

## Akzeptierter Artikel

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# Realization of an Al≡Al Triple Bond in the Gas-Phase Na<sub>3</sub>Al<sub>2</sub><sup>-</sup> Cluster via Double Electronic Transmutation

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**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 HC≡CH contains one  $\sigma$  bond and two  $\pi$  bonds constructed from the  $p$  orbitals perpendicular to the  $\sigma$  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 Na<sub>3</sub>Al<sub>2</sub><sup>-</sup> cluster predicted *in silico*, which was subsequently generated by pulsed arc discharge followed by mass spectrometry and photoelectron spectroscopy characterizations. Being effectively Al<sup>2-</sup> due to the electron donation from Na, the Al atoms in Na<sub>3</sub>Al<sub>2</sub><sup>-</sup> undergo a double electronic transmutation into Group 15 elements, thus the Al<sup>2-</sup>≡Al<sup>2-</sup> kernel mimics the P≡P and N≡N molecules. We anticipate this work will stimulate more endeavors in discovering materials using Al<sup>2-</sup>≡Al<sup>2-</sup> 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 (HC≡CH) molecules, homodinuclear triple bonds composed of main group elements are extremely scarce,<sup>[1,2]</sup> 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 coworkers' synthesis of the famous digallyne molecule Na<sub>2</sub>[ArGaGaAr] (Ar = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>2</sub>-2,4,6-iPr<sub>3</sub>)<sub>2</sub>) featuring the shortest Ga–Ga bond on record.<sup>[3]</sup> Even though the [ArGaGaAr]<sup>2-</sup> kernel is valence-isoelectronic to acetylene, its x-ray crystallography reveals a *trans*-bent structure. The nature of the Ga–Ga bond in this digallyne has attracted considerable debate afterwards.<sup>[4,5]</sup> Cotton *et al.* offered an opposing opinion by density functional theory (DFT) calculations that the Ga–Ga

bond had a  $\pi$ -type nonbonding orbital, and the short bond length was a result of the Ar-Na<sup>+</sup>-Ar attractions.<sup>[6]</sup> Power and coworkers provided similar arguments that the bonding in [RGaGaR]<sup>2-</sup> ions had considerable Lewis base character at the Ga centers where electron density was accumulated.<sup>[7]</sup> In a model system [PhGaGaPh]<sup>2-</sup>, 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.<sup>[8]</sup> Grunenberg and Goldberg pointed to the mechano-chemical weakness of this bond by calculating relaxed force constants (FCs).<sup>[9]</sup> According to their calculations of the inverted Hessian matrix, the Ga–Ga bond (0.87 aJ/Å<sup>2</sup>) in a "gallyne" model compound Ga<sub>2</sub>H<sub>2</sub>Na<sub>2</sub> was found to be weaker than the Ga–Ga double bond (1.20 aJ/Å<sup>2</sup>) in Ga<sub>2</sub>H<sub>4</sub>Na<sub>2</sub>. However, according to Schaefer, Schleyer, Robinson and coworkers' calculations,<sup>[10]</sup> the Ga≡Ga triple bond was composed of two dative bonds and one  $\pi$  bond, thus constituting a non-classical but genuine triple bond. Using a simplified model [Ga<sub>2</sub>H<sub>2</sub>]<sup>2-</sup>, Klinkhammer<sup>[11]</sup> supported the existence of the Ga≡Ga triple bond, which was claimed to be a combination of a  $\sigma$  bond, a  $\pi$  bond, and a non-classical "slipped"  $\pi$  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  $\sigma$  bond and two  $\pi$  bonds constructed from the  $p$  orbitals perpendicular to the  $\sigma$  bond, such as that in the linear HC≡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.*,<sup>[12]</sup> followed by a plethora of theoretical and experimental studies of the B<sub>2</sub> molecule stabilized by diatomic Lewis bases such as CO, CS, N<sub>2</sub>, NHC (N-heterocyclic carbene), BO<sup>-</sup>.<sup>[13-17]</sup> Braunschweig *et al.* synthesized the unprecedented NHC→B≡B←NHC crystal featured the first ambient-temperature isolable diboryne.<sup>[18]</sup> Köppe and Schnöckel questioned this triple bond based on electronic interactions between the B–B bond and the two B-(NHC) bonds.<sup>[19]</sup> However, later Grunenberg's<sup>[20a]</sup> and Frenking's calculations,<sup>[20b]</sup> Braunschweig's Raman<sup>[21a]</sup> and NMR<sup>[21b]</sup> spectroscopic measurements as well as chemical reactions<sup>[21c,d]</sup> 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, Uhl<sup>[22]</sup> synthesized the R<sub>2</sub>AlAIR<sub>2</sub> (R = CH(SiMe<sub>3</sub>)<sub>2</sub>) compound containing an Al–Al single bond. In the early 1990s, it was shown that this compound could be reduced to [R<sub>2</sub>AlAIR<sub>2</sub>]<sup>-</sup> anions with an increased formal bond order of 1.5.<sup>[23-26]</sup> Recently, Inoue and coworkers<sup>[27]</sup> reported the synthesis of a dialumene compound RR'AlAIRR' (R = *t*Bu<sub>2</sub>MeSi, R' = NHC) stabilized by N-heterocyclic carbenes, featuring a double Al=Al bond. Immediately after Inoue's work, the LiAl<sub>2</sub>H<sub>4</sub><sup>-</sup> cluster<sup>[28]</sup> produced in an ion beam was also found to exhibit an Al=Al double bond, with an Al<sub>2</sub>H<sub>4</sub><sup>2-</sup> kernel mimicking the

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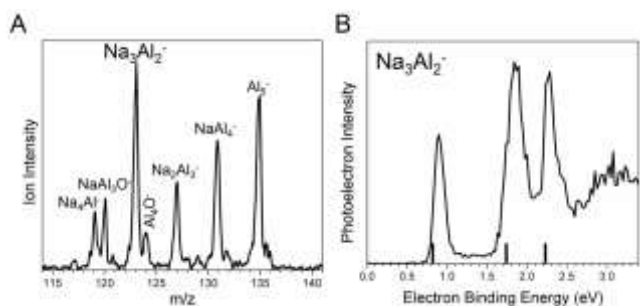
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isoelectronic  $\text{Si}_2\text{H}_4$  molecule. In 2006, Power<sup>[29]</sup> synthesized and characterized a stable  $\text{Na}_2[\text{Ar}'\text{AlAlAr}']$  ( $\text{Ar}' = \text{C}_6\text{H}_3-2,6-(\text{C}_6\text{H}_2-2,4,6-\text{iPr}_3)_2$ ) compound named dialuminyne, which was similar to digallyne<sup>[3]</sup> and featured a *trans*-bent structure, where the Al–Al triple bond was described to contain a slipped  $\pi$  bond.

In view of the above discussions, we aim to design a ligandless  $\text{Al}\equiv\text{Al}$  triple bond that is similar to  $\text{N}\equiv\text{N}$  and  $\text{P}\equiv\text{P}$ , so that it can rule out the possibilities of resonance structures, *trans*-bent geometry, and any non-classical bonding interactions such as the slipped  $\pi$  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,  $\text{Al}^{2-}\equiv\text{Al}^{2-}$  should be similar to  $\text{P}\equiv\text{P}$ . 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.<sup>[30]</sup> However, no compounds have been reported so far based on the DET concept.



**Figure 1.** The mass spectrum containing  $\text{Na}_3\text{Al}_2^-$  as the highest peak (A) and the anion photoelectron spectrum of  $\text{Na}_3\text{Al}_2^-$  taken with 355 nm photons. The vertical bars denote the calculated VDEs from the OVGf calculations (B).

To experimentally examine the  $\text{Al}^{2-}\equiv\text{Al}^{2-}$  prototype, we designed a  $\text{Na}_3\text{Al}_2^-$  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)<sup>[31]</sup> in the gas phase by discharging an Al/Na mixture target with  $\sim 1500$  A, 180 V, 20  $\mu\text{s}$  pulsed arc. Experimental details are provided in the Supporting Information (SI). The resulting mass spectrum is presented in Fig. 1A, where  $\text{Na}_x\text{Al}_{5-x}^-$  ( $x = 0-4$ ),  $\text{NaAl}_3\text{O}^-$  and  $\text{Al}_4\text{O}^-$  cluster anions are observed. Oxygen atoms are from the natural oxidation of sodium.  $\text{Na}_3\text{Al}_2^-$  is a magic number species with a reproducibly intense mass peak among its neighboring clusters, indicating an unusually high stability. Indeed, if  $\text{Na}_3\text{Al}_2^-$  is successfully “transmuted” into the  $\text{P}\equiv\text{P}$  analogue, it might well be very stable due to the closed-shell configuration and the triple bond.

The bonding situation of  $\text{Na}_3\text{Al}_2^-$  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  $\text{Na}_3\text{Al}_2^-$  is a transmuted version of  $\text{P}\equiv\text{P}$ , these three peaks should correspond to the photoelectrons detached from the three frontier orbitals, these being one  $\sigma$  bonding orbital and two  $\pi$  bonding orbitals, which is a direct observation of the  $\text{Al}\equiv\text{Al}$  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  $\text{Na}_3\text{Al}_2^-$ , 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  $\text{PBE0/6-311+G}^*$ , subsequently the lowest structures recalculated at higher levels of theory ( $\text{CCSD(T)/6-311+G}^*$  and  $\text{CCSD(T)/aug-cc-pVTZ/CCSD(T)/6-311+G}^*$ ), and further ranked according to their relative energies (Figure S1 and Table S1). The GM structure of  $\text{Na}_3\text{Al}_2^-$  ( $\text{C}_{2v}$ ,  $^1\text{A}_1$ ) exhibits a direct Al–Al contact of 2.49 Å ( $\text{CCSD(T)/6-311+G}^*$ ) with three surrounding Na atoms, which define a plane passing through the center of the  $\text{Al}_2$  core. The slight deviation from the perfect  $\text{D}_{3h}$  symmetry is stipulated by the pseudo-Jahn-Teller effect, which lowers the symmetry to  $\text{C}_{2v}$  (origin of the pseudo-Jahn-Teller distortion is presented in SI). To verify that the GM structure of  $\text{Na}_3\text{Al}_2^-$  describes the photoelectron spectrum, VDEs were computed at three levels of theory (DFT, OVGf, and  $\text{CCSD(T)}$ ). 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  $\text{Na}_3\text{Al}_2^-$  at three levels of theory.<sup>[a]</sup>

MO	VDE			
	EXPT.	OVGF	TD-B3LYP	CCSD(T)
HOMO ( $^2\text{a}_1$ )	0.89	0.82	0.67	0.807
HOMO-1 ( $^2\text{a}_1$ )	1.84	1.74	1.50	— <sup>[b]</sup>
HOMO-2 ( $^1\text{b}_1$ )	2.25	2.23	2.54	— <sup>[b]</sup>

<sup>[a]</sup> Aug-cc-pVTZ basis set was employed for all three methods.

<sup>[b]</sup> This VDE could not be obtained at this level of theory.

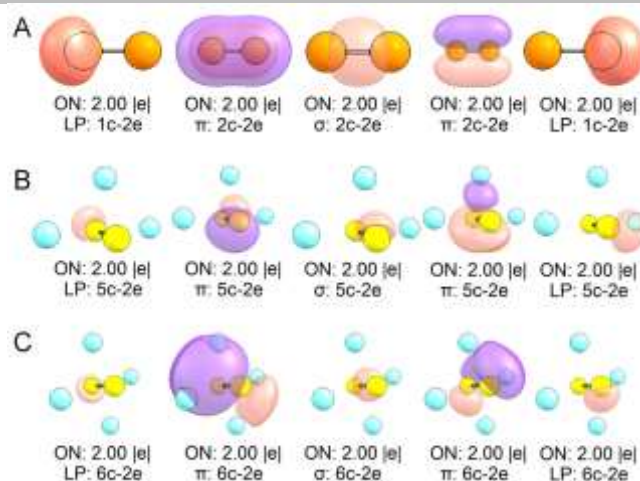
The GM of the neutral  $\text{Na}_4\text{Al}_2$  cluster (other isomers and their Cartesian coordinates are provided in Figure S2 and Table S2), which has four Na atoms positioned around the  $\text{Al}_2$  core in the  $\text{D}_{4h}$  manner, also possesses a quite short Al–Al bond length of 2.45 Å. Being isoelectronic, both clusters are expected to form a triple  $\text{Al}^{2-}\equiv\text{Al}^{2-}$  bond, which might be the shortest for dialuminum-containing species. However, they are comparable to the  $\text{Al}=\text{Al}$  double bond  $\text{LiAl}_2\text{H}_4^-$  (2.46 Å),<sup>[28]</sup> and somewhat longer than that of the di-tertbutyl(methyl)silyl-substituted dialumene (2.39 Å).<sup>[27]</sup> 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  $\text{FC}(\text{Al}-\text{Al})$  reflect a better measure of the bond order. According to our calculations at the  $\text{PBE0/Def2-SVP}$  level of theory employing normal coordinates within Gaussian 09 program,  $\text{FC}(\text{Al}-\text{Al})$  of  $\text{Na}_4\text{Al}_2$  is 2.30 mDyne/Å, and  $\text{FC}(\text{Al}-\text{Al})$  of  $\text{Na}_3\text{Al}_2^-$  is 2.02 mDyne/Å. These values are in excellent agreement with the coupled cluster values at  $\text{CCSD(T)/6-311+G}^*$ , i.e. 2.41 mDyne/Å and 2.00 mDyne/Å. Corresponding DFT values for the bulkier

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$R_2Al-AIR_2$  ( $R=CH(SiMe_3)_2$ )<sup>[22]</sup> and  $RR'Al=AIRR'$  ( $R=tBu_2MeSi$ ,  $R'=NHC$ )<sup>[27]</sup> complexes, for which single and double Al-Al bonds have been reported, are found to be 0.68 mDyne/Å and 1.00 mDyne/Å, respectively, thus supporting our interpretation of the  $Al\equiv Al$  triple bond in  $Na_3Al_2^-$  and  $Na_4Al_2$ . 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.<sup>[32]</sup> All these data are in accordance with the magic status of  $Na_3Al_2^-$  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.<sup>[9,33]</sup> To get more insight into the Al-Al interaction in the  $Na_3Al_2^-$  and  $Na_4Al_2$  clusters, we calculated the relaxed FC(Al-Al) values using the Compliance 3.0.2 program<sup>[34]</sup> at the PBE0/Def2-SVP level of theory for  $Na_3Al_2^-$ ,  $Na_4Al_2$ ,  $R_2Al-AIR_2$  ( $R=CH(SiMe_3)_2$ ),<sup>[22]</sup>  $RR'Al=AIRR'$  ( $R=tBu_2MeSi$ ,  $R'=NHC$ )<sup>[27]</sup> systems as well as for some other prototypical model clusters where single ( $Al_2H_6^{2-}$ ), double ( $Al_2H_4Na_2$ ), and triple ( $Al_2H_2Na_2$ ) Al-Al bonds are expected, in accordance with previous considerations of the corresponding Ga counterparts.<sup>[9]</sup> The relaxed FC(Al-Al) values (in mDyne/Å) of  $Na_3Al_2^-$  (0.95) and  $Na_4Al_2$  (1.08) are higher than those of the single-bonded  $Al_2H_6^{2-}$  (0.61) and  $R_2Al-AIR_2$  (0.80) systems, as well as of the triple-bonded  $Al_2H_2Na_2$  (0.79), and are comparable to that of the double-bonded  $Al_2H_4Na_2$  (1.03). Similarly to the case of model “gallyne”  $Ga_2H_2Na_2$  cluster,<sup>[9]</sup> the triple bond in  $Al_2H_2Na_2$  is found to be weaker than in its double-bonded counterpart  $Al_2H_4Na_2$ . However, the relaxed FCs of  $Na_3Al_2^-$  and  $Na_4Al_2$  are lower than that of the  $RR'Al=AIRR'$  molecule (1.43). Apparently, somewhat larger relaxed FC values of the species in solid state ( $R_2Al-AIR_2$ <sup>[22]</sup> and  $RR'Al=AIRR'$ <sup>[27]</sup>) in comparison to the corresponding model clusters ( $Al_2H_6^{2-}$  and  $Al_2H_4Na_2$ ) are associated with the presence of the bulky stabilizing ligands, which help increase the Al-Al bond strength. Hence, comparison of these numbers should be made with caution.

To further investigate the  $Al\equiv Al$  triple bond, we perform the Adaptive Natural Density Partitioning (AdNDP) analysis<sup>[35]</sup> of chemical bonding in  $P_2$ ,  $Na_3Al_2^-$  and  $Na_4Al_2$  at the  $\omega B97XD/Def2-TZVP$  level of theory (Figure 2). In both  $Na_3Al_2^-$  and  $Na_4Al_2$ , the bonding pattern is similar to  $P_2$ , though Na atoms contribute to the lone pair (LP) on each Al atom as well as to the  $\sigma$ - and  $\pi$ -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  $Na_3Al_2^-$  and 1.63 |e| in  $Na_4Al_2$ . The Al-Al  $\sigma$ -bond is found as a pure two-center two-electron (2c-2e)  $\sigma$ -bond with ON=1.85 |e| in  $Na_3Al_2^-$  and 1.97 |e| in  $Na_4Al_2$ . The two 2c-2e  $\pi$ -bonds have somewhat lower ON values: 1.30 |e|, 1.51 |e| in  $Na_3Al_2^-$ , and 1.60 |e|, 1.60 |e| in  $Na_4Al_2$ . It is noted that the deviation of the ON values of the  $\pi$ -bonds from the ideal value of 2.00 |e| is in agreement with the relaxed FC(Al-Al) values for  $Na_3Al_2^-$  and  $Na_4Al_2$ , which are comparable to that of the  $Al_2H_4Na_2$  cluster exhibiting Al=Al double bond. The analogous bonds in  $P_2$  have ON values close to 2.00 |e| (Figure 2A). Indeed, the remaining electron density in  $Na_3Al_2^-$  and  $Na_4Al_2$  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  $P_2$  (A),  $Na_3Al_2^-$  (B) and  $Na_4Al_2$  (C) clusters.

In summary, we have applied the DET concept to design two clusters,  $Na_3Al_2^-$  and  $Na_4Al_2$ , which are found to possess  $Al\equiv Al$  triple bonds. Excellent agreement between the experimental and calculated VDEs for the most stable isomer of  $Na_3Al_2^-$  confirms the proposed structure. Presence of the triple bond in  $Na_3Al_2^-$  is also supported by its reproducibly intense mass peak among the neighboring clusters, which indicates an unusually high stability. Similarity of the canonical MOs of the  $P\equiv P$  molecule with  $Na_3Al_2^-$  and  $Na_4Al_2$ , along with the AdNDP results, further confirm that Na atoms can “transmute” Al into P, and therefore, aid in the formation of the  $Al\equiv Al$  triple bonds. The  $Al^{2-}\equiv Al^{2-}$  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  $C_2^{2-}$  already functions as a building block of a large family of carbide compounds.<sup>[36]</sup> Furthermore, highly charged species of the heavier homologues of Al, such as the  $Tl_4^{8-}$  and  $In_4^{8-}$  cluster anions, represent more examples of experimentally observed building blocks, which are stabilized as solid-state Zintl phases via strong Coulomb interactions with  $Na^+$ .<sup>[37]</sup> 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  $Al^{2-}\equiv Al^{2-}$  triple bonds.

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**Keywords:** Al $\equiv$ Al triple bond • photoelectron spectroscopy • ab initio calculations • double electronic transmutation

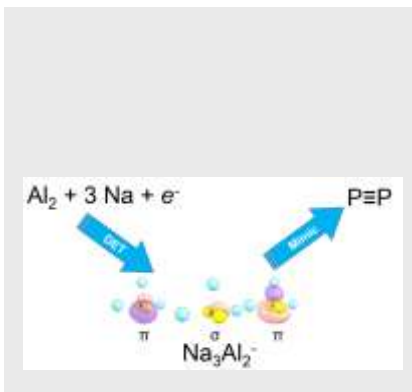
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## Entry for the Table of Contents (Please choose one layout)

Layout 1:

## COMMUNICATION

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<sub>3</sub>Al<sub>2</sub><sup>-</sup> cluster.



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**Realization of an Al≡Al Triple Bond in the Gas-Phase Na<sub>3</sub>Al<sub>2</sub><sup>-</sup> Cluster via Double Electronic Transmutation**