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PAPER

Aluminum chain in $\text{Li}_2\text{Al}_3\text{H}_8^-$ as suggested by photoelectron spectroscopy and ab initio calculations†

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Received 00th July 20xx,
Accepted 00th xxxx 20xx

DOI: 10.1039/x0xx00000x

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Group 13 elements are very rarely observed to catenate into linear chains and experimental observation of such species is challenging. Herein we report unique results obtained via combined photoelectron spectroscopy and ab initio studies of the $\text{Li}_2\text{Al}_3\text{H}_8^-$ cluster that confirm the formation of Al chain surrounded by hydrogen atoms in a very particular manner. Comprehensive searches for the most stable structure of the $\text{Li}_2\text{Al}_3\text{H}_8^-$ cluster have shown that the global minimum isomer I possesses a geometric structure, which resembles the structure of propane, similar to the experimentally known Zintl-phase $\text{Cs}_{10}\text{H}[\text{Ga}_3\text{H}_8]_3$ compound featuring the propane-like $[\text{Ga}_3\text{H}_8]^{3-}$ polyanions. Theoretical simulations of the photoelectron spectrum have demonstrated the presence of only one isomer (isomer I) in the molecular beam. Chemical bonding analysis of the $\text{Li}_2\text{Al}_3\text{H}_8^-$ cluster has revealed two classical Al-Al σ bonds constituting the propane-like kernel.

Introduction

Scarce examples of compounds featuring Group 13 metal–metal (M–M) single bonds represent unique cases deserving much attention. The chance for the experimental verification of the extended species featuring M–M bonding in a chain-like fashion is even smaller and hence fundamentally important. In contrast to Group 14 elements, which are quite frequently observed to form long and stable homonuclear chains,¹ Group 13 elements tend to form cluster-like species instead.² Homocatenated boron chains and rings of up to only eight boron atoms are known up to date.³ Catenation of boron by a metal and catenation of borylene subunits without the use of strong alkali metals as reducing agents has been recently made by Braunschweig et al. thus representing a unique example known for boron.⁴ Recent efforts to provide new, mild, functional-group-tolerant, and convenient synthetic methods for the formation of electron-precise B–B single bonds have been summarized elsewhere.⁵ The use of the electronic transmutation principle⁶ and similar Zintl–Klemm concept⁷ have enabled designing novel materials, which are isoelectronic and isostructural to existing compounds. Wörle and Nesper demonstrated the existence of pure-phase LiB_x samples (with the approximate range $0.82 < x < 1.0$) possessing

chains of boron atoms surrounded by a lithium shell that illustrate the structural analogy between borynide chains in LiB_x and isoelectronic polyyne and polycumulene chains.⁸ Fahlgvist et al. have shown the viability of this concept for gallium containing species: a hydrogenous Zintl-phase $\text{Cs}_{10}\text{H}[\text{Ga}_3\text{H}_8]_3$ featuring the propane-like polyanions⁹ $[\text{Ga}_3\text{H}_8]^{3-}$ and $(\text{K}_x\text{Rb}_{1-x})_n[\text{GaH}_2]_n$ ($0 \leq x \leq 1$) composed of $[\text{GaH}_2]_n^{n-}$ anionic chains with a polyethylene structure.¹⁰ Remarkably, six indium atoms were previously found to arrange into one line upon the treatment of indium(I) iodide with a protonated N-xylyl β -diketiminato and a strong potassium base in tetrahydrofuran.¹¹ Examples of the main-group homocatenated compounds are reported elsewhere.¹² Noteworthy, thus far there have been no experimental reports on the Al homocatenated compounds. The first remarkable example of a stable molecule with an Al–Al bond to be structurally characterized was R_2AlAlR_2 ($\text{R}=\text{CH}(\text{SiMe}_3)_2$).¹³ Later, a cyclic structure of the Al_3Cl_3 featuring direct Al–Al bonds was reported by matrix isolation tech technique using IR and Raman spectroscopies.¹⁴ The first “dialuminyne” ($\text{Na}_2[\text{Al}'\text{AlAl}'\text{Al}']$) synthesized has been shown to have Al–Al bond with the bond order of 1.13.¹⁵ It was also found that “cycloaluminene” ($\text{Na}_2[(\text{AlAr}')_3]$) features somewhat weakened Al–Al σ bonding, which is due the lone-pair character at the metal centers.¹⁵ Very recently, Gish et al.¹⁶ have theoretically predicted the existence of a new “Al homocatenated alkane” family $\text{Li}_n\text{Al}_n\text{H}_{2n+2}$, featuring striking similarities of the $\text{Al}_n\text{H}_{2n+2}$ kernel with their respective alkanes based on the electronic transmutation concept. In this communication we report a first experimental example of “Al homocatenated propane” $\text{Li}_2\text{Al}_3\text{H}_8^-$ species possessing direct Al–Al bonds arranged in a chain-like fashion.

Conceptually,⁶ a donation of one electron to Al atom might “transmute” it into Group 14 atoms. Thus, the theoretically proposed $\text{Li}_3\text{Al}_3\text{H}_8$ molecule was recently shown to be

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†Electronic Supplementary Information (ESI) available: optimized isomers of $\text{Li}_2\text{Al}_3\text{H}_8^-$ ($\Delta=20$ kcal/mol), the Cartesian coordinates of ten lowest energy isomers, comparison of the experimental, theoretically calculated VDEs for isomers I and II, and other theoretical details. See DOI: 10.1039/x0xx00000x

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isostructural analogue of propane.¹⁶ Here we utilized anion photoelectron spectroscopy (PES) to test the viability of this hypothesis using the $\text{Li}_2\text{Al}_3\text{H}_8^-$ anion species, which is isoelectronic to the neutral $\text{Li}_3\text{Al}_3\text{H}_8$ cluster.

Experimental and Computational Methods

Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. It is governed by the energy-conserving relationship, $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, EBE is the electron binding (transition) energy, and EKE is the electron kinetic energy. Our anion photoelectron spectrometer, which has been described previously,¹⁷ consists of one of many kinds of ion sources, a linear time-of-flight mass spectrometer, a mass gate, a momentum decelerator, a pulsed Nd:YAG photodetachment laser, and a magnetic bottle electron energy analyzer. Photoelectron spectra were taken with both 355 nm (3.49 eV) and 266 nm (4.66 eV) photon energies and calibrated against the well-known photoelectron spectrum of Cu^- .¹⁸ $\text{Li}_2\text{Al}_3\text{H}_8^-$ cluster anions were generated in a laser vaporization source. Briefly, an aluminum rod was coated by a very thin layer of LiAlH_4 powder, and then ablated by a pulsed Nd:YAG laser beam operating at a wavelength of 532 nm. The resulting plasma was cooled by supersonically expanding a plume of helium gas from a pulsed gas valve (backing pressure of ~ 100 psi). Negatively charged anions were then extracted into the spectrometer prior to mass selection and photodetachment.

In order to find the most energetically favorable arrangement of atoms for the $\text{Li}_2\text{Al}_3\text{H}_8^-$ stoichiometry, we have utilized an unbiased search for the global minimum (GM) and low-energy isomers using the Coalescence Kick (CK) program¹⁹ to follow the geometry optimization procedure with the Gaussian 09 program.²⁰ Exhaustive searches (30 thousand trial structures) for each multiplicity (singlet and triplet) were performed at the PBE0²¹/LanL2DZ²² to initially explore the potential energy surface of $\text{Li}_2\text{Al}_3\text{H}_8^-$. Afterwards, the low-lying isomers ($\Delta=20$ kcal/mol) were recalculated using the more expansive 6-311++G(d, p) basis set²³ (geometry optimization and follow-up frequency analyses to ensure that each structure is a minimum on the potential energy surface). Single-point coupled cluster calculations (CCSD(T)²⁴/aug-cc-pVTZ²⁵) at the DFT-optimized geometry were subsequently performed to give more precise relative energy ordering. VDEs of isomer I of $\text{Li}_2\text{Al}_3\text{H}_8^-$ were calculated at three different levels of theory: TD-DFT,²⁶ OVGF,²⁷ and CCSD(T)²⁴ (Table S3) and compared with experimental results. The chemical bonding analysis of the isomer I via Natural Bond Orbital (NBO)²⁸ method at the PBE0/6-311++G(d, p) level of theory are also presented. Molekel 5.4.0.8²⁹ program was used for structural and molecular orbitals visualization.

Results and discussion

The photoelectron spectra of $\text{Li}_2\text{Al}_3\text{H}_8^-$ taken with 3.49 eV and 4.66 eV photon energies are presented in Figure 1. Both spectra have an electron binding energy (EBE) band (X) starting from ~ 2.20 eV and peaking at 2.70 eV. In case of a sufficient Franck-Condon overlap between the ground state of the anion

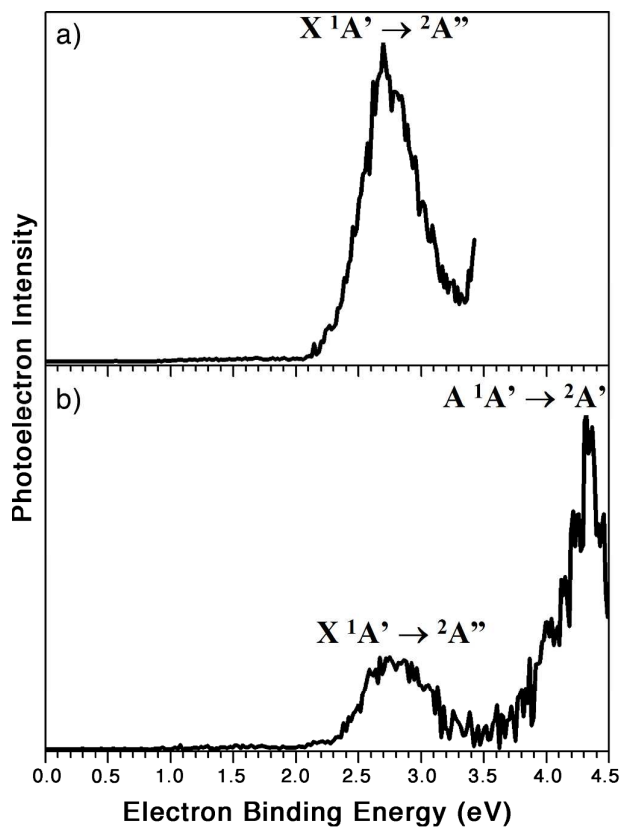


Fig. 1 Photoelectron spectra of $\text{Li}_2\text{Al}_3\text{H}_8^-$. a) at 355 nm (3.49 eV) and b) at 266 nm (4.661 eV).

and the ground state of the neutral, and given there is not much hot band signal, the threshold of the first EBE band (~ 2.20 eV) should be the electron affinity (EA). The first experimental vertical detachment energy (VDE, an energy difference between an anion and the corresponding neutral species at the geometry of the anion), corresponding to the peak position, is 2.70 eV. The width of the band X suggests an appreciable geometry change between the ground state of $\text{Li}_2\text{Al}_3\text{H}_8^-$ and that of its neutral. In Figure 1b, one can observe a second band (A) at the higher EBE end, which peaks at 4.32 eV that corresponds to the transition from the ground state of the anion to the first excited state of the neutral molecule.

Theoretically, twenty eight isomers were found within 20 kcal/mol range at PBE0/6-311++G(d, p) (Figure S1). One can see that all of them are in singlet state; the lowest energy isomer in triplet state appears to be 28.4 kcal/mol higher in energy than GM at CCSD(T). Interestingly, several low-lying isomers were found to have chiral enantiomers. As we expected, the GM isomer I (C_s , $^1A'$) was found to possess a

propane-like geometry with the $R(\text{Al-Al})=2.68 \text{ \AA}$, similar to the corresponding bond length (2.67 \AA)¹⁶ in its neutral isoelectronic analogue $\text{Li}_3\text{Al}_3\text{H}_8$. However, due to a different electrostatic field (different number of cations) in the global minimum structures of $\text{Li}_2\text{Al}_3\text{H}_8^-$ and $\text{Li}_3\text{Al}_3\text{H}_8$, locations of Li^+ cations in the first one is different than in the second one. Noteworthy, two closest in energy isomers (II and III in Figure 2) adopt similar $\text{Al}_n\text{H}_{2n+2}$ kernels with somewhat different arrangement of Li atoms. Akin to the neutral $\text{Li}_3\text{Al}_3\text{H}_8$ molecule,¹⁶ the GM structure of $\text{Li}_2\text{Al}_3\text{H}_8^-$ maintains the structural features of propane better than any other isomers (Table S1). Apparently,

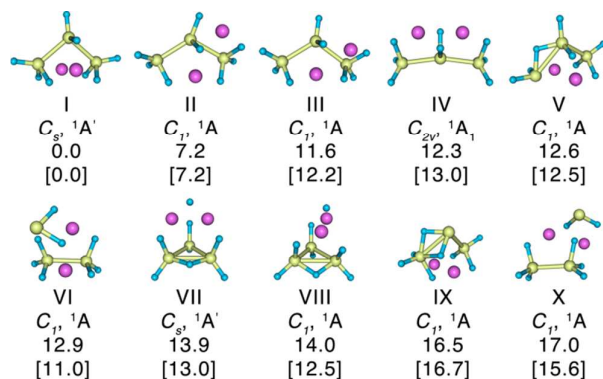


Fig. 2 Lowest energy isomers of $\text{Li}_2\text{Al}_3\text{H}_8^-$, their point group symmetries, ground electronic states, and ZPE corrected relative energies (in kcal/mol) at the PBE0/6-311++G(d, p) and CCSD(T)/aug-cc-pVTZ//PBE0/6-311++G(d, p) (in square brackets) levels of theory. The solid rods between atoms help visualization and do not necessarily represent 2c-2e σ bonds here and elsewhere. H is blue, Al is yellow, and Li is magenta.

higher Al-H perturbation caused by Li cations (the weaker the lithium-hydrogen interaction, the shorter the Al-H σ bond) evokes some deviation from the propane-like framework, and, probably, overall system destabilization. Thus, isomers II and III are 7.2 kcal/mol and 12.2 kcal/mol higher in energy than isomer I at CCSD(T). It should be noted that the valence Al-Al-Al angle in $\text{Li}_2\text{Al}_3\text{H}_8^-$ (100.0°) is almost the same as in propane molecule (112.8°). Relative to the experimentally synthesized ($\text{Cs}_{10}\text{H}[\text{Ga}_3\text{H}_8]_3$)⁹ and theoretically predicted ($\text{Li}_3\text{B}_3\text{H}_8$)⁶ X-homocatenated (X=B, Ga) propane-like species, $\text{Li}_2\text{Al}_3\text{H}_8^-$ cluster shows the smallest deviation in the valence angle from that of C_3H_8 molecule (Table S2).

To facilitate comparisons between the experimental and theoretical results, we calculated VDEs of isomer I of $\text{Li}_2\text{Al}_3\text{H}_8^-$ at three different levels of theory: TD-DFT,²⁶ OVGF,²⁷ and CCSD(T)²⁴ (Table S3). We found that the VDEs computed using all these methodologies are in excellent agreement with the first two detachment channels observed in the experiment (Figure 1). The electron detachment from $4a''$ -HOMO of the anion leads to a doublet final state for the neutral, thus giving rise to the first VDE of 2.78 eV (at CCSD(T)), compared with the

experimental VDE of 2.70 eV (peak X). The next electron detachment from the $6a'$ -HOMO-1 produces the second theoretically calculated VDE of 4.21 eV, in excellent agreement with the experimental value of 4.32 eV corresponding to the peak A. Furthermore, the calculated adiabatic detachment energy (ADE, an energy difference between an anion and the corresponding neutral species at the geometry of the anion and a neutral species, respectively) of isomer I (2.28 eV at CCSD(T)/aug-cc-pVTZ//PBE0/6-311++G(d, p)) is also in excellent agreement with the experimentally measured ADE value of 2.20 eV. As expected, appreciable geometry changes upon the electron detachment from $\text{Li}_2\text{Al}_3\text{H}_8^-$ were observed for the neutral $\text{Li}_2\text{Al}_3\text{H}_8$ cluster (Table S4), consistent with the broad X band observed in the PES spectra (Figure 1). We have also checked the VDEs of the second in energy isomer II (Table S3). However, the high relative energy of isomer II (Figure 2), as well as its somewhat higher theoretical first VDE of 2.94 eV, makes this isomer unlikely to be populated in the molecular beam in any appreciable amount. Thus, we believe that the propane-like structure I is the only one contributing to the PES.

Results of the chemical bonding analysis of the isomer I via Natural Bond Orbital (NBO)²⁸ method at the PBE0/6-311++G(d, p) level of theory are summarized in Figure 3. According to the NBO results, the $\text{Li}_2\text{Al}_3\text{H}_8^-$ cluster has two direct two-center two-electron (2c-2e) Al-Al σ bonds with $\text{ON}=1.79 |e|$ and eight 2c-2e Al-H σ bonds with $\text{ON}=1.85\text{--}1.99 |e|$. Li atoms are involved into the bonding primarily ionically, bearing charges of +0.49 and +0.56 (Table S5). These numbers are comparable to the existing studies on charge transfer from alkali metals to Al.³⁰ Al-H σ bonding is highly polarized towards hydrogen. On average, 70% of the electron density comes from hydrogen to form Al-H σ bonds. It should be pointed out that the obtained chemical bonding picture for $\text{Li}_2\text{Al}_3\text{H}_8^-$ confirms the fact of Al homocatenation and is in perfect agreement with the NBO pattern revealed for propane molecule (Figure S2). Although the positive charges on Li atoms are smaller than the ideal value of +1 according to the electronic transmutation principle,⁶ Al atoms gain enough electron density from lithium atoms to be able to transmute into Group 14 atoms and mimic the structural features of Group 14 hydrides.

Conclusions

In conclusion, thorough *ab initio* and PES studies of the $\text{Li}_2\text{Al}_3\text{H}_8^-$ cluster have reliably established the structure as well as deciphered the chemical bonding pattern of this unique species, thus introducing the first experimental example of Al homocatenation, yet unknown in chemistry. We hope that the current work will be of broad interest to scientists who are involved in synthesis of homocatenated chemical species across the Periodic Table as well as that our work will extend the view of chemical community on Al chemistry in particular.

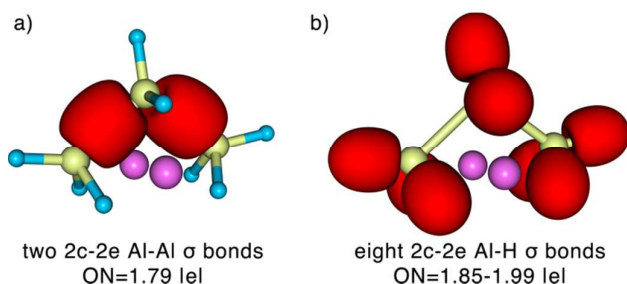


Fig. 3 Visualization of the NBO results for the $\text{Li}_2\text{Al}_3\text{H}_8^-$ cluster. a) Two aluminum-aluminum 2c-2e σ bonds (shown superimposed, left) b) Eight aluminum-hydrogen 2c-2e σ bonds (shown superimposed, right). ON denotes occupation number.

Acknowledgements

This work was supported in part by the National Science Foundation CHE-1361413 to A.I.B. Computer, storage and other resources from the Division of Research Computing in the Office of Research and Graduate Studies at Utah State University are gratefully acknowledged. This material is based in part upon work supported by the Air Force Office of Scientific Research (AFOSR), under Grant No. FA9550-15-1-0259 (K.H.B.)

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