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

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The interaction between the aluminum trimer and representative (super)halogens X (X = F, LiF₂, BeF₃, BF₄) and (super)alkalis M (M = Li, FLi₂, 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.

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1. Introduction

Clusters are extensively studied in physics because they represent the transition states between single atoms and bulk solid.¹⁻⁸ 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.⁹ 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.¹⁰⁻¹³ Two well-known subsets of superatoms are superhalogens¹⁴⁻¹⁷ and superalkalis,¹⁸⁻²¹ which have been extensively studied for more than 30 years. Superhalogens have higher electron affinities (EAs) than atomic EA limit (Cl: 3.617 eV)²² while superalkalis are

unique clusters possessing ionization potentials (IPs) lower than those of alkali atoms (5.39–3.89 eV).²³ Lately, the idea of combining superalkali with superhalogen clusters has been theoretically proposed and the generated superatom compounds include Al₁₃K₃O and Al₁₃Na₃O,²⁴ BF₄-M (M = Li, FLi₂, OLi₃, NLi₄),²⁵ BLi₆-X (X = F, LiF₂, BeF₃, BF₄),²⁶ and Li₃O-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, Al₃⁻, Al₄²⁻, and Al₆²⁻, *etc.*²⁸⁻³⁴ Besides, some pure or doped aluminum clusters, such as Al₁₃,³⁵ Al₁₄,³⁶ Al₇⁻,³⁷ Al₁₂Be,³⁸ Al₁₂Cu,³⁹ 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

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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.^{30,41–44} 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 Al_n 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,^{38,45–47} in which structures were generated by randomly distributing all atoms inside a sphere with radius $R = 5.0$ 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.⁵³

The intramolecular interaction energies (E_{int}) between Al₃ and X/M subunits and binding energy per atom (E_a) 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.^{25,38} We used the counterpoise (CP) procedure⁵⁴ to eliminate the basis set superposition error (BSSE) effect given by eqn (1):⁵⁵

$$E_{\text{int}} = E_{\text{AB}}(X_{\text{AB}}) - E_{\text{A}}(X_{\text{AB}}) - E_{\text{B}}(X_{\text{AB}}) \quad (1)$$

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

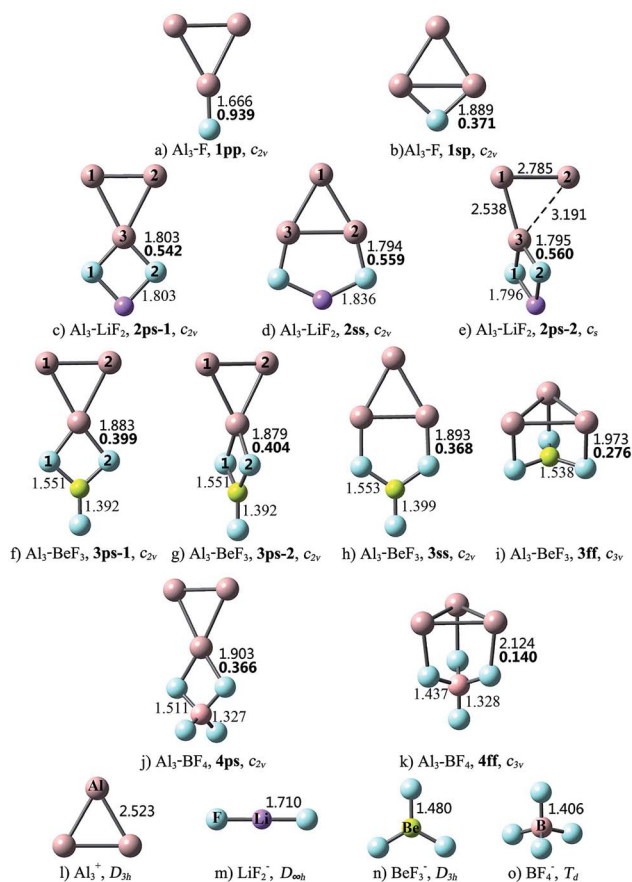


Fig. 1 Optimized structures of the Al₃-X compounds and Al₃⁺, LiF₂⁻, BeF₃⁻, BF₄⁻ ions at the MP2/6-311+G(3df) level, bond lengths (Å) and Laplacian of the electron density at a bond critical point $\nabla^2\rho(r)$ (in au., bold font) for the Al–F bonds that connect Al₃ and X subunits.



Table 1 Relative energies E_{rel} (kcal mol⁻¹), the lowest vibrational frequency ν_1 (cm⁻¹), NBO charge on the Al₃ subunit (Q^{Al_3} , |e|), HOMO–LUMO gaps (eV), binding energy per atom E_a (kcal mol⁻¹), bond energies E_b (kcal mol⁻¹), and the maximum negative NICS values of the Al₃–X compounds (NICS_{max}, ppm)

Species		Orientation	E_{rel}	ν_1	Q^{Al_3}	Gap	E_a	E_b	NICS _{max}
Al ₃ –F	1pp	Point-to-point	0.00	126	0.777	5.55	55.54	137.1	–28.5
	1sp	Side-to-point	23.03	174	0.818	4.80	51.17	120.1	–23.9
Al ₃ –LiF ₂	2ps-1	Point-to-side	0.00	49	0.685	4.97	68.55	178.8	–27.5
	2ss	Side-to-side	64.32	54	0.699	5.37	68.32	190.5	–37.6
	2ps-2	Point-to-side	84.34	29	0.685	4.53	66.05	174.7	—
Al ₃ –BeF ₃	3ps-1	Point-to-side	0.00	50	0.748	5.66	79.47	168.2	–30.6
	3ps-2	Point-to-side	2.61	39	0.756	5.40	78.99	164.6	–24.4
	3ss	Side-to-side	9.07	41	0.768	5.47	78.45	169.4	–32.0
	3ff	Face-to-face	12.51	134	1.375	6.34	78.31	180.8	–13.9
Al ₃ –BF ₄	4ps	Point-to-side	0.00	38	0.757	5.68	86.87	166.4	–30.8
	4ff	Face-to-face	19.99	89	0.824	5.64	85.38	166.7	–12.5

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 **1fp** and **1pp**, respectively), so there might also be Al–Li connections between Al₃ and LiF₂ units. The stability sequence is **2ps-1** > **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 (C_{2v}) than the latter (C_s). The Al–Be distance of 2.460 Å for **3ff** is close to that for the pyramidal Al₃Be cluster (2.370 Å),⁵⁸ 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

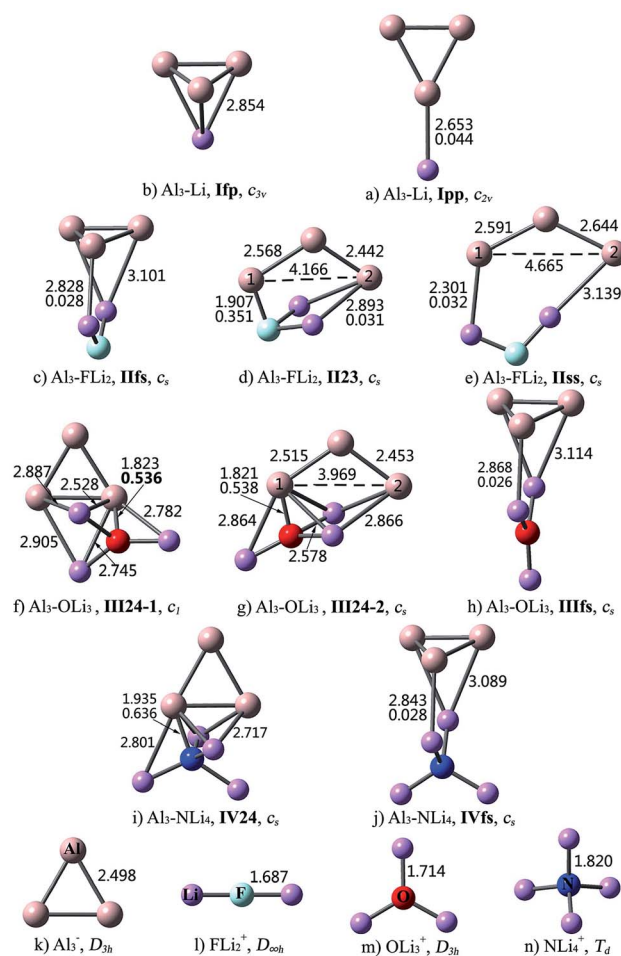


Fig. 2 Optimized structures of the Al₃–M compounds and Al₃⁻, FLi₂⁺, OLi₃⁺, NLi₄⁺ ions at the MP2/6-311+G(3df) level, bond lengths (Å) and Laplacian of the electron density at a bond critical point $\nabla^2\rho(r)$ (in a.u., bold font) for the bonds that connect Al₃ and M subunits.



corresponding lowest vibrational frequencies are listed in Table 2.

As can be seen from Fig. 2, the interaction between Al_3 and superalkalis M is a bit complex. In some structures, the Al_3 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 Al_3 unit. Accordingly, the nomenclature employed for the former kind of Al_3 –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 Al_3 and M, respectively. For example, **Iifs** represents an Al_3 – FLi_2 structure with face-to-side bonding pattern, while **II23** means that the interaction between Al_3 and FLi_2 involves two Al atoms, two Li atoms and the nonmetal F atom.

For Al_3 –Li, the Li atom may cap the Al_3 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 Al_3 and FLi_2 . Herein, isomer **Iifs** 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 Al_3 and FLi_2 moieties are linked together by two Al–Li bonds and an Al–F bond. Three structures were identified for the Al_3 – OLi_3 compound. Superalkali OLi_3 is bound to Al_3 by three Al–Li bonds in isomer **IIIifs**, where the Al_3 and OLi_3 planes are perpendicular to each other. In isomers **III24-1** and **III24-2**, all the four atoms of OLi_3 directly interact with the Al_3 unit. From Table 2, the stability order is **III24-1** > **III24-2** > **IIIifs**. As to Al_3 – NLi_4 , 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 Al_3 interacts with superalkali M, which leads to broken Al_3 ring in the **II23**, **Iiss** and **III24-2** structures. Nevertheless, the structural integrity of the Al_3 cluster and superalkali M are retained in the lowest-energy structure of each Al_3 –M compound.

The structural features of the Al_3 –M compounds indicate that Al_3 does not interact with superalkali M through the apex Al

atom as it does in superhalogen compounds. From Fig. 2, Al_3 prefers to bind with M through the ring plane in the Al_3 –Li and Al_3 – FLi_2 compounds, while in the other two species, it prefers to interact with M through the Al–Al edge. The isomer with more bonds between Al_3 and M generally exhibits relatively higher stability. Take Al_3 – OLi_3 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 Al_3 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 Al_3 –X and Al_3 –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 $\text{Al}_{13}\text{K}_3\text{O}^{36}$ (1.24 eV), suggesting better stability of the studied compounds.

The global chemical hardness (η),⁵⁹ 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 Al_6Be (2.751 eV),⁵⁸ and consequently, indicate considerable stability of the Al_3 –X and Al_3 –M compounds.

The relative stability of compounds can also be examined by binding energy per atom (E_a), and the larger the E_a value, the better the stability. It is found that the E_a values of the Al_3 –X compounds show an increasing tendency with increasing atom

Table 2 Relative energies E_{rel} (kcal mol^{−1}), the lowest vibrational frequency ν_1 (cm^{−1}), NBO charge on the Al_3 subunit (Q^{Al_3} , |e|), HOMO–LUMO gaps (eV), binding energy per atom E_a (kcal mol^{−1}), bond energies E_b (kcal mol^{−1}), and the maximum negative NICS values of the Al_3 –M compounds (NICS_{max}, ppm)

Species		Orientation	E_{rel}	ν_1	Q^{Al_3}	Gap	E_a	E_b	NICS _{max}
Al_3 –Li	Ifp	Face-to-point	0.00	180	−0.506	5.55	33.17	48.6	−39.0
	Ipp	Point-to-point	11.99	80	−0.675	4.93	30.00	37.2	−29.6
Al_3 – FLi_2	Iifs	Face-to-side	0.00	63	−0.519	5.62	52.55	61.7	−35.5
	II23	Side-to-face	16.28	119	−0.295	5.36	49.75	75.7	−17.9
	Iiss	Side-to-side	35.64	43	−0.422	4.95	47.84	58.0	—
Al_3 – OLi_3	III24-1	Side-to-face	0.00	60	−0.266	4.08	60.71	92.4	−34.8
	III24-2	Side-to-face	6.84	58	−0.314	4.21	59.72	101.0	−14.4
	IIIifs	Face-to-side	19.50	49	−0.454	4.91	58.21	65.5	−36.1
Al_3 – NLi_4	IV24	Side-to-face	0.00	24	−0.361	4.11	54.08	94.7	−26.1
	IVfs	Face-to-side	31.05	25	−0.350	4.90	50.58	55.0	−34.7



number. The lowest-energy structures can be taken as examples. From Table 1, the E_a values increase in the order $55.54 \text{ kcal mol}^{-1}$ ($\text{Al}_3\text{-F}$) < $68.55 \text{ kcal mol}^{-1}$ ($\text{Al}_3\text{-LiF}_2$) < $79.47 \text{ kcal mol}^{-1}$ ($\text{Al}_3\text{-BeF}_3$) < $86.87 \text{ kcal mol}^{-1}$ ($\text{Al}_3\text{-BF}_4$). By contrast, among the $\text{Al}_3\text{-M}$ compounds, the $\text{Al}_3\text{-OLi}_3$ species exhibit the largest E_a values of $58.21\text{--}60.71 \text{ kcal mol}^{-1}$. It is also noted that the $\text{Al}_3\text{-superhalogen}$ compounds possess larger E_a values than the $\text{Al}_3\text{-superalkali}$ compounds, which may reflect the superior stability of the former system.

The bond energies E_b of the $\text{Al}_3\text{-X}$ and $\text{Al}_3\text{-M}$ compounds are defined as the negative of E_{int} values. A larger E_b value implies a stronger interaction between Al_3 and (super)atoms. As can be seen from Table 1, the E_b values of the $\text{Al}_3\text{-X}$ compounds are as large as $120.1\text{--}190.5 \text{ kcal mol}^{-1}$, which are comparable to or much larger than traditional ionic bond energy of $133.5 \text{ kcal mol}^{-1}$ for LiF and bond energies ($117.5\text{--}128.45 \text{ kcal mol}^{-1}$) of superatom compounds $\text{Al}_{13}\text{K}_3\text{O}^{24}$ and $\text{Li}_3\text{O-X}$ ($\text{X} = \text{BF}_4, \text{BeF}_3, \text{NO}_3$).²⁷ Thus, the 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 $190.5 \text{ kcal mol}^{-1}$. This is due to the fact that isomer **2ss** contains one more Al-Li bond, and consequently, shows a stronger interaction between the Al_3 and LiF_2 moieties. Similarly, the **3ff** isomer with Al-Be connections has the largest bond energy among the $\text{Al}_3\text{-BeF}_3$ species. For the other $\text{Al}_3\text{-superhalogen}$ compounds without Al-metal atom interactions, the E_b value varies in the $164.6\text{--}169.4 \text{ kcal mol}^{-1}$ range. From Table 2, the bond energies of $37.2\text{--}101.0 \text{ kcal mol}^{-1}$ for $\text{Al}_3\text{-M}$ are smaller compared with those of the $\text{Al}_3\text{-X}$ compounds, but are large enough to guarantee the strong interaction between Al_3 and (super)alkali M. Besides, those $\text{Al}_3\text{-M}$ isomers involving nonmetal-atom- Al_3 connections, namely **II23**, **III24-1**, **III24-2**, **IV24**, exhibit much larger E_b values than the others.

To better understand the structures and stability of compounds assembled by Al_3 cluster and (super)atoms, we explored the bonding character of the $\text{Al}_3\text{-X}$ and $\text{Al}_3\text{-M}$ compounds on the basis of NBO and AIM analyses. Based on NBO analysis, the Al_3 unit exists in cationic state in $\text{Al}_3\text{-X}$ while in anionic state in the $\text{Al}_3\text{-M}$ compounds.

As shown in Table 1, the sum of NBO charges ($0.685\text{--}0.824|e|$) on the Al_3 subunit in each $\text{Al}_3\text{-X}$ compound is close to +1 (except for isomer **3ff**), denoting that an electron transfers from Al_3 to (super)halogen X. This is consistent with the recent work of Zhao *et al.*, where Al_3 has been indicated to be a superalkali cluster.⁶⁰ Structure **3ff** contains an Al_3Be unit, and the electron sharing between Al_3 and Be results in $1.375|e|$ NBO charge on the Al_3 subunit. Different from the case of $\text{Al}_3\text{-X}$, the Al_3 subunits are negatively charged with -0.266 to $-0.675|e|$ in the $\text{Al}_3\text{-M}$ compounds. It means that the (super)alkalis are capable of reducing the Al_3 cluster. To be specific, (super)alkali M is apt to lose an electron while the 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 $\text{Al}_3\text{-M}$ compounds, isomer **IIfs** is taken as an example and its valence molecular orbitals (MOs) are illustrated

in Fig. S1.† From the figure, the valence molecular orbitals of **IIfs** can be considered originated from Al_3^- and FLi_2^+ subunits, respectively. Obviously, both Al_3 and FLi_2 moieties obtain shell-closed electronic configurations ($1s^21p^62s^2$ and $1s^21p^6$, respectively, according to spherical jellium model^{61,62}) by charge transfer. As a result, the **IIfs** structure achieve high stability from the Al_3^- and FLi_2^+ segments, respectively. This is the same case for other $\text{Al}_3\text{-M}$ 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.^{50,51} Hence, the $\nabla^2\rho(r)$ values for dominant bonds that connect 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 Al-F bonds vary in the range of $0.140\text{--}0.939 \text{ au.}$, indicating that the Al_3 and (super)halogen subunits are connected by ionic bonds. These present a situation akin to that of superatom compounds $\text{BF}_4\text{-M}$ ($\text{M} = \text{Li}, \text{FLi}_2, \text{OLi}_3, \text{NLi}_4$)²⁵ and $\text{BLi}_6\text{-X}$ ($\text{X} = \text{F}, \text{LiF}_2, \text{BeF}_3, \text{BF}_4$).²⁶ The superhalogen and superalkali clusters are also ionically bonded in these compounds, and the ionic connections possess $0.106\text{--}0.361 \text{ au.}$ $\nabla^2\rho(r)$ values, which are comparable to those of the $\text{Al}_3\text{-X}$ compounds.

As can be seen from Fig. 2, the combination of Al_3 and (super)alkali M involves one or more Al-Li metallic bonds. Besides, the $\nabla^2\rho(r)$ values of $0.351\text{--}0.636 \text{ au.}$ confirm the ionic bonding nature of the Al-F/O/N bonds in the **II23**, **III24-1**, **III24-2**, **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 Al_3 and superalkali M. Similarly, ionic bonds play an important role in higher stability (namely larger binding energy and bond energy values) of $\text{Al}_3\text{-X}$ compared with the $\text{Al}_3\text{-M}$ system, since the former series are typical ionic compounds. It can be seen that both **1pp** and **II23** structures contain an Al-F ionic bond. Whereas, the 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 Al_3 when interacting with superhalogens can also be explained by the strength of Al-X ionic bonds. To be specific, for each $\text{Al}_3\text{-X}$ compound, the Al-F bond is the strongest, reflected by the shortest bond length and largest $\nabla^2\rho(r)$ value, when 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 Al-F bond lengths and corresponding $\nabla^2\rho(r)$ values. In contrast, the Al-F bond is the weakest, reflected by the longest bond length and smallest $\nabla^2\rho(r)$ value, when 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 $\text{Al}_3\text{-X}$ and $\text{Al}_3\text{-M}$ compounds behave differently upon including a solvent? To address these questions, we took $\text{Al}_3\text{-BF}_4$ (**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).^{63,64} 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 Al_3 and superatom subunits elongate in the presence of solvents. From Fig. S2,† the Al–Li metallic bonds of $\text{Al}_3\text{-NLi}_4$ 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 BF_4 toward Al_3 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 NLi_4 relative to Al_3 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 Al_3 and superatom clusters, especially superalkali NLi_4 . As a result, the stability of $\text{Al}_3\text{-NLi}_4$ is enhanced a lot in the presence of solvent molecules, which is reflected by the increased HOMO–LUMO gap, E_a , and E_b values. And this is particular the case when polar solvent (ethanol) is involved. For example, the bond energy of $\text{Al}_3\text{-NLi}_4$ reaches to 176.0 kcal mol^{-1} in ethanol environment. Note that this value is even larger than that of $\text{Al}_3\text{-BF}_4$. Hence, the Al_3 –superalkali compounds may be better stabilized in solvents than in gas phase. As far as $\text{Al}_3\text{-BF}_4$ 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 Al_3^- anion has double aromaticity.³⁹ From Fig. S4,† the σ -bonding HOMO orbital of Al_3^- renders σ -aromaticity, while the π -bonding HOMO–1 orbital renders π -aromaticity. The Al_3^+ ring, by contrast, is also expected to possess π -aromaticity arising from its π -bonding HOMO orbital. Since Al_3^- and Al_3^+ ions maintain their structural and electronic integrity in most $\text{Al}_3\text{-M}$ and $\text{Al}_3\text{-X}$ 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.⁵² To

examine the aromaticity of the studied superatom compounds, the NICS values were calculated at, above, and below the geometrical center of the Al_3 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 Al_3 moiety in structures **2ps-2** and **IIss**, their aromaticity is not considered in this work. Although the Al_3 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 $\text{Al}_3\text{-X}$ and $\text{Al}_3\text{-M}$ compounds are shown in Tables 1 and 2, respectively. From the tables, the NICS_{max} values range from -12.5 to -37.6 ppm for $\text{Al}_3\text{-X}$ and from -14.4 to -39.0 ppm for $\text{Al}_3\text{-M}$, confirming their aromatic nature. Nevertheless, it is worth noting that isomers **3ff** and **4ff** show considerably lower NICS_{max} values (-13.9 and -12.5 ppm, respectively) compared to isolated Al_3^+ ring (-31.4 ppm at the same computational level) and other $\text{Al}_3\text{-X}$ 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 Al_3 subunit and look like duplicates of those of isolated Al_3^+ ring. As a result, **4ps** exhibits π -aromaticity and its NICS_{max} value (-30.8 ppm) is close to that of isolated Al_3^+ . This is the same case for isomers **1pp**, **1sp**, **2ps-1**, **2ss**, **3ps-1**, **3ps-2**, and **3ss**. Interestingly, the MOs of the Al_3 cluster seem to have been rearranged while it interacts with superhalogen BeF_3 and BF_4 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 Al_3^+ ring can exhibit different aromaticity depending on how it combined with superhalogen anions. Besides, the σ -aromaticity of the Al_3^+ 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 NICS_{max} values of -17.9 and -14.4 ppm, respectively, are relatively low

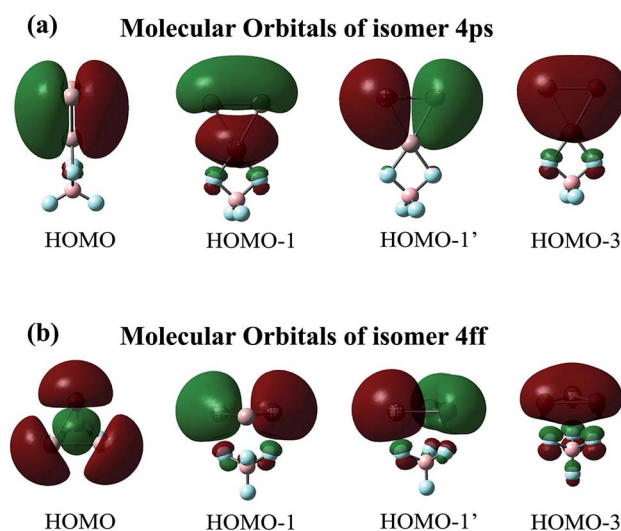


Fig. 3 Valence molecular orbitals of isomers (a) **4ps** and (b) **4ff**.



compared to other $\text{Al}_3\text{-M}$ compounds. Note that the aromaticity of these superatom compounds would reduce upon including solvent effect, which is reflected by decreased NICS_{max} values of **4ps** 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 ($X = \text{F}, \text{LiF}_2, \text{BeF}_3, \text{BF}_4$) or (super)alkalis M ($M = \text{Li}, \text{FLi}_2, \text{OLi}_3, \text{NLi}_4$). 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 $\text{Al}_3\text{-X}$ and $\text{Al}_3\text{-M}$ compounds. The most beneficial bonding pattern in the $\text{Al}_3\text{-X}$ systems is point-to-side, while the least favorable one is face-to-face. As for the $\text{Al}_3\text{-M}$ 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 $\text{Al}_3\text{-NLi}_4$ 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 (π or σ aromaticity) when combined with different superhalogen anions.

Conflicts of interest

There are no conflicts of interest to declare.

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