The behavior of the aluminum trimer when combining with different superatom clusters†

Hui Yang,ab Di Wu, Hui-Min He,a Dan Yu,a Ying Li,*a and Zhi-Ru Liaa

The interaction between the aluminum trimer and representative (super)halogens X (X = F, LiF2, BeF3, BF4) and (super)alkalis M (M = Li, LiF2, OLi3, NLI4) has been theoretically investigated at the MP2/6-311+ (3df) level. Various geometrical structures were obtained for the resulting Al3−X and Al3−M superatom compounds, respectively. Natural bond orbital analysis reveals that the Al3 moiety exists in a cationic state in Al3−X while in an anionic state in Al3−M compounds. And the charge transfer between Al3 and (super)atoms is found to be enhanced in either polar or nonpolar solvent. The studied superatom compounds feature large bond energies, binding energies, and HOMO–LUMO gaps, which not only reflect their stability but indicate strong interactions between Al3 and (super)atoms. Although the solvent effect is not significant for the stability of Al3−X, the Al3−superalkali compounds can be better stabilized in the presence of solvent molecules. In addition, these superatom compounds exhibit aromaticity both in the gas phase and in solution.

1. Introduction

Clusters are extensively studied in physics because they represent the transition states between single atoms and bulk solid. On the one hand, clusters possess properties that are neither atomic-like nor solid-like but depend on their composition, size, geometry, charge state, etc. On the other hand, stable clusters can serve as basic building blocks in chemistry. Hence, the research of clusters is also of significance in developing novel cluster-assembled materials with tunable properties.

One of the most exciting developments in the research area of clusters is the realization that specific clusters exhibit similar chemical behavior to atoms in the periodic table. Such clusters are consequently termed superatoms. Two well-known subsets of superatoms are superhalogens and superalkalis which have been extensively studied for more than 30 years. Superhalogens have higher electron affinities (EAs) than atomic EA limit (Cl: 3.617 eV) while superalkalis are unique clusters possessing ionization potentials (IPs) lower than those of alkali atoms (5.39–3.89 eV). Lately, the idea of combining superalkali with superhalogen clusters has been theoretically proposed and the generated superatom compounds include Al13K2O and Al13Na3O524 BF4−M (M = Li, FLi2, OLi3, NLI4)22 BLi2−X (X = F, LiF2, BeF3, BF4)26 and LiO−X (X = BF4, BeF3, NO3)27 etc. It has been found that both superhalogens and superalkalis play the role of building block in the resulting ionic compounds that are named as “supersalts” by Jena et al.27 These inspiring results motivate us to think about the following questions: can superatoms combine with other clusters, especially metal clusters? If so, what are the preferred structures as well as bonding nature of such superatom compounds? Will the structural and electronic integrity of the metal cluster break when it interacts with superatoms? How does the metal cluster behave when combining with superalkalis and superhalogens, respectively?

During the last two decades, aluminum clusters have become a rich area of research in cluster physics and chemistry. In addition to providing a basic understanding of size-dependent physical and chemical properties of simple metal clusters, researches also bring out some special characteristics of aluminum clusters. These include the potentially multivalent character of the bonding in aluminum clusters, the free electron character of aluminum which makes aluminum clusters an archetypal example of the shell model, all-metal aromaticity found in small Al-based clusters, for example, Al13−, Al12−, and Al9−, etc.28–34 Besides, some pure or doped aluminum clusters, such as Al118, Al141, Al7−, Al12Be, Al12Cu,36 have been proven to show superatom features. Furthermore, small aluminum clusters share some properties in common with the more electronically complex transition metal clusters. Thus, the
studies of p-block aluminum clusters are good complements to those of the less computationally tractable d-block metal clusters.40

As one of the smallest and thus most foundational components of aluminum clusters, aluminum trimer has been extensively studied and its electronic and geometrical structures are well understood.36,41-44 Hence, it has been chosen in our work as a representative metal cluster to interact with differently shaped (super)halogens X (X = F, LiF2, BeF3, BF4) and (super)alkalis M (M = Li, FLi2, OLi3, NLi4). The main objectives of this contribution are (1) to reveal different behaviors of Al3 when combining with different (super)atoms, (2) to examine stability of the resulting Al3–X and Al3–M compounds both in gas phase and in solution. Besides, aromaticity of these superatom compounds is analyzed as well. We hope that the results we provide in this work can further enrich our knowledge on superatoms and the principles obtained may work well for a variety of superatom compounds involving metal cluster building blocks, especially the Al3 group.

2. Computational details

The minima on the potential-energy surfaces of the Al3–X (X = F, LiF2, BeF3, BF4) and Al3–M (M = Li, FLi2, OLi3, NLi4) compounds were explored by using two approaches. The first one is to construct initial geometries artificially by considering all the possible bonding orientations between Al3 cluster and (super)atoms X/M. The second one employs a random search procedure,36,45-47 in which structures were generated by randomly distributing all atoms inside a sphere with radius \( R = 5.0 \text{ Å} \). The resulting geometries were optimized at the B3LYP/3-21G level automatically. Then, all the geometries obtained by the first method and the minimum structures from the second method were optimized using the second order Møller–Plesset (MP2) method48 with the 6-311+G(3df) basis set, followed by vibrational frequency calculations. Note that only those minimum structures where the Al3 and superatom subunits retain their respective integrity are discussed in the present work since the interaction between Al3 and superatom clusters is the focus of our attention. Natural bond orbital (NBO)49 and atom in molecules (AIM)50-51 analyses were performed at the same level. The nucleus-independent chemical shifts (NICS)52 values were obtained employing the GIAO-B3LYP/6-311+G(3df) method.51

The intramolecular interaction energies (\( E_{\text{int}} \)) between Al3 and X/M subunits and binding energy per atom (\( E_{\text{b}} \)) for these Al3–X and Al3–M species were calculated at the higher CCSD(T)//MP2/6-311+G(3df) level based on the MP2 geometries.25,28 We used the counterpoise (CP) procedure44 to eliminate the basis set superposition error (BSSE) effect given by eqn (1):55

\[
E_{\text{int}} = E_{\text{AB}}(X_{\text{AB}}) - E_{\text{A}}(X_{\text{AB}}) - E_{\text{B}}(X_{\text{AB}}) \tag{1}
\]

where the same basis set, \( X_{\text{AB}} \), was used for the subunit energy (\( E_{\text{A}} \) and \( E_{\text{B}} \)) calculation as for the complex energy (\( E_{\text{AB}} \)) calculation.

All calculations were performed using the GAUSSIAN 09 program package.56 The plots of molecular configurations and orbitals were generated by the GaussView program.57

3. Results and discussion

3.1. Geometrical structures

3.1.1. Al3–X. Eleven equilibrium structures with real frequencies were gained for the Al3–X compounds. The optimized geometries of Al3–X and their ionic components are displayed in Fig. 1, and their corresponding lowest vibrational frequencies are listed in Table 1.

Different from linear diatomic molecules, the Al3–X compounds have a variety of structures (see Fig. 1). The eleven Al3–X structures can be classified into five types according to the relative orientation (bonding pattern) between Al3 and X, namely, point-to-point (pp), point-to-side (ps), side-to-point (sp), side-to-side (ss), and face-to-face (ff). These geometries were employed for an Al3–X isomer designates the number of F atoms in Arabic numerals, followed by the bonding pattern. For example, 3ss represents an Al3–BeF3 structure with side-to-side bonding pattern.

Fig. 1 Optimized structures of the Al3–X compounds and Al3+ ions at the MP2/6-311+G(3df) level, bond lengths (Å) and Laplacian of the electron density at a bond critical point \( \nabla^2 \rho(r) \) (in au., bold font) for the Al–F bonds that connect Al3 and X subunits.
As shown in Fig. 1, the structural integrity of superhalogens X is maintained in all the Al₃-X compounds. For Al₃-F, the F atom is either bound to an apex Al atom (1pp), or side-on bound to the Al₃ triangle (1sp). From Table 1, the former is 23.03 kcal mol⁻¹ more stable than the latter. There are two kinds of interaction orientations between Al₃ and LiF₂, namely, point-to-side (2ps-1 and 2ps-2) and side-to-side (2ss). From Fig. 1, the relative position between Al₃ and LiF₂ units in isomer 2ps-1 is different from that in 2ps-2. To be specific, line Al₁Al₂ is parallel to line F₁F₂ in 2ps-1, but is perpendicular to line F₁F₂ in 2ps-2. The Al₃–Li distances are 2.629, 2.850 and 2.610 Å for the 2ps-1, 2ss and 2ps-2 structures, respectively. Note that these lengths are close to those of Al₃–Li (2.854 and 2.653 Å for 1pp and 1sp, respectively), so there might also be Al–Li connections between Al₃ and LiF₂ units. The stability sequence is 2pp > 2ss > 2ps-2 for the three Al₃–LiF₂ structures in accordance to the total energy order. Four isomers were found for the Al₃–BeF₃ compound. From Table 1, the point-to-side orientation (3ps-1, 3ps-2) is superior to the side-to-side orientation (3ss), and the least favorable structure is 3ff with the face-to-face orientation. Herein, the bonding pattern in 3ps-1 is similar to that in 2ps-1. It is worth to mention that, though 3ps-2 exhibits a similar bonding pattern to that for 2ps-2, the former has a higher symmetry (C₂ᵥ) than the latter (C₃ᵥ). The Al–Be distance of 2.460 Å for 3ff is close to that for the pyramidal Al₃Be cluster (2.370 Å), hence structure 3ff can also be regarded as three F atoms side-on attached to an Al₃Be unit. As to Al₃–BF₄, two structures were obtained with point-to-side (4ps) and face-to-face (4ff) bonding patterns, respectively. Isomer 4ff is 19.99 kcal mol⁻¹ less stable than isomer 4ps.

According to the above results, when Al₃ interacts with superhalogens, the preferred sequence of interaction site is apex Al atom > Al–Al side > Al₃ ring plane, for the Al₃ cluster. As to superhalogens, the F–F side is superior to the plane consisting of three F atoms. Therefore, the most beneficial bonding pattern for the Al₃–X systems is point-to-side, while the least favorable one is face-to-face. The only exception is that 2ps-2 is 20.02 kcal mol⁻¹ less stable than isomer 2ss, which may be attributed to the evidently distorted Al₃ triangle in the former. In contrast, the Al₃ ring is almost intact in the four structural isomers of Al₃–BeF₃, hence the 3ps-1 and 3ps-2 isomers with point-to-side orientation possess lower total energy than the others (3ss, 3ff).

3.1.2. Al₃-M. Ten minimum structures were identified for the Al₃-(super)alkali compounds at the MP2/6-311+G(3df) level. The optimized geometries of Al₃-M (M = Li, FLi₂, OLi₃, NLi₄) and their ionic components are displayed in Fig. 2, and their

Table 1  Relative energies E_rel (kcal mol⁻¹), the lowest vibrational frequency ν₁ (cm⁻¹), NBO charge on the Al₃ subunit (Q^Al), HOMO–LUMO gaps (eV), binding energy per atom E_b (kcal mol⁻¹), and the maximum negative NICS values of the Al₃–X compounds (NICS_max, ppm).

<table>
<thead>
<tr>
<th>Species</th>
<th>Orientation</th>
<th>E_rel</th>
<th>ν₁</th>
<th>Q^Al</th>
<th>Gap</th>
<th>E_b</th>
<th>NICS_max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₃–F</td>
<td>1pp</td>
<td>0.00</td>
<td>126</td>
<td>0.777</td>
<td>5.55</td>
<td>55.54</td>
<td>137.1</td>
</tr>
<tr>
<td></td>
<td>1sp</td>
<td>23.03</td>
<td>174</td>
<td>0.818</td>
<td>4.80</td>
<td>51.17</td>
<td>120.1</td>
</tr>
<tr>
<td>Al₃–LiF₂</td>
<td>2ps-1</td>
<td>0.00</td>
<td>49</td>
<td>0.685</td>
<td>4.97</td>
<td>68.55</td>
<td>178.8</td>
</tr>
<tr>
<td></td>
<td>2ps-2</td>
<td>84.34</td>
<td>29</td>
<td>0.685</td>
<td>4.53</td>
<td>66.05</td>
<td>174.7</td>
</tr>
<tr>
<td>Al₃–BeF₃</td>
<td>3ps-1</td>
<td>0.00</td>
<td>50</td>
<td>0.748</td>
<td>5.66</td>
<td>79.47</td>
<td>164.6</td>
</tr>
<tr>
<td></td>
<td>3ps-2</td>
<td>2.61</td>
<td>39</td>
<td>0.756</td>
<td>5.40</td>
<td>78.99</td>
<td>164.6</td>
</tr>
<tr>
<td></td>
<td>3ss</td>
<td>9.07</td>
<td>41</td>
<td>0.768</td>
<td>5.47</td>
<td>78.45</td>
<td>169.4</td>
</tr>
<tr>
<td></td>
<td>3ff</td>
<td>12.51</td>
<td>134</td>
<td>1.375</td>
<td>6.34</td>
<td>78.31</td>
<td>180.8</td>
</tr>
<tr>
<td>Al₃–BF₄</td>
<td>4ps</td>
<td>0.00</td>
<td>38</td>
<td>0.757</td>
<td>5.68</td>
<td>86.87</td>
<td>166.4</td>
</tr>
<tr>
<td></td>
<td>4ff</td>
<td>19.99</td>
<td>89</td>
<td>0.824</td>
<td>5.64</td>
<td>85.38</td>
<td>166.7</td>
</tr>
</tbody>
</table>

Fig. 2  Optimized structures of the Al₃-M compounds and Al₃–, FLi₂⁺, OLi₃⁺, NLi₄⁺ ions at the MP2/6-311+G(3df) level, bond lengths (Å) and Laplacian of the electron density at a bond critical point \( \nabla \rho(\mathbf{r}) \) (in au., bold font) for the bonds that connect Al₃ and M subunits.
corresponding lowest vibrational frequencies are listed in Table 2.

As can be seen from Fig. 2, the interaction between Al3 and superalkalis M is a bit complex. In some structures, the Al3 and M subunits are connected via Al–Li bonds, while in the other structures, the central nonmetal atom of superalkali M also takes part in the intramolecular interaction and directly binds to the Al3 unit. Accordingly, the nomenclature employed for the former kind of Al3–M structures designates the number of Li atoms in Roman numerals, followed by the bonding pattern. Differently, for the latter kind of structures, the Roman numerals are followed by the number of atoms participating in the intramolecular interaction, from Al3 and M, respectively. For example, IIIfs represents an Al3–FLi2 structure with face-to-side bonding pattern, while II23 means that the interaction between Al3 and OLi3 involves two Al atoms, two Li atoms and the nonmetal F atom.

For Al3–Li, the Li atom may cap the Al3 triangle (Ifp) or bind with the apex Al atom (Ipp). Isomer Ifp with the face-to-point bonding pattern is more stable. There are three types of interactions between Al3 and FLi2. Herein, isomer IIIfs with face-to-side bonding pattern is the lowest-energy structure, and isomer IIss with side-to-side bonding orientation is the least favorable one. As for isomer II23, the Al3 and FLi2 moieties are linked together by two Al–Li bonds and an Al–F bond. Three structures were identified for the Al3–OLi3 compound. Superalkali OLi3 is bound to Al3 by three Al–Li bonds in isomer IIIfs, where the Al3 and OLi3 planes are perpendicular to each other. In isomers II24-1 and II24-2, all the four atoms of OLi3 directly interact with the Al3 unit. From Table 2, the stability order is III24-1 > III24-2 > IIIfs. As to Al3–NLi4, two isomers were found and isomer IV24 is 31.05 kcal mol−1 more stable than IVfs. From Fig. 2, the bonding patterns in structures IV24 and IVfs are similar to those in structures III24-1 and IIIIfs, respectively.

As shown in Fig. 2, intercluster fusion occurs when Al3 interacts with superalkali M, which leads to broken Al3 ring in the II23, IIss and III24-2 structures. Nevertheless, the structural integrity of the Al3 cluster and superalkali M are retained in the lowest-energy structure of each Al3–M compound.

The structural features of the Al3–M compounds indicate that Al3 does not interact with superalkali M through the apex Al atom as it does in superhalogen compounds. From Fig. 2, Al3 prefers to bind with M through the ring plane in the Al3–Li and Al3–FLi2 compounds, while in the other two species, it prefers to interact with M through the Al–Al edge. The isomer with more bonds between Al3 and M generally exhibits relatively higher stability. Take Al3–OLi3 as an example. The III24 isomer involving five Al–Li bonds and an Al–O bond is more stable than IIIIfs with three Al–Li bonds. For two isomers with the same bonding mode, the one containing intact Al3 ring is more favorable. This is why III24-1 is 6.84 kcal mol−1 more stable than III24-2.

### 3.2. Stability and bonding nature

The HOMO–LUMO energy gap is considered to be an important index of electronic stability and chemical inertness of clusters. From Tables 1 and 2, the HOMO–LUMO gaps of the Al3–X and Al3–M compounds are comparable to each other, which are ranging from 4.53 to 6.34 eV and from 4.08 to 5.62 eV, respectively. These gap values are considerably large compared with that of superatom compound Al13K3O36 (1.24 eV), suggesting better stability of the studied compounds.

The global chemical hardness (η), which can be approximately obtained as follows,

$$\eta \approx \frac{\text{VIP} - \text{VEA}}{2}$$

was also calculated to measure the stability of the studied compounds. VIP and VEA in the formula represent vertical ionization potential and vertical electron affinity, respectively. Structures with large hardness are often considered to be harder, namely, less reactive and more stable. We took the lowest-energy structures of each compound as examples. Their hardness values are presented in Table S1 in ESI.† From the table, the η values range from 1.959 to 2.569 eV, which are comparable to that of magic cluster Al6Be (2.751 eV), and consequently, indicate considerable stability of the Al3–X and Al3–M compounds.

The relative stability of compounds can also be examined by binding energy per atom ($E_b$), and the larger the $E_b$ value, the better the stability. It is found that the $E_b$ values of the Al3–X compounds show an increasing tendency with increasing atom

Table 2. Relative energies $E_{rel}$ (kcal mol−1), the lowest vibrational frequency $\nu_1$ (cm−1), NBO charge on the Al3 subunit ($Q^{Al_3}$, [e]), HOMO–LUMO gaps (eV), binding energy per atom $E_b$ (kcal mol−1), bond energies $E_b$ (kcal mol−1), and the maximum negative NICS values of the Al3–M compounds (NICSmax, ppm)

<table>
<thead>
<tr>
<th>Species</th>
<th>Orientation</th>
<th>$E_{rel}$</th>
<th>$\nu_1$</th>
<th>$Q^{Al_3}$</th>
<th>Gap</th>
<th>$E_b$</th>
<th>$E_b$</th>
<th>NICSmax</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al3–Li</td>
<td>Ifp</td>
<td>0.00</td>
<td>180</td>
<td>-0.506</td>
<td>5.55</td>
<td>33.17</td>
<td>48.6</td>
<td>-39.0</td>
</tr>
<tr>
<td></td>
<td>Ipp</td>
<td>11.99</td>
<td>80</td>
<td>-0.675</td>
<td>4.93</td>
<td>30.00</td>
<td>37.2</td>
<td>-29.6</td>
</tr>
<tr>
<td>Al3–FLi2</td>
<td>IIIfs</td>
<td>0.00</td>
<td>63</td>
<td>-0.539</td>
<td>5.62</td>
<td>32.55</td>
<td>61.7</td>
<td>-35.5</td>
</tr>
<tr>
<td></td>
<td>II23</td>
<td>16.28</td>
<td>119</td>
<td>-0.295</td>
<td>5.36</td>
<td>49.75</td>
<td>75.7</td>
<td>-17.9</td>
</tr>
<tr>
<td></td>
<td>IIss</td>
<td>35.64</td>
<td>43</td>
<td>-0.422</td>
<td>4.95</td>
<td>47.84</td>
<td>58.0</td>
<td>-</td>
</tr>
<tr>
<td>Al3–OLi3</td>
<td>III24-1</td>
<td>0.00</td>
<td>60</td>
<td>-0.266</td>
<td>4.08</td>
<td>60.71</td>
<td>92.4</td>
<td>-34.8</td>
</tr>
<tr>
<td></td>
<td>III24-2</td>
<td>6.84</td>
<td>58</td>
<td>-0.314</td>
<td>4.21</td>
<td>59.72</td>
<td>101.0</td>
<td>-14.4</td>
</tr>
<tr>
<td></td>
<td>IIIIfs</td>
<td>19.50</td>
<td>49</td>
<td>-0.454</td>
<td>4.91</td>
<td>58.21</td>
<td>65.5</td>
<td>-36.1</td>
</tr>
<tr>
<td>Al3–NLi4</td>
<td>IV24</td>
<td>0.00</td>
<td>24</td>
<td>-0.361</td>
<td>4.11</td>
<td>54.08</td>
<td>94.7</td>
<td>-26.1</td>
</tr>
<tr>
<td></td>
<td>IVfs</td>
<td>31.05</td>
<td>25</td>
<td>-0.350</td>
<td>4.90</td>
<td>50.58</td>
<td>55.0</td>
<td>-34.7</td>
</tr>
</tbody>
</table>
The bond energies $E_b$ of the $\text{Al}_3$–X and $\text{Al}_3$–M compounds are defined as the negative of $\Delta E_{\text{en}}$ values. A larger $E_b$ value implies a stronger interaction between $\text{Al}_3$ and (super)atoms. As can be seen from Table 1, the $E_b$ values of the $\text{Al}_3$–X compounds are as large as 120.1–190.5 kcal mol$^{-1}$, which are comparable to or much larger than traditional ionic bond energy of 133.5 kcal mol$^{-1}$ for LiF and bond energies (117.5–128.45 kcal mol$^{-1}$) of superatom compounds $\text{Al}_3K_2O^4$ and $\text{Li}_2O$–$X$ ($X = \text{BF}_4^-$, $\text{BeF}_3$, $\text{NO}_3^-$).\textsuperscript{27} Thus, the $\text{Al}_3$ cluster can tightly bind with (super)halogen $X$. Note that the bond energy sequence is not completely consistent with the stability sequence of the isomers. For example, the total energy of 2ps$-1$ is much lower than that of 2ss, but the latter has a larger $E_b$ value of 190.5 kcal mol$^{-1}$. This is due to the fact that isomer 2ss contains one more Al–Li bond, and consequently, shows a stronger interaction between the $\text{Al}_3$ and $\text{LiF}_2$ moieties. Similarly, the 3ff isomer with Al–Be connections has the largest bond energy among the $\text{Al}_3$–$\text{BeF}_2$ species. For the other $\text{Al}_3$–superhalogen compounds without Al–metal atom interactions, the $E_b$ value varies in the 164.6–169.4 kcal mol$^{-1}$ range. From Table 2, the bond energies of 37.2–101.0 kcal mol$^{-1}$ for $\text{Al}_3$–M are smaller compared with those of the $\text{Al}_3$–X compounds, but are large enough to guarantee the strong interaction between $\text{Al}_3$ and (super)alkali M. Besides, those $\text{Al}_3$–M isomers involving nonmetal–$\text{Al}_3$ connections, namely II23, II24-1, II24-2, IV24, exhibit much larger $E_b$ values than the others.

To better understand the structures and stability of compounds assembled by $\text{Al}_3$ cluster and (super)atoms, we explored the bonding character of the $\text{Al}_3$–X and $\text{Al}_3$–M compounds on the basis of NBO and AIM analyses. Based on NBO analysis, the $\text{Al}_3$ unit exists in cationic state in $\text{Al}_3$–X while in anionic state in $\text{Al}_3$–M compounds.

As shown in Table 1, the sum of NBO charges (0.685–0.824|e|) on the $\text{Al}_3$ subunit in each $\text{Al}_3$–X compound is close to +1 (except for isomer 3ff), denoting that an electron transfers from $\text{Al}_3$ to (super)halogen $X$. This is consistent with the recent work of Zhao et al.,\textsuperscript{29} where $\text{Al}_3$ has been indicated to be a superalkali cluster.\textsuperscript{29} Structure 3ff contains an $\text{Al}_3$Be unit, and the electron sharing between $\text{Al}_3$ and Be results in 1.375|e| NBO charge on the $\text{Al}_3$ subunit. Different from the case of $\text{Al}_3$–X, the $\text{Al}_3$ subunits are negatively charged with $-0.266$ to $-0.675|e|$ in the $\text{Al}_3$–M compounds. It means that the (super)alkalis are capable of reducing the $\text{Al}_3$ cluster. To be specific, (super) alkali M is apt to lose an electron while the $\text{Al}_3$ cluster longs for an electron to achieve a closed-shell configuration. To clearly show the electron-shell structure and molecular orbital characteristics of the $\text{Al}_3$–M compounds, isomer IIff is taken as an example and its valence molecular orbitals (MOs) are illustrated in Fig. S1.\textsuperscript{†} From the figure, the valence molecular orbitals of IIff can be considered originated from $\text{Al}_3^-$ and $\text{FLi}_3^-$ subunits, respectively. Obviously, both $\text{Al}_3$ and $\text{FLi}_3$ moieties obtain shell-closed electronic configurations (1s$^2$1p$^2$2s$^2$ and 1s$^2$1p$^5$), respectively, according to spherical jellium model\textsuperscript{44,45} by charge transfer. As a result, the IIff structure achieve high stability from the $\text{Al}_3^-$ and $\text{FLi}_3^-$ segments, respectively. This is the same case for other $\text{Al}_3$–M compounds.

The Laplacian of the electron density at a bond critical point (BCP), $\nabla^2\rho(r)$, is an important quantity based on the AIM theory for describing the chemical bonding nature.\textsuperscript{56,57} Hence, the $\nabla^2\rho(r)$ values for dominant bonds that connect $\text{Al}_3$ and $X$/M subunits were calculated, and are shown in Fig. 1 and 2, respectively. From Fig. 1, the $\nabla^2\rho(r)$ values of $\text{Al}$–$F$ bonds vary in the range of 0.140–0.939 au, indicating that the $\text{Al}_3$ and (super) halogen subunits are connected by ionic bonds. These present a situation akin to that of superatom compounds $\text{BF}_4^-$–$M$ ($M = \text{Li, FLi}_2$, $\text{OLi}_3$, $\text{NLi}_4$)\textsuperscript{29} and $\text{FLi}_2$–$X$ ($X = \text{F, LiF}_2$, $\text{BeF}_3$, $\text{BF}_4$).\textsuperscript{26} The superhalogen and superalkali clusters are also ionically bonded in these compounds, and the ionic connections possess 0.106–0.361 au. $\nabla^2\rho(r)$ values, which are comparable to those of the $\text{Al}_3$–X compounds.

As can be seen from Fig. 2, the combination of $\text{Al}_3$ and (super)alkali M involves one or more Al–Li metallic bonds. Besides, the $\nabla^2\rho(r)$ values of 0.351–0.636 au. confirm the ionic bonding nature of the $\text{Al}$–$F$/O/N bonds in the II23, II24-1, II24-2, IV24 structures. Note that these compounds have much larger bond energies compared with the others, suggesting that the ionic bonds contribute a lot to the interaction between $\text{Al}_3$ and superalkali M. Similarly, ionic bonds play an important role in higher stability (namely larger binding energy and bond energy values) of $\text{Al}_3$–X compared with the $\text{Al}_3$–M system, since the former series are typical ionic compounds. It can be seen that both 1pp and II23 structures contain an $\text{Al}$–$F$ ionic bond. Whereas, the $\text{Al}$–$F$ bond in 1pp is much stronger compared with that in II23, as reflected by shorter bond length and larger $\nabla^2\rho(r)$ value of the former. Hence, the bond energy of 1pp is quite larger than that of II23. Besides, the preferred interaction site sequence of $\text{Al}_3$ when interacting with superhalogens can also be explained by the strength of $\text{Al}$–$X$ ionic bonds. To be specific, for each $\text{Al}_3$–$X$ compound, the $\text{Al}$–$F$ bond is the strongest, reflected by the shortest bond length and largest $\nabla^2\rho(r)$ value, when $\text{Al}_3$ binds with superhalogens through an apex Al atom. The only exception is the $\text{Al}_3$–$\text{LiF}_2$ compound. Its three isomers have similar $\text{Al}$–$F$ bond lengths and corresponding $\nabla^2\rho(r)$ values. In contrast, the $\text{Al}$–$F$ bond is the weakest, reflected by the longest bond length and smallest $\nabla^2\rho(r)$ value, when $\text{Al}_3$ interacts with superhalogens through its ring plane (see Fig. 1).

Since the aforementioned investigations were performed within the gas-phase approximation, one may wonder to what extent the calculations would be affected when solvent effects are taken into account. Besides, do $\text{Al}_3$–$X$ and $\text{Al}_3$–M compounds behave differently upon including a solvent? To address these questions, we took $\text{Al}_3$–$\text{BF}_2$ (4ps) and $\text{Al}_3$–$\text{NLi}_4$ (IV-24) as examples and ran parallel calculations by employing a self-consistent reaction-field (SCRF) treatment with a polarizable continuum model (PCM).\textsuperscript{53,64} Thereby, their optimized structures were...
obtained in polar (ethanol) and nonpolar (cyclohexane) environments, respectively, and are displayed in Fig. S2.† The corresponding physicochemical properties of 4ps and IV-24 were also calculated by using the PCM model, and are listed in Table S2.†

Compared with the optimized structures in gas-phase, all the ionic bonds that connect Al₃ and superatom subunits elongate in the presence of solvents. From Fig. S2,† the Al–Li metallic bond of Al₃–NLi₄ elongate in polar solvent but shorten in nonpolar solvent. Nevertheless, it can be concluded that solvent effect on the geometrical structures of superatom compounds is not significant since the 4ps and IV-24 structures do not change much in solution.

To explore the solvent effect on infrared (IR) spectrum of the 4ps and IV-24 isomers, their characteristic vibrations with the largest IR intensity were selected and examined with the PCM model. The stretching movement of superhalogen BF₄ toward Al₃ cluster is the characteristic vibration of 4ps both in gas-phase and in solution (see Fig. S3a†). From Table S2,† the stretching frequency is red-shifted by 28.7 and 12.8 cm⁻¹, and the corresponding IR intensity increases 213.2 and 93.8 km mol⁻¹ in the presence of polar and nonpolar solvents, respectively. As to IV-24, its characteristic vibration is the stretching mode of superalkali NLi₄ relative to Al₃, no matter whether in gas phase or in solution (see Fig. S3b†). Meanwhile, the characteristic vibrational frequency of IV-24 also undergoes redshifts of 10.4 and 54.4 cm⁻¹ in polar and nonpolar solvents, respectively. Moreover, it can be found that both polar and nonpolar solvents promote the charge transfer between Al₃ and superatom clusters, especially superalkali NLi₄. As a result, the stability of Al₃–NLi₄ is enhanced a lot in the presence of solvent molecules, which is reflected by the increased HOMO–LUMO gap, Eₐ, and E₀ values. This is particular the case when polar solvent (ethanol) is involved. For example, the bond energy of Al₃–NLi₄ reaches to 176.0 kcal mol⁻¹ in ethanol environment. Note that this value is even larger than that of Al₃–BF₄. Hence, the Al₃–superalkali compounds may be better stabilized in solvents than in gas phase. As far as Al₃–BF₄ is concerned, the HOMO–LUMO gap value becomes a bit larger according to the prediction of PCM solvation model. Apart from that, solvent effect hardly influences its stability.

3.3. Aromaticity

According to previous report, the Al₃⁻ anion has double aromaticity.28 From Fig. S4,† the σ-bonding HOMO orbital of Al₃⁻ renders σ-aromaticity, while the π-bonding HOMO–1 orbital renders π-aromaticity. The Al₃⁺ ring, by contrast, is also expected to possess π-aromaticity arising from its π-bonding HOMO orbital. Since Al₃⁻ and Al₃⁺ ions maintain their structural and electronic integrity in most Al₃–M and Al₃–X compounds, respectively, the resulting superatom compounds are supposed to be aromatic as well.

The nucleus-independent chemical shift (NICS), proposed by Schleyer and coworkers, is an efficient method to probe aromaticity of a molecule. Negative and positive NICS values denote aromaticity and antiaromaticity, respectively.53 To examine the aromaticity of the studied superatom compounds, the NICS values were calculated at, above, and below the geometrical center of the Al₃ subunits,53,65 and the spatial locations of the maximum NICS values are listed in Tables S3 and S4.† Because of the serious deformation of Al₃ moiety in structures 2ps-2 and 1ls, their aromaticity is not considered in this work. Although the Al₃ moiety also undergoes severe deformation in isomers II23 and III24-2, the three Al atoms and two Li atoms are seen to form a metal cage which might have three-dimensional (3-D) aromaticity.

The maximum NICS values for the Al₃–X and Al₃–M compounds are shown in Tables 1 and 2, respectively. From the tables, the NICSmax values range from −12.5 to −37.6 ppm for Al₃–X and from −14.4 to −39.0 ppm for Al₃–M, confirming their aromatic nature. Nevertheless, it is worth noting that isomers 3ff and 4ff show considerably lower NICSmax values (−13.9 and −12.5 ppm, respectively) compared to isolated Al₃⁺ ring (−31.4 ppm at the same computational level) and other Al₃–X structures. To explore the reason behind this, isomers 4ff and 4ps are taken as examples. Their first four valence MOs are shown in Fig. 3. From the figure, the four MOs of 4ps originate from the Al₃ subunit and look like duplicates of those of isolated Al₃⁺ ring. As a result, 4ps exhibits π-aromaticity and its NICSmax value (−30.8 ppm) is close to that of isolated Al₃⁺. This is the same case for isomers 1pp, 1sp, 2ps-1, 2ss, 3ps-1, 3ps-2, and 3ss. Interestingly, the MOs of the Al₃ cluster seem to have been rearranged while it interacts with superhalogen BeF₃ and BF₄ in the face-to-face orientation. As shown in Fig. 3, the HOMO orbital of 4ff turns out to be a σ-bonding orbital formed from in-plane 3p orbital of Al atoms, which renders σ-aromaticity to this structure. The same holds true for the 3ff isomer. Thus, the Al₃⁺ ring can exhibit different aromaticity depending on how it combined with superhalogen anions. Besides, the σ-aromaticity of the Al₃⁺ subunit corresponds to a smaller NICS value compared with its π-aromaticity. In addition, isomers II23 and III24-2 do possess 3-D aromaticity although their NICSmax values of −17.9 and −14.4 ppm, respectively, are relatively low.

![Fig. 3 Valence molecular orbitals of isomers (a) 4ps and (b) 4ff.](image-url)
compared to other Al$_3$–M compounds. Note that the aromaticity of these superatom compounds would reduce upon including solvent effect, which is reflected by decreased NICS$_{\text{max}}$ values of 4$\text{ps}$ and IV–24 in both polar and nonpolar environments (see Table S2†). It implies that the delocalized valence electron cloud of the Al$_3$ subunit becomes less concentrated due to the interaction with solvent molecules.

4. Conclusions

In summary, we have theoretically studied two types of superatom compounds by combining the Al$_3$ trimer with different shaped (super)halogens X (X = F, LiF$_2$, BeF$_3$, BF$_4$) or (super)alkalis M (M = Li, FLi$_2$, OLi$_3$, NLi$_4$). NBO analysis reveals that the Al$_3$ cluster donates electron to the former whereas gains electron from the latter species. Diverse structures have been obtained for the resulting Al$_3$–X and Al$_3$–M compounds. The most beneficial bonding pattern in the Al$_3$–X systems is point-to-side, while the least favorable one is face-to-face. As for the Al$_3$–M compounds, Al$_3$ prefers to bind with Li and FLi$_2$ through its ring plane, while prefers to interact with OLi$_3$ and NLi$_4$ through the Al–Al edge. All the studied superatom compounds possess large bond energies, indicating strong interactions between Al$_3$ and (super)atoms. Although the geometrical structures of the studied compounds do not change much when solvent effects are taken into account, the stability of Al$_3$–NLi$_4$ is obviously enhanced in the presence of solvent molecules. As expected, the Al$_3$ ring brings aromaticity to these superatom compounds no matter whether in gas phase or in solution. What is intriguing is that the Al$_3^{+}$ ring can exhibit different aromaticity ($\pi$ or $\sigma$ aromaticity) when combined with different superhalogen anions.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Grant No. 21375017, 21603032) and State Key Development Program for Basic Research of China (Grant No. 2013CB834801).

References