



The reaction of aluminum cluster anions with tetrakis(dimethylamino)ethylene (TDMAE): Insertion of an aluminum anion into a C–N bond

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ABSTRACT

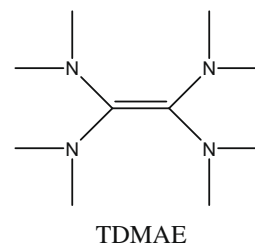
The reactivity of aluminum cluster anions with tetrakis(dimethylamino)ethylene (TDMAE) has been studied using mass spectrometry. All aluminum cluster anions, regardless of their size, disappeared from the mass spectrum upon introduction of TDMAE, leaving behind the single anionic reaction product, $[\text{Al}(\text{TDMAE})]^-$. The combination of anionic photoelectron spectroscopy and density functional theory was then employed to probe the structure of this anion. Contrary to the π -complex structure known in Al-alkene systems, $[\text{Al}(\text{TDMAE})]^-$ was found to prefer a 2 eV more stable geometry in which Al⁻ inserted into one of the C–N bonds in TDMAE.

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The reactivity of aluminum clusters in their anionic, cationic, and neutral charge states has received considerable attention over the last two decades [1–4]. These studies provide not only useful insight into the size-dependence of reactivity with various molecular reagents, but also evidence of the unique electronic and geometric structures which allow particular aluminum cluster species to resist chemical ‘erosion’. Among aluminum clusters, Al_{13}^- has shown the greatest resistance to reactivity, making it a promising candidate as a building block of cluster-assembled materials [4–8].

In a recent study, the interaction of aluminum cluster anions with propene has been investigated in a flow tube reactor [9]. There, it was found that while most aluminum cluster anions did not react at all, a few cluster anion sizes formed π -bonded complexes. These findings are consistent with the fact that aluminum is known to form π -complexes with alkenes [10–14].

Here, we present a study of the interaction of aluminum cluster anions with the nitrogen-containing organic molecule, tetrakis(dimethylamino)ethylene (TDMAE). We were motivated by the prospect that TDMAE’s unusually low ionization potential of ~ 5.4 eV [15] might allow it to form cluster-assembled, salt ‘molecules’ of the form, $(\text{TDMAE})^+\text{Al}_{13}^-$, and that these could provide a basis for forming ionic, cluster-assembled materials. Alkali⁺- Al_{13}^- salt ‘molecules’ have been reported in molecular beam studies [8,16].



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Aluminum cluster anions were generated in a pulsed arc cluster ionization source (PACIS) that has been described in detail elsewhere [17,18]. Briefly, a discharge is triggered between an anode and a grounded aluminum cathode that vaporizes metal from the cathode. About 14 bar of UHP helium gas propels the resultant plasma into a 20 cm flow tube, where the evaporated material cools and forms clusters. In this study a pulse of TDMAE, seeded in 4 bar of UHP He gas, was also injected via a second pulsed valve about 10 cm down the flow tube. The TDMAE concentration was controlled by heating the pulsed valve storing the TDMAE. Reaction products were monitored by a time-of-flight mass spectrometer (TOF-MS) which is an in-line component of our magnetic bottle photoelectron spectrometer (MBPES). Details of our apparatus are described elsewhere [19]. Due to TDMAE’s unavailability commercially, we synthesized it following a literature recipe [20]. The product was identified through observation of its distinctive green light chemiluminescence upon its exposure to oxygen (air). Further confirmation was provided by its correct mass appearing in mass spectra of $[\text{Al}(\text{TDMAE})]^-$.

Mass spectra obtained at different TDMAE concentration levels are presented in Fig. 1. Increasing the concentration of injected TDMAE led to a dramatic increase in a species with $m/z = 227$ amu and an equally dramatic decrease in all sizes of aluminum cluster anions. We attribute this to the formation of $[\text{Al}(\text{TDMAE})]^-$ at $m/z = 227$ amu. This assignment is also confirmed by the observation of the expected ^{13}C peak intensity at $m/z = 228$ amu (10% of $m/z = 227$ amu) in a higher resolution mass spectrum. While all sizes of aluminum cluster anions are etched away by exposure to TDMAE, the small sizes appear to be destroyed at a faster rate.

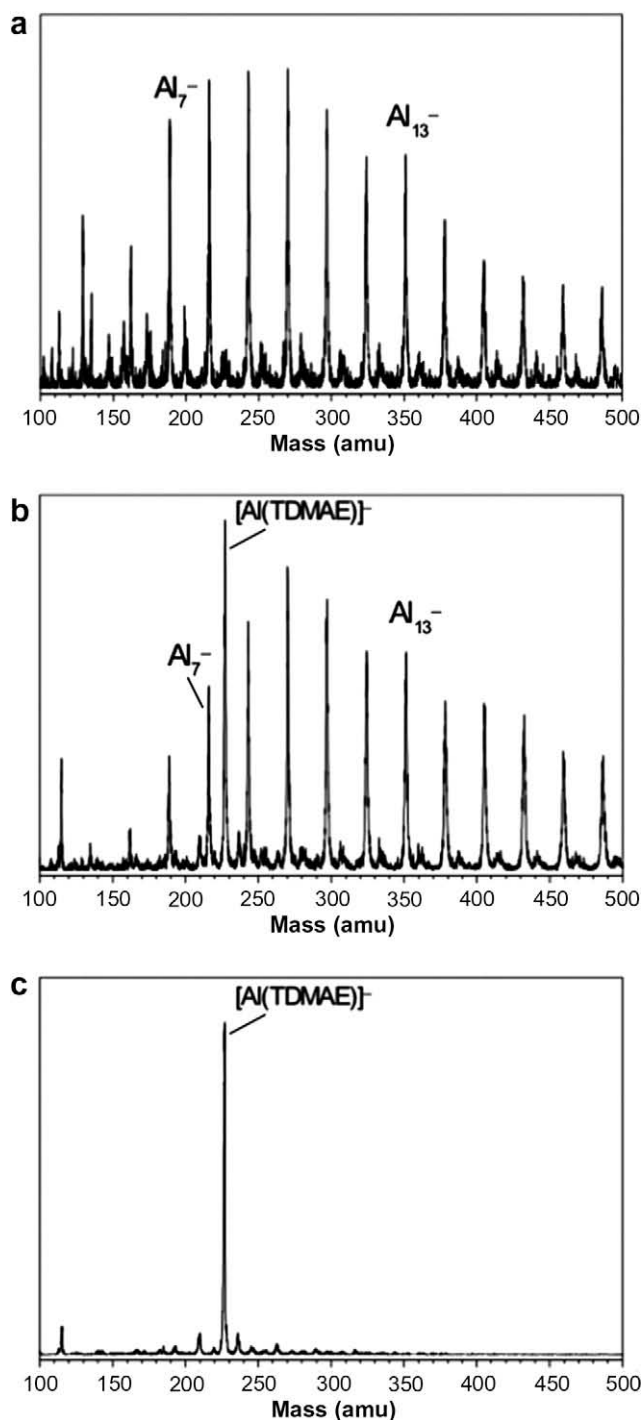
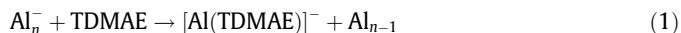


Fig. 1. Mass spectra obtained at increasing concentrations of TDMAE seeded in He carrier gas. (a) Al_n^- with no TDMAE; (b) Al_n^- with a low concentration of TDMAE; (c) Al_n^- with a high concentration of TDMAE.

(Weak intensities of AlC^- cluster anions were also observed but had no effect on the results.)

These observations led us to assume the following mechanism for the observed behavior of all studied Al_{n-20}^- clusters:



Note that, unlike in the case of $[\text{Al}_n(\text{propene})]^-$, there appear to be no multi-aluminum $[\text{Al}_n(\text{TDMAE})]^-$ species present in the mass spectrum. Presumably, the observed difference in behavior between these two organic molecules, both of which contain $\text{C}=\text{C}$ as well as $\text{C}-\text{H}$ bonds, can be attributed to the presence of nitrogen in TDMAE. The differences become even more apparent when considering the energetics of the proposed mechanism, which involves the extraction of an aluminum anion from the cluster anion to which it is bound by 2.5 eV or more [21]. Clearly, the $[\text{Al}(\text{TDMAE})]^-$ anion must be sufficiently stable in order to drive this reaction. The $[\text{Al}(\text{alkene})]^-$ π -complexes, on the other hand, are known to be bound by only about 1 eV [22]. To better understand the nature of the chemical interaction between the aluminum metal anion and its nitrogen-containing organic moiety and to elucidate the structure of $[\text{Al}(\text{TDMAE})]^-$, we utilized a synergistic combination of anion photoelectron spectroscopy and density functional theory (DFT) calculations.

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. The photodetachment process 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 energy, and EKE is the electron kinetic energy. In this study, the fourth harmonic of a Nd:YAG laser (266 nm, 4.661 eV) was employed for photodetachment, and a magnetic bottle type photoelectron spectrometer with an instrumental resolution of ~ 35 meV at $\text{EKE} = 1$ eV was used to energy analyze the resultant electrons [19]. The photoelectron spectrum of $[\text{Al}(\text{TDMAE})]^-$ is presented in Fig. 2. Peaks in this spectrum correspond to the photodetachment transitions between the ground electronic state of the singlet anion and the ground and excited electronic states of the resulting doublet neutral cluster at the geometry of the anion. Peaks are broadened due to the presence of a vibrational manifold in each electronic state. Of particular interest is the lowest EBE peak, which ties together the ground

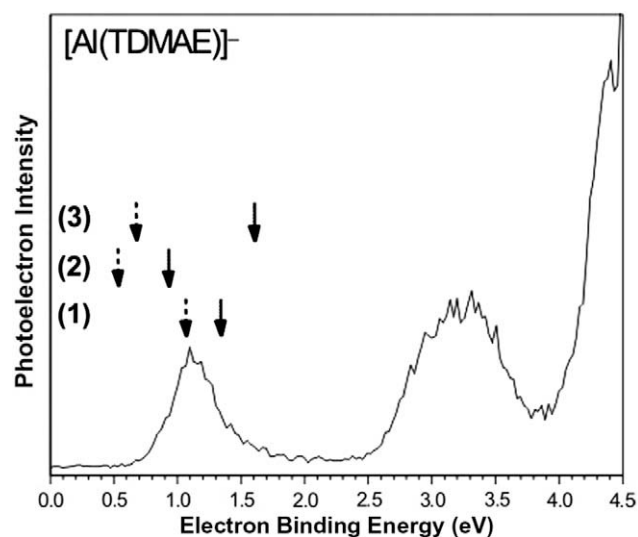


Fig. 2. Anion photoelectron spectrum of $[\text{Al}(\text{TDMAE})]^-$ recorded with 4.661 eV photons. Arrows indicate the theoretically-predicted vertical detachment energy (solid) and the adiabatic electron affinity (dashed) values for the studied isomers. The symbols (1)–(3) refer to the structures in Fig. 3.

electronic states of the anion and its corresponding neutral, thereby providing a measurement of the adiabatic electron affinity (EA_a). The threshold region of this peak is utilized to provide an estimate of the EA_a value, which we determined to be 0.7 ± 0.2 eV. The EBE of the photoelectron intensity maximum in this peak is the vertical detachment energy (VDE), which represents the photodetachment transition having the greatest Franck–Condon overlap between the vibronic states of the anion and its corresponding neutral. The VDE is thus a well-defined quantity, and its value is measured to be 1.1 ± 0.1 eV. In addition, the ~ 2.1 eV spacing between the lowest and the next higher EBE peaks is a measure of the ground to first excited electronic state splitting in neutral Al(TDMAE). Such low lying electronic states are not unusual in open shell species. Furthermore, the spacing between the second highest EBE peak and the highest EBE feature in the spectrum implies that the splitting between the first and second excited states of neutral Al(TDMAE) is at least 1.2 eV.

For performing geometry optimizations and obtaining equilibrium structures, density functional theory B3LYP/6-31+G was employed, while for determining photoelectron spectroscopic values, DFT with the 6-311++G(2d,p) basis set and with the PW91 exchange and correlation functional was utilized. All calculations were carried out with the GAUSSIAN 03 suite of programs [23]. Several isomeric forms of the $[Al(TDMAE)]^-$ anion were found, and those structures with the lowest total energies are presented in Fig. 3. (While both singlet and triplet states were considered, singlet state structures were found to be more stable.) As can be seen, the lowest energy geometries are those in which an Al^- anion has inserted into a C–N bond in TDMAE. The π -complex (as can be seen in Fig. 3(3)), however, which had been observed to be so prevalent in Al-alkene systems, was found to be energetically unfavorable by about 2 eV relative to the inserted structures of $[Al(TDMAE)]^-$. In addition, the experimentally-determined photoelectron spectroscopic values agree significantly better with those predicted by theory for inserted structures than for the π -complex (see calculated VDE and EA_a values for the various isomers in Fig. 3), further supporting our interpretation that the observed $[Al(TDMAE)]^-$ product anion is an inserted isomer. This determination hinges on the greater reliability of well-defined VDE values over estimated EA values and on their energy difference better matching the half-width of the lowest EBE peak. Moreover, the ~ 2 eV energy difference between the inserted complex and the π -complex would account for the energy demands needed in extracting an aluminum anion from the bare metal cluster anion as proposed in mechanism (1).

While the computational uncertainty of ~ 0.2 eV makes it difficult to distinguish between the two inserted structures shown in Fig. 3, their low total energies and the reasonably good fit between experimentally-measured and theoretically-predicted photoelectron values strongly suggests that $[Al(TDMAE)]^-$ is formed with an Al^- inserted into a C–N bond. Although there have been other studies [24–28] which showed metal insertion in carbon-containing bonds, e.g., transition metal anions inserting into C–SH bonds [24], the present work is the first observation of an aluminum atom inserting into an organic molecule. Since no such insertions are known for hydrocarbons, it appears that a larger electronegativity difference between adjacent atoms, i.e., between carbon and nitrogen, is necessary for insertion to occur. It would furthermore be interesting to explore whether isolated C–N bonds, for instance in substituted amines, can be broken in a similar fashion or whether the presence of another functional group, such as C=C, is necessary to facilitate the insertion. In any case, we saw no evidence in this study for cluster anion stoichiometries containing both TDMAE and Al_{13} moieties as we had hoped. However, this work has provided significant guidance in selecting other less aggressive candidates for forming organic cation/aluminum cluster

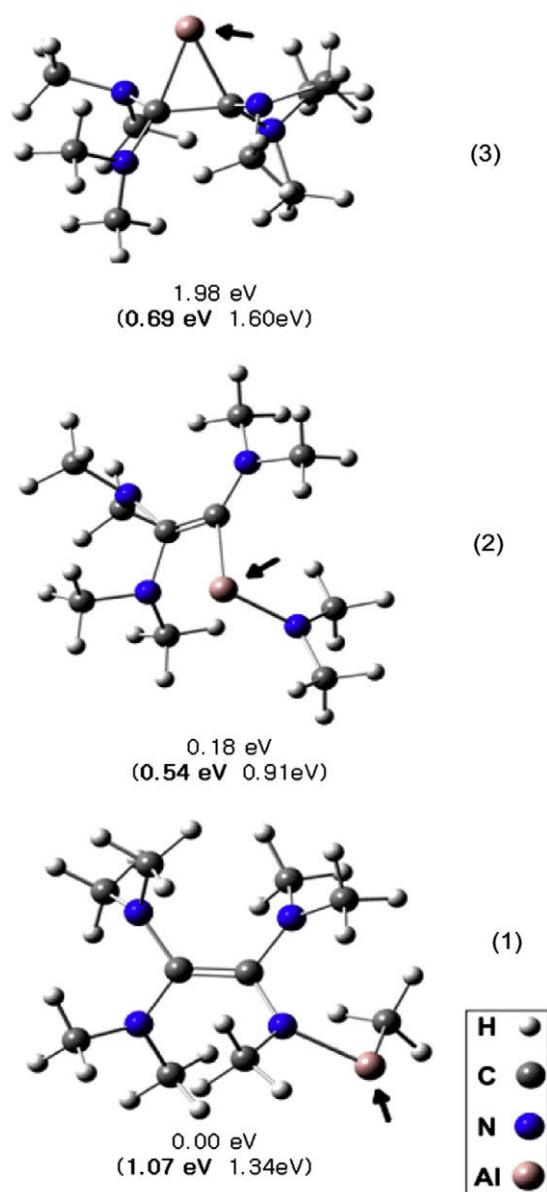


Fig. 3. Calculated structures of representative $[Al(TDMAE)]^-$ anionic isomers found in this study. Carbon atoms are shown in gray, nitrogen in blue, and aluminum in pink. Relative total energies are given below each structure. The two values in parentheses correspond to calculated VDE and EA_a (in bold) values, respectively. Aluminum atoms in each structure are indicated with an arrow. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

anion salts, and these may yet form the basis for making aluminum cluster-containing, cluster-assembled materials.

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