasingly evident that nanoparticles would