

Main-Group Bonding

International Edition: DOI: 10.1002/anie.201710338

German Edition: DOI: 10.1002/ange.201710338

The Existence of a Designer Al=Al Double Bond in the $\text{LiAl}_2\text{H}_4^-$ Cluster Formed by Electronic TransmutationKatie A. Lundell[†], Xinxing Zhang[†], Alexander I. Boldyrev,^{*} and Kit H. Bowen^{*}

Abstract: The Al=Al double bond is elusive in chemistry. Herein we report the results obtained via combined photoelectron spectroscopy and *ab initio* studies of the $\text{LiAl}_2\text{H}_4^-$ cluster that confirm the formation of a conventional Al=Al double bond. Comprehensive searches for the most stable structures of the $\text{LiAl}_2\text{H}_4^-$ cluster have shown that the global minimum isomer I possesses a geometric structure which resembles that of Si_2H_4 , demonstrating a successful example of the transmutation of Al atoms into Si atoms by electron donation. Theoretical simulations of the photoelectron spectrum discovered the coexistence of two isomers in the ion beam, including the one with the Al=Al double bond.

Aluminum–hydrogen clusters are known to be stabilized by multicenter bonding.^[1] Yet, it was recently shown that formation of conventional Al–Al bonds is possible in clusters^[2,3] and in solid-state compounds.^[4] Reports of double Al=Al and triple Al≡Al bonds are scarce.^[5,6] Chesnut^[5d] performed topological study in di- and tetra-hydrides Al_2H_2 and Al_2H_4 molecules. Based on the ELF analysis, he concluded that in the *trans*-bent HAlAlH isomer (though not a global minimum structure), chemical bonding can be described as a resonance between a no-bond and double bond situation between two the aluminum atoms. In 1988 Uhl^[6a] synthesized the R_2AlAlR_2 ($\text{R} = \text{CH}(\text{SiMe}_3)_2$) compound containing an Al–Al bond. In the early 1990s it was shown that this compound could be reduced to $[\text{R}_2\text{AlAlR}_2]^-$ anions ($\text{R} = \text{CH}(\text{SiMe}_3)_2$ ^[6b,c] or $\text{C}_6\text{H}_5-2,4,6\text{-iPr}_3$)^[6d,e] which had Al–Al bonds of formal order 1.5 owing to the occupation of a π -orbital by a single electron. In 2003, Power and co-workers^[6d] reported the [2+4] Diels–Alder cycloaddition product of a probable dialuminene, $\text{Ar}'\text{AlAlAr}'$ ($\text{Ar}' = \text{C}_6\text{H}_3-2,6\text{-Dipp}_2$; $\text{Dipp} = \text{C}_6\text{H}_3-2,6\text{-Pri}_2$), with toluene. However, the dialuminene was not isolated. Three years later, Power^[6f] synthesized and characterized a stable $\text{Na}_2[\text{Ar}'\text{AlAlAr}']$ compound with the Al–Al bond order of 1.13. Very recently, Inoue and co-workers reported an Al=Al

containing compound stabilized by the *N*-heterocyclic carbene ligands.^[7] The utilization of electron-donating, bulky ligands forced the s and p valence electrons of Al to hybridize and form homodinuclear multiple bonds to fulfill the octet rule, which is in a similar way that the B≡B triple bonds were synthesized by Zhou^[8a] and Braunschweig.^[8b]

Our strategy for designing an Al=Al double bond is different. Herein we adopt the electronic transmutation method that was developed by our group;^[9] briefly, when an atom acquires an extra electron, it starts to behave as the isoelectronic, neighboring element. We have discovered many examples that such approach indeed works.^[2,3,9,10] Based on this, it could be anticipated that by adding one electron to each Al atom in the H_2AlAlH_2 molecule, Al might be transmuted into Si, yielding a molecule that is isoelectronic to the $\text{H}_2\text{Si}=\text{SiH}_2$ molecule. The doubly charged $\text{H}_2\text{AlAlH}_2^{2-}$ anion is not expected to be stable in the isolated state owing to the Coulomb repulsion between the two excess electrons. Indeed a crude evaluation shows that the $\text{Al}_2\text{H}_4^{2-}$ dianion is not stable owing to electron autodetachment (vertical electron detachment energy is -3.1 eV). To stabilize this dianion we counter the $\text{Al}_2\text{H}_4^{2-}$ dianion with the Li^+ cation. The final $\text{LiAl}_2\text{H}_4^-$ anion is expected to be stable due to the electrostatic stabilization from the Li^+ cation.

The photoelectron spectrum of $\text{LiAl}_2\text{H}_4^-$ taken with a 3.49 eV (355 nm) laser is presented in Figure 1. Details of

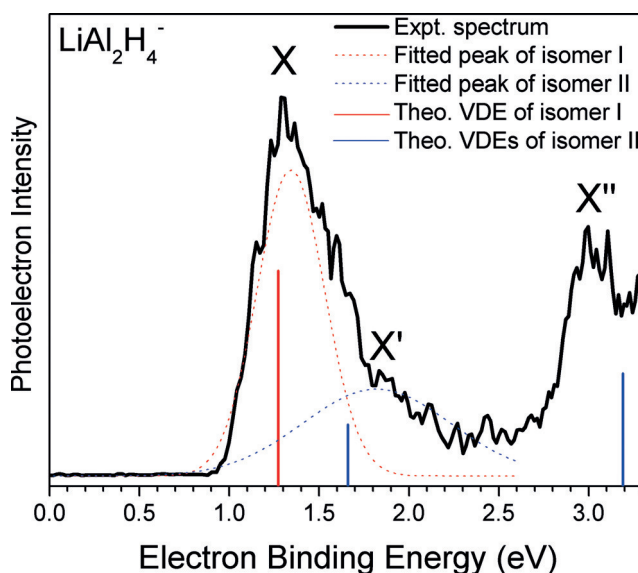


Figure 1. Experimental photoelectron spectrum of $\text{LiAl}_2\text{H}_4^-$ using 355 nm laser (black line), Gaussian fitting of isomer I and II (red and blue dotted lines), and calculated stick spectra of isomer I and II (red and blue vertical lines).

[*] K. A. Lundell,^[†] Prof. Dr. A. I. Boldyrev
Department of Chemistry and Biochemistry, Utah State University
0300 Old Main Hill, Logan, UT 84322-0300 (USA)
E-mail: a.i.boldyrev@usu.edu

Dr. X. Zhang,^[†] Prof. Dr. K. H. Bowen
Departments of Chemistry and Material Science
Johns Hopkins University
Baltimore, MD 21218 (USA)
E-mail: kbowen@jhu.edu

[†] These authors contributed equally to this work.

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/anie.201710338>.

the experiment and the apparatus are given in the Supporting Information. The spectrum has an electron binding energy (EBE) band starting from about 1.0 eV and peaks at 1.30 eV. In case of a sufficient Franck–Condon overlap between the ground state of the anion and the ground state of the neutral species, and given there is not much hot band signal, the threshold of the first EBE band (ca. 1.0 eV) should be the electron affinity (EA). The first experimental vertical detachment energy (VDE) is the photodetachment transition at which the Franck–Condon overlap between the wavefunctions of the anion and its neutral counterpart is maximal, corresponding to the peak position, 1.30 eV. The width of the band suggests an appreciable geometry change between the ground state of $\text{LiAl}_2\text{H}_4^-$ and that of its neutral.

To find the experimentally observed structure, we initially performed an unbiased search (10000 trial structures) for the singlet configuration of the $\text{LiAl}_2\text{H}_4^-$ stoichiometry using the coalescence-kick method^[11] with the Gaussian09 program^[12] at the PBE0^[13]/3-21G^[14] level of theory. Afterwards, the lowest-lying isomers ($\Delta E \leq 20 \text{ kcal mol}^{-1}$) were recalculated at the more expensive PBE0/6-311++G** level of theory^[15] with geometry optimization and frequency analysis to ensure that each structure was a minimum on the potential energy surface. Single-point couple cluster calculations (CCSD(T)^[16]/6-311++G** and CCSD(T)/aug-cc-pVTZ^[17]) at the DFT-optimized geometry were subsequently performed to give more precise relative energies. VDEs of the lowest isomers were calculated as the energy difference between the ground states of the anions and different states of the neutral counterparts at the same geometry of the anions using three different levels of theory: TD-DFT,^[18] OVGF,^[19,20] and CCSD(T), and compared with experimental results. The chemical bonding analysis of the two lowest isomers, isomers I and II, via Adaptive Natural Density Partitioning (AdNDP)^[21] method at the PBE0/6-311++G** level of theory is also presented. Chemcraft v1.8 (build 165)^[22] was used for structural and molecular orbital visualization.

The lowest ten isomers found at PBE0/6-311++G** and CCSD(T)/aug-cc-pVTZ level of the $\text{LiAl}_2\text{H}_4^-$ stoichiometry are presented in Figure 2. The 3D coordinates of all of these structures are provided in the Supporting Information. As designed, the global minimum structure I is similar to the Si_2H_4 structure. Because of an imaginary frequency, the planar C_{2v} (1A_1) structure is not a minimum. Geometry optimization following this imaginary frequency mode leads to a slightly non-planar structure C_2 (1A) symmetry with hydrogen atoms lying above and below the Al–Li–Al plane by 0.27 and 0.35 Å. However, the barrier for planarization is very small ($0.01 \text{ kcal mol}^{-1}$) and thus this structure is effectively planar if we include ZPE corrections. The similar distortion is known for the Si_2H_4 molecule. According to our calculations, the planar Si_2H_4 molecule is not a minimum at the planar D_{2h} symmetry and undergoes the pseudo Jahn–Teller distortion towards a *trans*-bent structure (see the Supporting Information for details). However, as in the case of $\text{LiAl}_2\text{H}_4^-$, the barrier for the planarization in Si_2H_4 is small ($0.14 \text{ kcal mol}^{-1}$ at PBE0/6-311++G**) and the vibrationally averaged structure is effectively planar. The optimal bond length between the two Al atoms in $\text{LiAl}_2\text{H}_4^-$ structure is 2.46 Å

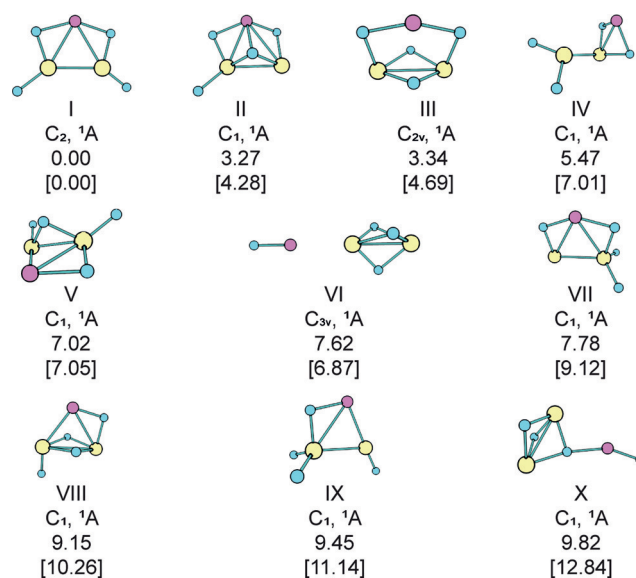


Figure 2. Lowest energy isomers of $\text{LiAl}_2\text{H}_4^-$, their point group symmetries, ground electronic states, and ZPE corrected relative energies [kcal mol⁻¹] at the CCSD(T)/aug-cc-pVTZ (in parentheses) and PBE0/6-311++G** (in square brackets) levels of theory. The solid rods between atoms help visualize and do not necessarily represent σ -bonds here and elsewhere. H blue, Al yellow, Li pink.

(PBE0/6-311++G**), which is shorter than the single Al–Al σ -bond (2.59 Å, PBE0/6-311++G**) in the H_2AlAlH_2 molecule and the single Al–Al σ -bond (2.55 Å) in the $\text{H}_3\text{AlAlH}_3^{2-}$ crystal structure.^[4] The appreciably shorter Al–Al distance in structure I indicates that there could be a double bond between the two aluminum atoms.

Before further analysis of the chemical bonding, we need to confirm that the calculated VDEs agree with the experimentally observed values. Table 1 summarizes the calculated and experimental VDE data. First, calculated VDEs for both isomers I and II using three different methods are in a reasonable agreement among themselves. The first calculated VDE from HOMO 3b for the global minimum structure I is 1.27 eV (CCSD(T)), in excellent agreement with the experimentally observed 1.30 eV value (Figure 1, peak X, fitted by a red dotted line), confirming that the Si_2H_4 -like structure for $\text{LiAl}_2\text{H}_4^-$ was indeed observed in the ion beam. However, the experimental EBE intensity at around 1.8 eV (X', fitted by a blue dotted line) and the peak at 3.0 eV (X'') do

Table 1. Calculated and experimental VDEs (eV) of isomers I and II of the $\text{LiAl}_2\text{H}_4^-$ anion.

Isomer I	VDE _{EXPT}	VDE _{TD-DFT} ^[a]	VDE _{OVGF} ^[b]	VDE _{CCSD(T)} ^[c]
HOMO (3b)	1.3	1.224	1.178	1.273
HOMO–1 (3a)	NA	3.685	4.059	3.852
HOMO–2 (2b)	NA	5.465	6.270	6.225
Isomer II	VDE _{EXPT}	TD-DFT	OVGF	CCSD(T)
HOMO (6a)	1.8	1.615	1.632	1.649
HOMO–1 (5a)	3.0	3.034	3.009	3.187

[a] TD-DFT/6-311++G**. [b] OVGF/aug-cc-pVTZ. [c] CCSD(T)/aug-cc-pVTZ.

not agree with the other calculated VDE (HOMO-1, 3a) of isomer I. They might correspond to coexisting low-lying isomers, which is not uncommon for laser vaporization generated ion beams. According to the calculations, the first VDE (HOMO 6a) of isomer II at 1.64 eV (CCSD(T)) is in reasonable agreement with the PES intensity at 1.8 eV (X'). The next experimental EBE band at 3.0 eV (X') is also in good agreement with the second VDE (HOMO-1, 5a) of isomer II at 3.19 eV (CCSD(T)). Thus, from the comparison of theoretical and experimental data, we can confirm that two isomers were experimentally observed in the ion beam. Since the third isomer was found to be very close in energy to isomer II, we performed VDE calculations for it as well (Supporting Information, Table S1). The two first VDEs have energies at 2.4–2.5 eV and there are no corresponding peaks in the experimental spectrum. Most importantly, our expectation of the Si₂H₄-like LiAl₂H₄⁻ isomer was indeed produced by experiment.

The next obvious question is whether the Al=Al double bond exist in the global minimum structure. To answer this question, we performed AdNDP analysis for the global minimum isomer I (Figure 3) and isomer II (Supporting Information, Figure S1). From Figure 3, two 2c-2e σ Al-H

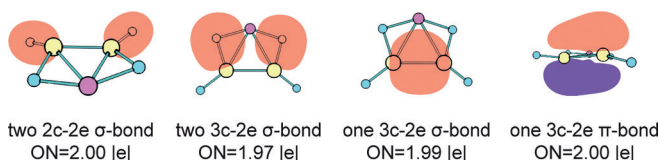


Figure 3. Chemical bonds recovered by the AdNDP analysis for isomer I.

bonds (ON = 2.00 |e|), two 3c-2e σ Li-H-Al bonds (ON = 1.97 |e|); these four bonds are analogous to the σ Si-H bonds in Si₂H₄, one σ 3c-2e Al-Li-Al bond (ON = 1.99 |e|; an analogue of the σ Si-Si bond in Si₂H₄), and one π Al-Li-Al bond (ON = 2.00 |e|) (an analogue of the π Si-Si bond in Si₂H₄) can be observed. To claim the presence of the Al=Al double bond we need to evaluate how much the lithium atom contributes to the σ 3c-2e Al-Li-Al and π 3c-2e Al-Li-Al bonds. The AdNDP method allows us to view this bond as a 2c-2e bond. We found that the σ 3c-2e Al-Li-Al bond (ON = 1.99 |e|) can be seen as one σ 2c-2e Al-Al bond (ON = 1.87 |e|) and the π 3c-2e Al-Li-Al bond (ON = 2.00 |e|) can be found as one π 2c-2e Al-Al bond (ON = 1.65 |e|). That gives us the 1.76 bond order for Al=Al double bond in our cluster. Therefore, the global minimum isomer I does have an Al=Al double bond. This is further supported by each Al demonstrating an electronic transmutation of their natural charge from +0.7 in H₂AlAlH₂ to +0.0 in LiAl₂H₄⁻ through the addition of one electron and one Li atom to the system (see the Supporting Information, Table S3 for full natural population analysis charges).

In summary, on the basis of the electronic transmutation model, we have designed and observed a LiAl₂H₄⁻ cluster with a global minimum that has a Si₂H₄-like structure and an Al=Al double bond. Photoelectron spectroscopy study and the comparison with the theory reveal that the LiAl₂H₄⁻ ion

beam consists of two isomers, including the calculated global minimum (isomer I) and the second low-lying isomer (isomer II). The AdNDP analysis indicates that the Al=Al double bond of isomer I possesses one σ and one π bond. Our results provide the viability of the electronic transmutation strategy in designing Al-Al multiple bonds, and shed light on the future discovery of the Al≡Al triple bond. Also, molecules with the Al=Al double bonds are important for further synthesis of new unusual molecules through [2+2] or [2+4] reactions.

Acknowledgements

This material is based upon work supported by the Air Force Office of Scientific Research (AFOSR) under Grant No. FA9550-15-1-0259 (K.H.B.). The theoretical work was supported by the National Science Foundation (CHE-1664379 to A.I.B.).

Conflict of interest

The authors declare no conflict of interest.

Keywords: ab initio calculations · aluminum hydride · double bonds · electronic transmutation · photoelectron spectroscopy

How to cite: *Angew. Chem. Int. Ed.* **2017**, *56*, 16593–16596
Angew. Chem. **2017**, *129*, 16820–16823

- [1] a) A. Grubisic, X. Li, S. T. Stokes, J. Cordes, G. F. Ganteför, K. H. Bowen, B. Kiran, P. Jena, R. Burgert, H. Schnöckel, *J. Am. Chem. Soc.* **2007**, *129*, 5969–5975; b) X. Li, A. Grubisic, S. T. Stokes, J. Cordes, G. F. Ganteför, K. H. Bowen, B. Kiran, M. Willis, P. Jena, R. Burgert, H. Schnöckel, *Science* **2007**, *315*, 356–358; c) X. Li, A. Grubisic, K. H. Bowen, A. K. Kandalam, B. Kiran, G. F. Ganteför, P. Jena, *J. Chem. Phys.* **2010**, *132*, 241103; d) B. Kiran, A. K. Kandalam, J. Xu, Y. H. Ding, M. Sierka, K. H. Bowen, H. Schnöckel, *J. Chem. Phys.* **2012**, *137*, 134303; e) B. Kiran, P. Jena, X. Li, A. Grubisic, S. T. Stokes, G. F. Ganteför, K. H. Bowen, R. Burgert, H. Schnöckel, *Phys. Rev. Lett.* **2007**, *98*, 256802; f) C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 564–565; *Angew. Chem.* **1991**, *103*, 594–595.
- [2] T. J. Gish, I. A. Popov, A. I. Boldyrev, *Chem. Eur. J.* **2015**, *21*, 5307–5310.
- [3] I. A. Popov, X. Zhang, B. W. Eichhorn, A. I. Boldyrev, K. H. Bowen, *Phys. Chem. Chem. Phys.* **2015**, *17*, 26079–26083.
- [4] S. Bonyhady, J. N. Holzmann, G. Frenking, A. Stasch, C. Jones, *Angew. Chem. Int. Ed.* **2017**, *56*, 8527–8531; *Angew. Chem.* **2017**, *129*, 8647–8651.
- [5] a) Z. Palagyi, R. S. Grev, H. F. Schaefer III, *J. Am. Chem. Soc.* **1993**, *115*, 1936; b) B. S. Jursic, *J. Mol. Struct. Theochem* **1998**, *453*, 123; c) K. Lammertsma, O. F. Güner, R. M. Drewes, A. E. Reed, P. v. R. Schleyer, *Inorg. Chem.* **1989**, *28*, 313; d) D. B. Chesnut, *Chem. Phys.* **2006**, *321*, 269–276.
- [6] a) W. Uhl, *Z. Naturforsch. B* **1988**, *43*, 1113; b) C. Pluta, K. R. Pörschke, C. Krueger, K. Hildenbrand, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 388; *Angew. Chem.* **1993**, *105*, 451; c) W. Uhl, A. Vester, W. Kaim, J. Poppe, *J. Organomet. Chem.* **1993**, *454*, 9; d) R. J. Wright, A. D. Phillips, P. P. Power, *J. Am. Chem. Soc.*

- 2003**, 125, 10784–10785; e) P. P. Power, *Chem. Rev.* **1999**, 99, 3463–3503; f) R. J. Wright, J. C. Fettinger, P. P. Power, *Angew. Chem. Int. Ed.* **2006**, 45, 5953–5956; *Angew. Chem.* **2006**, 118, 6099–6102.
- [7] P. Bag, A. Porzelt, P. J. Altmann, S. Inoue, *J. Am. Chem. Soc.* **2017**, DOI: <https://doi.org/10.1021/jacs.7b08890>.
- [8] a) M. Zhou, N. Tsumori, Z. Li, K. Fan, L. Andrews, Q. Xu, *J. Am. Chem. Soc.* **2002**, 124, 12936–129367; b) H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. Vargas, *Science* **2012**, 336, 1420–1422.
- [9] J. K. Olson, A. I. Boldyrev, *Chem. Phys. Lett.* **2012**, 523, 83–86.
- [10] a) A. S. Ivanov, A. J. Morris, K. V. Bozhenko, C. J. Pickard, A. I. Boldyrev, *Angew. Chem. Int. Ed.* **2012**, 51, 8330–8333; *Angew. Chem.* **2012**, 124, 8455–8458; b) J. K. Olson, A. S. Ivanov, A. I. Boldyrev, *Chem. Eur. J.* **2014**, 20, 6636–6640; c) A. S. Ivanov, A. I. Boldyrev, G. Frenking, *Chem. Eur. J.* **2014**, 20, 2431–2435A; d) A. S. Ivanov, T. Kar, A. I. Boldyrev, *Nanoscale* **2016**, 8, 3454–3460.
- [11] A. P. Sergeeva, B. B. Averkiev, H. J. Zhai, A. I. Boldyrev, L. S. Wang, *J. Chem. Phys.* **2011**, 134, 224304.
- [12] Gaussian 09 (Revision B.0.1), M. J. Frisch et al., Gaussian, Inc., Wallingford CT, **2009**.
- [13] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, 110, 6158.
- [14] J. B. Collins, J. A. Pople, W. J. Hehre, *J. Am. Chem. Soc.* **1980**, 102, 939.
- [15] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, 72, 650.
- [16] H. B. Schlegel, M. A. Robb, *Chem. Phys. Lett.* **1982**, 93, 43.
- [17] a) G. D. Purvis, R. J. Bartlett, *J. Chem. Phys.* **1982**, 76, 1910; b) K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, 157, 479.
- [18] E. Runge, E. K. U. Gross, *Phys. Rev. Lett.* **1984**, 52, 997–1000.
- [19] L. S. Cederbaum, *J. Phys. Chem.* **1975**, 8, 290–303.
- [20] J. Lin, J. V. Ortiz, *Chem. Phys. Lett.* **1990**, 171, 197–200.
- [21] D. Y. Zubarev, A. I. Boldyrev, *Phys. Chem. Chem. Phys.* **2008**, 10, 5207–5217.
- [22] G. Andrenko, **2014**, Chemcraft V1.8 (build 165).

Manuscript received: October 6, 2017

Revised manuscript received: October 28, 2017

Accepted manuscript online: November 2, 2017

Version of record online: November 28, 2017