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 15 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 homodinuclear triple bonds composed of Group 13 elements started with Robinson and co-workers’ synthesis of the famous digallene molecule Na₂[ArGaGaAr] (Ar = C₂H₂-2,6-(C₆H₅-2,4,6-iPr)₃) featuring the shortest Ga–Ga bond on record.[3] Even though the [ArGaGaAr]⁺ kernel is valence-isoelectronic to acetylene, its X-ray crystallography reveals a trans-bent structure. The nature of the Ga–Ga bond in this digallene 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 π-type nonbonding orbital, and the short bond length was a result of the Ar-Na⁺-Ar attractions.[6] Power and co-workers provided similar arguments that the bonding in [RGaGaR]⁻ ions had considerable Lewis base character at the Ga centers where electron density was accumulated.[7] In a model system [PhGaGaPh]⁻, Frenking and co-workers 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] Grünenberg and Goldberg pointed to the mecano-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 aJ Å⁻¹) featuring the shortest Ga–Ga bond in this “gallyne” model compound GaH₃Na₂ was found to be weaker than the Ga–Ga double bond (1.20 aJ Å⁻¹) in GaH₆N₂. However, according to Schaefer, Schleyer, Robinson and co-workers’ calculations[10] the Ga≡Ga triple bond was composed of two diaxial bonds and one π bond, thus constituting a non-classical but genuine triple bond. Using a simplified model [GaH₃]⁺[GaH₃]⁻, 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” π bond. These studies in this phenomenal “digallene 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 at 8 K 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, NHC (N-heterocyclic carbene), BO.[13-15] Braunsgeweg et al. synthesized the unprecedented NHC−B≡B−NHC crystal featured the first ambient-temperature isolable diboryne.[14] Köppe and Schnöckel questioned this triple bond based on electronic interactions between the B−B bond and the two B−(NHC) bonds.[15] However, later Grünenberg’s[16]
and Frenking’s calculations,[30b] Braunschweig’s Raman[21a] and NMR[21b] spectroscopic measurements as well as chemical reactions[27c–d] supported the existence of the B=B triple bond in NHCH=N=B—NHC.

The search for multiple Al=Al bonds has proceeded in a step-by-step manner. In 1988, Uhl[30] synthesized the R₂AlAlR₂ (R = CH(SiMe₃)) compound containing an Al–Al single bond. In the early 1990s, it was shown that this compound could be reduced to [R₂AlAlR₂−] anions with an increased formal bond order of 1.5.[32–36] Recently, Inoue and co-workers[37] reported the synthesis of a dialumene compound RR’AlAlRR’ (R = Bu₂MeSi, R’ = NHCH) stabilized by N-heterocyclic carbene, featuring a double Al=Al bond. Immediately after Inoue’s work, the Li₃AlH₄ cluster[28] produced in an ion beam was also found to exhibit an Al=Al double bond, with an Al–H₂⁻ kernel mimicking the isoelectronic SiH₂ molecule. In 2006, Power[29] synthesized and characterized a stable Na₂[Ar’AlAlAr’] (Ar’ = C₆H₅−2,4,6-(CH₂)₂,2,4,6-iPr₃) compound named dialumine, which was similar to digalline[38] 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 N≡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 used 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, Al²⁺≡Al²⁺ 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[30b] including those with single[30a] and double[28] Al=Al bonds. However, no compounds have been reported so far based on the DET concept.

To experimentally examine the Al²⁺≡Al²⁺ prototype, we designed a Na₃Al₂⁺ 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. Na-Al clusters of various stoichiometries were generated with a pulsed arc cluster ionization source (PACIS)[32] in the gas phase by discharging an Al/Na mixture target with about 1500 A, 180 V, 20 μs pulsed arc. Experimental details are provided in the Supporting Information. The resulting mass spectrum is presented in Figure 1A, where Na₂Al₃⁺− (x = 0–4), Na₃AlO and Al₂O₃ cluster anions are observed. Oxygen atoms are from the natural oxidation of sodium. Na₃Al₂⁺ is a magic number species with a reproducibly intense mass peak among its neighboring clusters, indicating an unusually high stability. Indeed, if the Al-Al core is successfully “transmutated” into P≡P, the Na₃Al₂⁺ cluster might well be very stable due to the closed-shell configuration and the triple Al²⁺≡Al²⁺ bond.

The bonding situation of Na₃Al₂⁺ can be better interpreted by photoelectron spectroscopy, 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 Na₃Al₂⁻ is a transmutated 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 find the most thermodynamically stable structure of Na₃Al₂⁺, 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, 10000 trial structures (in singlet and triplet states) underwent geometry optimizations at PBE0/6-311 + G*, subsequently the lowest structures were 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 in the Supporting Information). The GM structure of Na₃Al₂⁺ (C₂ᵥ, 1A₁) 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 Al₂ core. The slight deviation from the perfect D₃h symmetry is stipulated by the pseudo-Jahn–Teller effect, which lowers the symmetry to C₃h (origin of the pseudo-Jahn–Teller distortion is presented in the Supporting Information). To verify that the GM structure of Na₃Al₂⁺ 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.

The GM of the neutral Na₃Al₂ cluster (other isomers and their Cartesian coordinates are provided in Figure S2 and Table S2), which has four Na atoms positioned around the Al₂ core in the D₃h manner, also possesses a quite short Al–Al bond length of 2.45 Å. Being isoelectronic, both clusters are

Figure 1. The mass spectrum containing Na₃Al₂⁺ as the highest peak (A) and the anion photoelectron spectrum of Na₃Al₂⁻ taken with 355 nm photons. The vertical bars denote the calculated VDEs from the OVGF calculations (B).
expected to form a triple Al≡Al bond, which might be the shortest for diatomic-containing species. However, they are comparable to the Al=Al double bond LiAlH₄⁻ (2.46 Å), and somewhat longer than that of the divinyl(methyl)vinyl-substituted diacylumene (2.39 Å). 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 Gaussian09 program, FC(Al–Al) of Na₂Al₂ is 2.30 mDyne Å⁻¹, and FC(Al–Al) of Na₃Al₃ is 2.02 mDyne Å⁻¹. These values are in excellent agreement with the coupled cluster values at CCSD(T)/6-311+G*, that is, 2.41 mDyne Å⁻¹ and 2.00 mDyne Å⁻¹. Corresponding DFT values for the bulkier R₂Al–AIR₂ (R = CH(SiMe₃)) [22] and RR'Al = AIRR' (R = Bu₃MeSi, R' = NHC) [23] complexes, for which single and double Al–Al bonds have been reported, are found to be 0.68 mDyne Å⁻¹ and 1.00 mDyne Å⁻¹, respectively, thus supporting our interpretation of the Al–Al triple bond in Na₂Al₃ and Na₃Al₃. This argument is further confirmed by the relation of FC(P–P) of molecules with single, double and triple P–P bonds: 1.9:3.4:5.5 mDyne Å⁻¹. All these data are in accordance with the magic status of Na₂Al₃ in the mass spectrum (Figure 1A). Contrary to the “real space” FCs, which are not invariant to the choice of the used coordinate system, relaxed FCs (compliance constants) were previously shown to provide a better measurement of the interaction strength between two atoms. To get more insight into the Al–Al interaction in the Na₃Al₃ and Na₄Al₃ clusters, we calculated the relaxed FC(Al–Al) values using the compliance 3.0.2 program [23] at the PBE0/Def2-SVP level of theory for Na₂Al₂, Na₃Al₂, R₂Al–AIR₂ (R = CH(SiMe₃)), [22] RR’Al = AIRR’ (R = Bu₃MeSi, R’ = NHC) [23] systems as well as for some other prototypical model clusters where single (Al₄H₆), double (Al₃H₆Na), and triple (Al₂H₆Na) Al–Al bonds are expected, in accordance with previous considerations of the corresponding Ga counterparts. [10] The relaxed FC(Al–Al) values (in mDyne Å⁻¹) of Na₂Al₃ (0.95) and Na₃Al₂ (1.08) are higher than those of the single-bonded Al₄H₆ (0.61) and R₂Al–AIR₂ (0.80) systems, as well as of the triple-bonded Al₂H₆Na (0.79), and are comparable to that of the double-bonded Al₃H₆Na (1.03). Similarly to the case of model “gallyne” Ga₃H₆Na₂ cluster, the triple bond in Al₃H₆Na is found to be weaker than in its double-bonded counterpart Al₂H₆Na. However, the relaxed FCs of Na₂Al₃ and Na₃Al₂ are lower than that of the RR’Al = AIRR’ molecule (1.43).

Table 1: Experimental and calculated VDEs (eV) for the GM of Na₂Al₃ at three levels of theory. [a]  

<table>
<thead>
<tr>
<th>MO</th>
<th>EXPT</th>
<th>OVGF</th>
<th>TD-B3LYP</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO (s)</td>
<td>0.89</td>
<td>0.82</td>
<td>0.67</td>
<td>0.807</td>
</tr>
<tr>
<td>HOMO-1 (s)</td>
<td>1.84</td>
<td>1.74</td>
<td>1.50</td>
<td>1.06</td>
</tr>
<tr>
<td>HOMO-2 (p)</td>
<td>2.25</td>
<td>2.23</td>
<td>2.54</td>
<td>2.89</td>
</tr>
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[a] Aug-cc-pVTZ basis set was employed for all three methods. [b] This VDE could not be obtained at this level of theory.

Figure 2. Summary of the AdNDP analysis of the P₂ (A), Na₂Al₃ (B) and Na₄Al₃ (C) clusters.
clusters, which indicates an unusually high stability. Similarity of the canonical MOs of the P=P molecule with Na$_3$Al$_2$ and Na$_3$Al$_2$, along with the AdNDP results, further confirm that Na atoms can “transmutate” Al into P, and therefore, aid in the formation of the Al@Al triple bond. The AlF$_3$@AlF$_3$ 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$_{2}^{2-}$ already functions as a building block of a large family of carbide compounds.$^{36}$ Furthermore, highly charged species of the heavier homologs of Al, such as the Ti$_6^{-}$ and In$_6^{-}$ cluster anions, represent more examples of experimentally observed building blocks, which are stabilized as solid-state Zintl phases via strong Coulomb interactions with Na$^{+}$. 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 AlF$_3$@AlF$_3$ triple bonds.

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Conflict of interest

The authors declare no conflict of interest.

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