6-28-2010

Communications: Chain and double-ring polymeric structures: Observation of AlnH3n+1 − (n=4–8) and Al4H14 −

Xiang Li
*Johns Hopkins University*

Andrej Grubisic
*Johns Hopkins University*

Kit H. Bowen
*Johns Hopkins University*

Anil K. Kandalam
*West Chester University of Pennsylvania, akandalam@wcupa.edu*

Boggavarapu Kiran
*McNeese State University*

*See next page for additional authors*

Follow this and additional works at: [http://digitalcommons.wcupa.edu/phys_facpub](http://digitalcommons.wcupa.edu/phys_facpub)

Part of the Atomic, Molecular and Optical Physics Commons

**Recommended Citation**


This Article is brought to you for free and open access by the College of Arts & Sciences at Digital Commons @ West Chester University. It has been accepted for inclusion in Physics by an authorized administrator of Digital Commons @ West Chester University. For more information, please contact wcressler@wcupa.edu.
Authors
Xiang Li, Andrej Grubisic, Kit H. Bowen, Anil K. Kandalam, Boggavarapu Kiran, Gerd F. Gantefoer, and Puru Jena
Communications: Chain and double-ring polymeric structures: Observation of $\text{Al}_n\text{H}_{3n+1}^-$ ($n=4–8$) and $\text{Al}_4\text{H}_{14}^-$

Xiang Li, Andrej Grubisic, Kit H. Bowen, Anil K. Kandalam, Boggavarapu Kiran, Gerd F. Gantefoer, and Puru Jena

1Department of Chemistry and Department of Materials Science, Johns Hopkins University, Baltimore, Maryland 21218, USA
2Department of Physics and Department of Chemistry, McNeese State University, Lake Charles, Louisiana 70609, USA
3Department of Physics, Konstanz University, 78457 Konstanz, Germany
4Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284, USA

(Received 17 May 2010; accepted 10 June 2010; published online 24 June 2010)

A pulsed arc discharge source was used to prepare gas-phase, aluminum hydride cluster anions, $\text{Al}_n\text{H}_{m}^-$, exhibiting enhanced hydrogen content. The maximum number of hydrogen atoms in $\text{Al}_n\text{H}_{m}^-$ species was $m=3n+1$ for $n=5–8$, i.e., $\text{Al}_n\text{H}_{3n+1}^-$, and $m=3n+2$ for $n=4$, i.e., $\text{Al}_4\text{H}_{14}^-$, as observed in their mass spectra. These are the most hydrogen-rich aluminum hydrides to be observed thus far, transcending the 3:1 hydrogen-to-aluminum ratio in alane. Even more striking, ion intensities for $\text{Al}_n\text{H}_{m}^-$ species with $m=3n+1$ and $m=3n+2$ hydrogen atoms were significantly higher than those of nearby $\text{Al}_n\text{H}_{m}^-$ mass peaks for which $m<3n+1$, i.e., the ion intensities for $\text{Al}_n\text{H}_{3n+1}^-$ and for $\text{Al}_4\text{H}_{14}^-$ deviated from the roughly bell-shaped ion intensity patterns seen for most $\text{Al}_n\text{H}_{m}^-$ species, in which $m$ ranges from 1 to $3n$. Calculations based on density functional theory showed that $\text{Al}_n\text{H}_{3n+1}^-$ clusters have chain and/or double-ring polymeric structures. © 2010 American Institute of Physics. [doi:10.1063/1.3458912]

Complex aluminum hydrides may have uses both as propellants and as hydrogen storage materials since both applications prize substances which are light-weight and hydrogen-rich. Until recently, however, aluminum hydride chemistry was largely limited to alane, $\text{AlH}_{3}$, and the alanates, e.g., $\text{LiAlH}_{4}$. Solid alane has eight known phases, and these are usually described as hydrogen-bridged polymeric networks. Also, molecular alane and dialane ($\text{Al}_2\text{H}_{6}$) have been studied in both cryogenic matrices and the gas phase as well as on surfaces. Alanates are alkali metal salts with $\text{AlH}_{4}^-$, an anion whose aluminum atom is tetrahedrally coordinated and in which the octet rule is satisfied.

Over the past several years, efforts to investigate other compositions of aluminum hydrides have moved into the gas phase, where many different compositions can be prepared, identified via mass spectrometry, and separately characterized. As a result, both beam experiments and computational studies have been conducted. Theoretical studies include work on $\text{Al}_n\text{H}_{3n}$ neutral clusters, where they were found to have cyclic structures, as well as work on small $\text{Al}_n\text{H}_{3n}$ anionic clusters, where their electron binding energies were computed. Experimental studies have focused on photoelectron spectroscopy of aluminum hydride cluster anions, $\text{Al}_n\text{H}_{m}^-$, generated in both laser vaporization and pulsed arc discharge sources.

In the present paper, we report on the formation of homologous series of $\text{Al}_n\text{H}_{m}^-$ cluster anions, generated in a pulsed arc discharge source, identified by mass spectrometry, and structurally characterized by calculations based on density functional theory (DFT). Among these species, the maximum number of hydrogen atoms bonded to their aluminum moieties is $m=3n+1$ for $n=5–8$, i.e., $\text{Al}_n\text{H}_{3n+1}^-$, and $m=3n+2$ for $n=4$, i.e., $\text{Al}_4\text{H}_{14}^-$. Typically, aluminum hydride cluster anions have hydrogen-to-aluminum ratios ($m:n$) that are not larger than that of alane, i.e., 3:1. However, under some source conditions, strong ion intensities of hydrogen-rich aluminum hydride cluster anions with $m>3n$ were reproducibly observed. Our calculations showed that $\text{Al}_n\text{H}_{3n+1}^-$ ($n=4–8$) clusters have both chain and cyclic double-ring polymeric structures, which are nearly degenerate energetically. These structural motifs afford them a mechanism for propagation and self-assembly.

In a pulsed arc discharge source, electrical discharges are periodically struck between an anode and a grounded cathode of conducting sample material, while helium gas from a pulsed valve flows through the discharge region. In the present experiments, the cathode was aluminum metal, and hydrogen gas was injected into the source’s condensation channel via a second pulsed valve. Upon initiation of the discharge, a plasma containing aluminum and hydrogen atoms (the latter formed by the dissociation of $\text{H}_2$) expanded down the condensation channel, where the mixture cooled, clustered, and reacted. (Typical operating conditions included discharge voltages of 100–200 V and pulsed valve backing pressures of 200 psi for both helium and hydrogen.) Extending the condensation channel tended to enhance the formation of hydrogen-rich aluminum hydride anions. After expanding into vacuum, the resulting anions were extracted into a time-of-flight mass spectrometer and mass analyzed.

aAuthors to whom correspondence should be addressed. Electronic addresses: kbowen@jhu.edu and akandalam@mcneese.edu.
A typical mass spectrum showing Al\textsubscript{n}H\textsubscript{m}\textsuperscript{−} species that were produced in these experiments is presented in Fig. 1. Figures 2\textsubscript{a}–2\textsubscript{d} provide magnified, separate versions of these mass spectra for \(n=4–7\), respectively. Several observations can be made from these mass spectra. The maximum number of hydrogen atoms in Al\textsubscript{n}H\textsubscript{m}\textsuperscript{−} species was observed to be \(m=3n+1\) for \(n=5–8\), i.e., Al\textsubscript{5}H\textsubscript{14}\textsuperscript{−} and Al\textsubscript{6}H\textsubscript{17}\textsuperscript{−}. These are the most hydrogen-rich aluminum hydrides to be observed thus far, transcending the 3:1 hydrogen-to-aluminum ratio of alanate. Even more striking, ion intensities for Al\textsubscript{n}H\textsubscript{m}\textsuperscript{−} species with \(m=3n+1\) and \(m=3n+2\) hydrogen atoms were significantly stronger than the ion intensities of nearby Al\textsubscript{n}H\textsubscript{m}\textsuperscript{−} species for which \(m<3n+1\). Typically, for a given \(n\), the ion intensities of Al\textsubscript{n}H\textsubscript{m}\textsuperscript{−} species in the mass spectra grow with increasing \(m\) until reaching a maximum after which they decrease; this pattern suggests governance by kinetics. Under many source conditions, this series terminates at \(m=3n\). In these studies, however, the ion intensities for Al\textsubscript{n}H\textsubscript{3n+1}\textsuperscript{−} and for Al\textsubscript{4}H\textsubscript{14}\textsuperscript{−} deviated from the usual roughly bell-shaped ion intensity patterns, instead exhibiting relatively intense ion signals which may suggest enhanced stabilities. In regard to species with the stoichiometry, Al\textsubscript{n}H\textsubscript{3n+2}\textsuperscript{−}, this was observed only for \(n=4\). Interestingly, the ion intensity of Al\textsubscript{4}H\textsubscript{14}\textsuperscript{−} was even stronger than that of Al\textsubscript{5}H\textsubscript{13}\textsuperscript{−}.

We took care to exclude the possibility that the existence of contaminants may cause the unexpected pattern in the mass spectrum. Based on the stoichiometries seen in the mass spectra, we speculated that polymer chain structures would provide an explanation for the \(m=3n+1\) species. In order to explore our hypothesis and provide further insights into the electronic structure, we carried out DFT calculations on Al\textsubscript{n}H\textsubscript{3n+1}\textsuperscript{−} anionic clusters. We employed Becke’s three parameter hybrid functional with Lee, Yang, and Parr correlation functional form\textsuperscript{29,30} and an all electron 6−311++G(3df, 3pd) basis set for Al and H atoms. All calculations were carried out using GAUSSIAN 03 code.\textsuperscript{31} In the geometry optimization procedure, the convergence criterion for energy was set to \(10^{-9}\) hartree, while the gradient was converged to \(10^{-4}\) hartree/Å.

The lowest energy structures of Al\textsubscript{n}H\textsubscript{3n+1}\textsuperscript{−} \((n=4–7)\) obtained from our calculations are shown in Fig. 3.
lations found polymerlike chain structures to be the most stable isomers for these anionic species. As expected, in these polymeric structures each Al atom has tetrahedral coordination. These results confirm our speculation regarding the possibility of open structures for these hydrogen-rich clusters. In addition, however, cyclic (ringlike) structures were also found to be very close in energy to the ground state open structures. In these cyclic structures, the additional hydrogen atom bridges two nonadjacent aluminum atoms, dividing the cyclic structure into two double-ring structures, and those two aluminum atoms exhibit a fivefold coordination. Although Al atoms are usually tetrahedrally coordinated, it is noteworthy here that in an earlier study on neutral Al\(_n\)H\(_3\)\(_n\) clusters, dibridged linear structures containing fivefold coordinated Al atoms were also reported to be energetically very close to the ground state cyclic structures. Lastly, structures with higher symmetry (e.g., planar-Al framework) were found not to be energetically favorable.

In both chain and double-ring polymeric isomers, the average Al–H\(_{\text{bridge}}\) bond length remained approximately constant at 1.74 Å even as the size of the cluster increased from Al\(_{10}\)H\(_{13}^-\) to Al\(_{12}\)H\(_{19}^-\). This distance is slightly larger than the Al–H\(_{\text{bridge}}\) bond length (1.70 Å) observed for neutral Al\(_{10}\)H\(_{14}^+\) clusters. The thermodynamic stability of these hydrogen-rich species was studied by calculating the relative stability of Al\(_n\)H\(_{3n+1}^-\) against fragmentation into Al\(_{n-1}\)H\(_{3n-2}^-\) and AlH\(_3^+\) units as follows:

\[
E_n = -[E(\text{Al}_n\text{H}_{3n+1}^-) - E(\text{Al}_{n-1}\text{H}_{3n-2}^-) - E(\text{AlH}_3^+)],
\]

where \(n = 5-7\). The fragmentation energies, thus calculated are \(E_5 = 1.06\) eV, \(E_6 = 1.04\) eV, and \(E_7 = 0.98\) eV. Thus, we see that energy gain in sequential addition of AlH\(_3^+\) units is more or less independent of the size of the cluster, \(n\). This trend once again clearly supports our conclusion regarding the polymerlike nature of the Al\(_n\)H\(_{3n+1}^-\) cluster, where addition of a monomer (AlH\(_3^+\)) does not result in substantial energy gain.

One of the observed Al\(_{4}\)H\(_{m}^-\) species presents an unresolved issue. While the situation for Al\(_{4}\)H\(_{12}^-\) and Al\(_{4}\)H\(_{13}^-\) is similar to that of the other Al\(_n\)H\(_{3n}^-\) and Al\(_n\)H\(_{3n+1}^-\) clusters described above, the observation of Al\(_{4}\)H\(_{14}^-\) (the only \(m = 3n + 2\) species to be observed) defied our computational efforts to define it. Moreover, the ion intensity of Al\(_{4}\)H\(_{14}^-\) is typically double that of Al\(_{4}\)H\(_{13}^-\). According to our calculations, neither chain nor the cyclic Al\(_{4}\)H\(_{13}^-\) isomers can accommodate another hydrogen atom. Other trial explanations have also failed in one or more critical ways. This enigmatic species remains a subject of our computational studies.

This report extends our knowledge of aluminum hydride cluster chemistry. Our experiments found that a maximum of \(3n + 1\) hydrogen atoms can attach to aluminum cluster anions for \(n = 5-8\), while \(3n + 2\) can do so for \(n = 4\). Our computational calculations revealed that Al\(_n\)H\(_{3n+1}^-\) clusters can have chain and/or cyclic double-ring polymeric structures. In view of the fivefold coordination of aluminum atoms in the double-ring structures and the existence of Al\(_4\)H\(_{14}^-\), it can be
anticipated that still other stoichiometries and structures might be possible among aluminum hydride cluster anions. These may provide pathways for synthesizing novel hydrogen-containing materials.

K.H.B. thanks the (U.S.) Air Force Office of Scientific Research for support of this work. A.K.K. acknowledges the faculty start-up funds made available through the Louisiana Board of Regents-Research Commercialization/Educational Enhancement Program (RC/EEP). B.K. acknowledges the support from Research Corporation.

31 M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.