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Realization of an Al≡Al Triple Bond in the Gas-Phase Na₃Al₂⁻
Cluster via Double Electronic Transmutation

Xinxing Zhang,* Ivan A. Popov, Katie A. Lundell, Haopeng Wang, Chaonan Mu, Wei Wang, Hansgeorg Schnöckel, Alexander I. Boldyrev* and Kit H. Bowen*

Abstract: The discovery of homodinuclear multiple bonds composed of Group 13 elements represents one of the most challenging frontiers in modern chemistry. A classical triple bond such as N≡N and HCC≡CH contains one σ bond and two π bonds constructed from the p orbitals perpendicular to the σ bond. However, the traditional textbook triple bond between two Al atoms has remained elusive. Here we report an Al≡Al triple bond in the designer Na₃Al₂⁻ cluster predicted in silico, which was subsequently generated by pulsed arc discharge followed by mass spectrometry and photoelectron spectroscopy characterizations. Being effectively Al²⁻ due to the electron donation from Na, the Al atoms in Na₃Al₂⁻ undergo a double electronic transmutation into Group 13 elements, thus the Al²⁻≡Al²⁻ kernel mimics the P≡P and N≡N molecules. We anticipate this work will stimulate more endeavors in discovering materials using Al²⁻≡Al²⁻ as a building block in the gas phase and in the solid state.

Other than the well-known dinitrogen (N≡N), diphosphorus (P≡P), and acetylene (HCC≡CH) molecules, homodinuclear triple bonds composed of main group elements are extremely scarce,[1,2] and the synthesis of such species imposes a great challenge to modern chemistry. The narrative of the famous digallane molecule Na₂[ArGaGaAr] (Ar = C₆H₅-2,6-(C₆H₅-2,4,6-iPr)₃) featuring the shortest Ga–Ga bond on record.[3] Even though the [ArGaGaAr]²⁻ kernel is valence-isoelectronic to acetylene, its x-ray crystallography reveals a trans-bent structure. The nature of the Ga–Ga bond in this digallane has attracted considerable debate afterwards.[4,5] Cotton et al. offered an opposing opinion by density functional theory (DFT) calculations that the Ga–Ga bond had a μ-type nonbonding orbital, and the short bond length was a result of the Ar–Na⁺–Ar⁺ attractions.[6] Power and coworkers provided similar arguments that the bonding in [RGaGar]²⁻ ions had considerable Lewis base character at the Ga centers where electron density was accumulated.[7] In a model system [PhGaGaPh]²⁻, Frenking and coworkers pointed out that two of the three electron pairs of the Ga–Ga bond had partial lone-pair character, hence the calculated bond order had a value typical for single bonds.[8] Grunenberg and Goldberg pointed to the mechano-chemical weakness of this bond by calculating relaxed force constants (FCs).[9] According to their calculations of the inverted Hessian matrix, the Ga–Ga bond (0.87 auÅ¹) in a “gallyne” model compound Ga₃H₆Na₂ was found to be weaker than the Ga–Ga double bond (1.20 auÅ¹) in Ga₂H₂Na₂. However, according to Schaefer, Schleyer, Robinson and coworkers’ calculations,[10] the Ga≡Ga triple bond was composed of two dative bonds and one π bond, thus constituting a non-classical but genuine triple bond. Using a simplified model [Ga₃H₆]²⁻, Klinkhammer[11] supported the existence of the Ga≡Ga triple bond, which was claimed to be a combination of a σ bond, a π bond, and a non-classical “slipped” τ bond. These studies in this phenomenal “digallyne debate” have been significant contributions to Group 13 chemistry. However, due to the trans-bent nature, the Ga–Ga bonding situation of these compounds does not correspond to the classical triple bond that is composed of one σ bond and two π bonds constructed from the p orbitals perpendicular to the σ bond, such as that in the linear HCC≡CH.

The discovery of the B≡B triple bond has more fruitful results, which starts from the isolation of the OC–B≡B–CO molecule in an argon matrix by Zhou et al.[12] followed by a plethora of theoretical and experimental studies of the B₂ molecule stabilized by diatomic Lewis bases such as CO, CS, N₂, NH₃ (N-heterocyclic carbene), BO⁻,[13,14] Braunischweig et al. synthesized the unprecedented NHC–B≡B–NHC crystal featured the first ambient-temperature isolable diborane.[15] Köppe and Schnöckel questioned this triple bond based on electronic interactions between the B–B bond and the two B–(NHC) bonds.[16] However, later Grunenberg[17] and Frenking’s calculations[18] and Braunischweig’s Raman[19] and NMR[20] spectroscopic measurements as well as chemical reactions[21] supported the existence of the B≡B triple bond in NHC–B≡B–NHC.

The search for multiple Al–Al bonds has proceeded in a step-by-step manner. In 1988, Uno[22] synthesized the R₂AlIAR₂ (R = CH(SiMe₃)₂) compound containing an Al–Al single bond. In the early 1990s, it was shown that this compound could be reduced to [R₂AlIAR₂]⁻ anions with an increased formal bond order of 1.5.[23–26] Recently, Inoue and coworkers[27] reported the synthesis of a dialumene compound R₂AlIAR₂ (R = Si₂Me₅, R = NH₂) stabilized by N-heterocyclic carbene, featuring a double Al–Al bond. Immediately after Inoue’s work, the LiAl₂⁺ cluster[28] produced in an ion beam was also found to exhibit an Al–Al double bond, with an Al₂H₂⁺ kernel mimicking the...
iso-electronic Si$_2$H$_4$ molecule. In 2006, Power$^{29}$ synthesized and characterized a stable Na$_2$[Ar$^*$/AlAr$^*$] (Ar$^*$ = C$_2$H$_2$/2.6-(C$_2$H$_2$/2.4,6-$i$Pr)$_3$) compound named dialumynine, which was similar to digalynine$^{30}$ and featured a trans-bent structure, where the Al-Al triple bond was described to contain a slipped π bond. In view of the above discussions, we aim to design a ligandless Al≡Al triple bond that is similar to Na≡N and P≡P, so that it can rule out the possibilities of resonance structures, trans-bent geometry, and any non-classical bonding interactions such as the slipped π bond. Hence, we utilized the concept of double electronic transmutation (DET), which depicts the process that by acquiring two extra electrons, an element with the atomic number Z begins to have properties that were known to only belong to the element with the atomic number Z+2. Based on DET, AlP$_2$≈AlP$^2$ should be similar to P≡P. Being a stricter and narrower notion of the widely-used valence-isoelectronic principle, single electronic transmutation (SET) has been successfully applied for predicting structures of various compounds as reviewed elsewhere.$^{30}$ However, no compounds have been reported so far based on the DET concept.

To experimentally explore the AlP$_2$≈AlP$^2$ prototype, we designed a Na$_2$Al$^2$- cluster in the hope that each Na atom could function as an electron donor, and the fourth electron is in the form of a negative charge. The clusters were generated with a pulsed arc cluster ionization source (PACIS)$^{31}$ in the gas phase by discharging an Al/Na mixture target with ~1500 A, 180 V, 20 μs pulsed arc. Experimental details are provided in the Supporting Information (SI). The resulting mass spectrum is presented in Fig. 1A, where Na$_2$Al$_{x}$- $^-$ (x = 0–4). NaAl$_2$O$^-$ and Al$_2$O$^-$ cluster anions are observed. Oxygen atoms are from the natural oxidation of sodium. Na$_2$Al$^2$- is a magic number species with a reproducibly intense mass peak among its neighboring clusters, indicating an unusually high stability. Indeed, if Na$_2$Al$^2$- is successfully “transmuted” into the P≡P analogue, it might well be very stable due to the closed-shell configuration and the triple bond.

The bonding situation of Na$_2$Al$^2$- can be better interpreted by photoelectron spectroscopy (Si), a direct means to investigate the electronic structures of the occupied molecular orbitals (MOs). In Figure 1B, several electron binding energy (EBE) peaks at 0.89, 1.84 and 2.25 eV are assigned as the vertical detachment energies (VDE). If Na$_2$Al$^2$- is a transmuted version of P≡P, these three peaks should correspond to the photoelectrons detached from the three frontier orbitals, these being one σ bonding orbital and two π bonding orbitals, which is a direct observation of the Al≡Al triple bond.

Isolated and well-defined gas-phase systems are ideally suited for simulations employing state-of-the-art quantum theoretical methods. The unmatched high complementarity and comparability of experiment and theory in the case of gas-phase investigations bear an enormous potential for modeling challenging tasks such as global minimum (GM) search and chemical bonding analysis. To better understand Na$_2$Al$^2$-, we employed an unbiased search for the GM on the potential energy surface, which was expected to be the main contributor to the photoelectron spectrum. Using the Coalescence Kick (CK) program, 10,000 trial structures (in singlet and triplet states) underwent geometry optimizations at PBE0/6-311+G*$^{*}$, subsequently the lowest structures recalculated at higher levels of theory (CCSD(T)/6-311+G*$^{*}$ and CCSD(T)/aug-cc-pVTZ/CCSD(T)/6-311+G*$^{*}$), and further ranked according to their relative energies (Figure S1 and Table S1). The GM structure of Na$_2$Al$_2$- (Co$_{ov}$, A$_1$) exhibits a direct Al–Al contact of 2.49 Å (CCSD(T)/6-311+G*$^{*}$) with three surrounding Na atoms, which define a plane passing through the center of the Al$_2$ core. The slight deviation from the perfect D$_6h$ symmetry is stipulated by the pseudo-Jahn-Teller effect, which lowers the symmetry to C$_{2v}$ (origin of the pseudo-Jahn-Teller distortion is presented in SI). To verify that the GM structure of Na$_2$Al$_2$- describes the photoelectron spectrum, VDEs were computed at three levels of theory (DFT, OVGF, and CCSD(T)). As shown in Table 1, the first three VDEs unambiguously coincide with the experimental VDEs, thus confirming the computationally predicted GM structure.

Table 1. Experimental and calculated VDEs (eV) for the GM of Na$_2$Al$^2$- at three levels of theory.$^{[a]}$

<table>
<thead>
<tr>
<th>MO</th>
<th>EXPT</th>
<th>OVGF</th>
<th>TD-BLYP</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO (ε$_{a_2}$)</td>
<td>0.89</td>
<td>0.82</td>
<td>0.67</td>
<td>0.807</td>
</tr>
<tr>
<td>HOMO-1 (ε$_{a_1}$)</td>
<td>1.84</td>
<td>1.74</td>
<td>1.50</td>
<td>_</td>
</tr>
<tr>
<td>HOMO-2 (ε$_{b_1}$)</td>
<td>2.25</td>
<td>2.23</td>
<td>2.54</td>
<td>_</td>
</tr>
</tbody>
</table>

$^{[a]}$ Aug-cc-pVTZ basis set was employed for all three methods.

This VDE could not be obtained at this level of theory.

The GM of the neutral Na$_2$Al$_2$ cluster (other isomers and their Cartesian coordinates are provided in Figure S2 and Table S2), which has four Na atoms positioned around the Al$_2$ core in the D$_6h$ manner, also possesses a quite short Al–Al bond length of 2.45 Å. Being isoelectronic, both clusters are expected to form a triple AlP$_2$≈AlP$^2$- bond, which might be the shortest for dialumino-containing species. However, they are comparable to the Al–Al double bond LiAlH$_4$ – (2.46 Å),$^{[29]}$ and somewhat longer than that of the di-tertbutyl(methyl)silyl-substituted dialumene (2.39 Å).$^{[37]}$ We opine that it is because Al atoms carry large negative charges, which repulse each other. Other than the Al–Al distances, the Al–Al force constants FC(Al–Al) reflect a better measure of the bond order. According to our calculations at the PBE0/Def2-SVP level of theory employing normal coordinates within Gaussian 09 program, FC(Al–Al) of Na$_2$Al$_2$ is 2.30 mDyne/Å, and FC(Al–Al) of Na$_2$Al$^2$- is 2.02 mDyne/Å. These values are in excellent agreement with the coupled cluster values at CCSD(T)/6-311+G*$^{*}$, i.e. 2.41 mDyne/Å and 2.00 mDyne/Å. Corresponding DFT values for the bulkier...
To further investigate the Al\textsubscript{2} triple bond, we perform the Adaptive Natural Density Partitioning (AdNDP) analysis\cite{9,10} of chemical bonding in P\textsubscript{2}, Na\textsubscript{2}Al\textsubscript{2} and Na\textsubscript{2}Al at the wB97XD/Def2-TZVP level of theory (Figure 2). In both Na\textsubscript{2}Al\textsubscript{2} and Na\textsubscript{2}Al, the bonding pattern is similar to P\textsubscript{2}, though Na atoms contribute to the lone pair (LP) on each Al atom as well as to the σ- and τ-bonds. According to AdNDP, there are two s-type lone pairs on the two Al atoms (one on each) with occupation numbers (ONs) equal to 1.64 \[e^{-}\] in Na\textsubscript{2}Al\textsubscript{2} and 1.63 \[e^{-}\] in Na\textsubscript{2}Al. The Al-Al σ-bond is found as a pure two-center two-electron (2c-2e) σ-bond with ON=1.85 \[e^{-}\] in Na\textsubscript{2}Al\textsubscript{2} and 1.97 \[e^{-}\] in Na\textsubscript{2}Al. The two 2c-2e τ-bonds have somewhat lower ON values: 1.30 \[e^{-}\], 1.51 \[e^{-}\] in Na\textsubscript{2}Al\textsubscript{2} and 1.60 \[e^{-}\], 1.60 \[e^{-}\] in Na\textsubscript{2}Al. It is noted that the deviation of the ON values of the τ-bonds from the ideal value of 2.00 \[e^{-}\] is in agreement with the relaxed FC(Al-Al) values for Na\textsubscript{2}Al\textsubscript{2} and Na\textsubscript{2}Al, which are comparable to that of the Al\textsubscript{2}H\textsubscript{2}N\textsubscript{2} cluster exhibiting Al=Al double bond. The analogous bonds in P\textsubscript{2} have ON values close to 2.00 \[e^{-}\] (Figure 2A). Indeed, the remaining electron density in Na\textsubscript{2}Al\textsubscript{2} and Na\textsubscript{2}Al is found on the Na atoms. Inclusion of the Na atoms into the bond search produces multicenter bonds with ON=2.00 \[e^{-}\], thus allowing to assess the contribution of Na atoms (Figure 2B, 2C).

**Figure 2. Summary of the AdNDP analysis of the P\textsubscript{2} (A), Na\textsubscript{2}Al\textsubscript{2} (B) and Na\textsubscript{2}Al (C) clusters.**

In summary, we have applied the DET concept to design two clusters, Na\textsubscript{2}Al\textsubscript{2} and Na\textsubscript{2}Al, which are found to possess Al=Al triple bonds. Excellent agreement between the experimental and calculated VDEs for the most stable isomer of Na\textsubscript{2}Al\textsubscript{2} confirms the proposed structure. Presence of the triple bond in Na\textsubscript{2}Al\textsubscript{2} is also supported by its reproduced intense mass peak among the neighboring clusters, which indicates an unusually high stability. Similarity of the canonical MOs of the P\textsubscript{2}S\textsubscript{6} molecule with Na\textsubscript{2}Al\textsubscript{2} and Na\textsubscript{2}Al, along with the AdNDP results, further confirm that Na atoms can "transmute" Al into P, and therefore, aid in the formation of the Al=Al triple bonds. The Al\textsuperscript{2}≡Al\textsuperscript{2} core may serve as a building block in other gas-phase clusters, and it also holds potential to be realized in periodically extended solid-state compounds. Similarly, the valence-isoelectronic triple bonded C\textsuperscript{2+} already functions as a building block of a large family of carbide compounds.\cite{8} Furthermore, highly charged species of the heavier homologues of Al, such as the Tl\textsuperscript{2+} and In\textsuperscript{2+} clusters, represent more examples of experimentally observed building blocks, which are stabilized as solid-state Zintl phases via strong Coulomb interactions with Na\textsuperscript{+}.\cite{7} Hence, this work will not only serve as a general guideline for predicting novel DET clusters, but also stimulate synthesis of the unprecedented chemical solids featuring Al\textsuperscript{2+}≡Al\textsuperscript{2+} triple bonds.

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Keywords: Al-Al triple bond • photoelectron spectroscopy • ab initio calculations • double electronic transmutation

The experimental observation of an Al≡Al triple bond is achieved from the double electronic transmutation of Al atoms into P atoms by electron donation from Na in the Na$_3$Al$_2$ cluster.

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