

Cluster-assembled compounds comprising an all-metal subunit Li_3Al_4^- †

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The recent, experimentally-discovered, all-metal antiaromatic Li_3Al_4^- has attracted great interest and extensive investigations due to its unique chemical bonds and exotic properties. Although a very recent theoretical study demonstrated that the all-metal species Li_3Al_4^- can be effectively stabilized by complexation with 3d transition metals, unfortunately such stabilization is at the expense of losing antiaromaticity (rectangular Al_4) to become aromatic (square Al_4). Here, we predict theoretically a series of cluster-assembled compounds $[\text{DM}(\text{Li}_3\text{Al}_4)]^{q-}$ ($\text{D} = \text{Li}_3\text{Al}_4^-$, Cp^- ; $\text{M} = \text{Li, Na, K, Be, Mg, Ca}$). The assembled species are ground states containing the all-metal antiaromatic Li_3Al_4^- subunits. Many fusion isomers are energetically lower than the homo-decked cluster-assembled compounds, thus, the homo-decked assembly species $[\text{M}(\text{Li}_3\text{Al}_4)_2]^{q-}$ are less likely due to their thermodynamic instability. In addition, the well-retained all-metal antiaromaticity is mainly ascribed to the ionic electrostatic interactions and the protections of rigid organic aromatic Cp-deck avoiding the fusion of Li_3Al_4^- . Our results represent the first example that the all-metal antiaromaticity is well retained in assembled compounds as that in the free Li_3Al_4^- cluster. Sufficiently large interaction energies make the realization of all-metal antiaromatic Li_3Al_4^- -incorporated compounds very promising.

1. Introduction

Recently, the experimental discovery of an Li_3Al_4^- cluster¹ in a laser vaporization technique, has led the concept of “antiaromaticity”, which is well-known in organic chemistry,² to enter the novel all-metal realm. As a result, the all-metal antiaromatic species have now received extensive attention in various aspects.³ Although whether Li_3Al_4^- is net antiaromatic or aromatic has been the focus of many debates and discussions,⁴ it is now generally agreed that Li_3Al_4^- possesses all-metal π -antiaromaticity with a rectangular Al_4^{4-} structure. In addition to the significant fundamental interest, recent theoretical studies^{5a,b} have shown that Al_4M_4 ($\text{M} = \text{Li, Na, and K}$) could be very good candidates for higher order nonlinear optical (NLO) materials due to charge transfer from the alkali-metal atoms (M) to the Al_4 rings. Moreover, if stable, all-metal antiaromatic clusters might have potential applications as new inorganic ligands and building blocks in chemistry and materials science. The ultimate goal may be to design novel two-dimensional (2D) and three-dimensional (3D) cluster-assembled materials based on the concept of “all-metal antiaromaticity”.

Surely, the key issue is whether and how the all-metal antiaromatic species like Li_3Al_4^- can be assembled into more

complex and stable compounds while retaining their antiaromatic features. Design of such compounds may help future laboratory synthesis for better structural characterization and property investigations. Very recently, Datta and Pati^{5b-d} found that the all-metal species Li_3Al_4^- can be stabilized by complexation with 3d transition metals very similar to an organic counterpart, C_4H_4 . Unfortunately, such “complexation to transition metal ions reduces the frontier orbital energies and introduces aromatic characteristics”,^{5c} i.e., the nature of Li_3Al_4^- is changed from the antiaromatic (in bare cluster) to aromatic (in complex). To the best of knowledge, *an assembled compound with a genuine subunit Li_3Al_4^- is still missing!* In this paper, we for the first time report a series of sandwich-like assembled compounds $[\text{DM}(\text{Li}_3\text{Al}_4)]^{q-}$ ($\text{D} = \text{Li}_3\text{Al}_4^-$, Cp^- ; $\text{M} = \text{Li, Na, K, Be, Mg, Ca}$) that each consist of an all-metal antiaromatic subunit Li_3Al_4^- . In contrast to the case for Datta and Pati, the antiaromaticity \rightarrow aromaticity conversion^{5c} is effectively avoided here through introducing the alkali- and alkaline metals.

2. Computational methods

Initially, we fully optimized the geometries of $[\text{DM}(\text{Li}_3\text{Al}_4)]^{q-}$ ($\text{D} = \text{Li}_3\text{Al}_4^-$, Cp^- ; $\text{M} = \text{Li, Na, K, } q = 1$; $\text{Be, Mg, Ca, } q = 0$) employing analytical gradients with polarized split-valence basis set (6-311 + G(d))⁶ using pure functional BP86^{7a,b} and the hybrid functional B3LYP^{7c,e} i.e., Becke’s hybrid three-parameter exchange functional with the Lee–Yang–Parr correlation functional within Kohn–Sham theory, which is implemented in the Gaussian 03 package.⁸ After geometrical optimization, normal mode vibrational analysis was performed to check whether the obtained structure is a true minimum point with all real frequencies or a first-order saddle

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† Electronic supplementary information (ESI) available: Full citations for ref. 8, the section of the homo-decked sandwich complexes, the mechanism of cluster assembly of all-metal antiaromatic cluster Li_3Al_4^- , the structures, Descartes coordinates, frequencies, absolute energies of our designed cluster-assembled compounds. See DOI: 10.1039/b716362b

point with only one imaginary frequency or high-order saddle points with many imaginary frequencies. The higher theoretical method CCSD(T)⁹ with 6-311+G(d) and 6-311++G(d, p) basis sets based on the B3LYP/6-311+G(d) geometries (a series of single point energy calculations) were also used to test the reliability of the results obtained at B3LYP/6-311+G(d) for some selected species. In order to get insight into the nature of our designed homo- and hetero-decked sandwich-type complexes, we performed detailed natural bond orbital (NBO)¹⁰ (NPA charge distributions) and orbital¹¹ (characterized orbitals) analyses on the designed sandwich-like species at the 6-311+G(d)–B3LYP/BP86 level. All calculations were performed with the Gaussian-03 program.⁸

3. Theoretical results and discussions

Initially, we consider the assembly and stabilization of the all-metal antiaromatic Li_3Al_4^- unit in the homo-decked sandwich scheme. We find that many fusion isomers are energetically lower than the homo-decked sandwich compounds, thus the homo-decked sandwich complexes are thermodynamically unstable (detailed information can be found in the electronic supporting information (ESI)[†]). In summary, it is less likely to incorporate the all-metal antiaromatic Li_3Al_4^- unit into cluster-assembled compounds in the homo-decked sandwich scheme.

The above “discouraging” results drive us to ask the questions again: “How to incorporate the all-metal antiaromatic unit into the assembled compounds?” and “How to retain the antiaromaticity, rather than to convert or destroy it in the assembled compounds?” The rich and mature chemistry of metallocenes assured us that Cp^- is a powerful sandwiching deck and versatile building block. We were thus promoted to wonder whether the all-metal antiaromatic Li_3Al_4^- can cooperate with the organic aromatic deck Cp^- to sandwich metal atoms. Luckily, it is indeed the case!

We apply the “hetero-decked sandwich” scheme for assembly of the all-metal antiaromatic Li_3Al_4^- unit into molecular complexes. A new class of sandwich compounds $\text{CpM}(\text{Li}_3\text{Al}_4)^{q-}$ can be designed. Such compounds are intuitively of special interest because they contain both the classic organic aromatic unit Cp^- and novel all-metal antiaromatic unit Li_3Al_4^- . At the 6-311+G(d)–B3LYP/BP86 level, some selected low-lying species are listed in Fig. 1a–f. Among all the considered $[\text{CpM}(\text{Li}_3\text{Al}_4)]^{q-}$ systems, the planar Cp^- structure is well maintained, indicative of the unique “rigidity” of this organic unit. Fusion of the Cp^- and Li_3Al_4^- decks to form new C–Al, C–Li or C–M bonds is energetically unfavorable, in sharp contrast to the situation for the $[\text{Li}_6\text{Al}_8\text{M}]^{q-}$ systems (see the ESI[†]). This results in the high stability of the hetero-decked assembled species $[\text{CpM}(\text{Li}_3\text{Al}_4)]^{q-}$. Thus, the rigid organic deck Cp^- can effectively assist the all-metal antiaromatic unit Li_3Al_4^- to sandwich metal atoms. The “hetero-decked sandwich” scheme can effectively stabilize the antiaromatic Li_3Al_4^- unit by avoiding fusion. For the purpose of actual synthesis, we also designed neutral species $(\text{Li})^+[\text{CpM}(\text{Li}_3\text{Al}_4)]^-$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, q = 1$) (see Fig. 1g–i) with counterions Li^+ . For each M , the low-lying sandwich isomers in charged

$[\text{CpM}(\text{Li}_3\text{Al}_4)]^{q-}$ are also the low-lying structures in neutral $(\text{Li})^+[\text{CpM}(\text{Li}_3\text{Al}_4)]^-$. Surely, the counterions have little influence on the low-lying structures. The results of the above calculations have demonstrated that the face (Cp^-)–face (Al_4 -ring) (f–f) and face (Cp^-)–side (Al–Al bond) interaction types are common phenomena in the extended systems. Such an interesting growth pattern might be applicable to the assembly of all-metal antiaromatic Li_3Al_4^- into the highly extended sandwich-like compounds.

In order to evaluate the stabilities of our designed cluster-assembled species, we consider some dissociation channels and calculate corresponding interaction energies. Firstly, we consider the two viable dissociation channels. (a) Extrusion of Li_3Al_4^- : $[\text{CpM}(\text{Li}_3\text{Al}_4)]^{q-} \rightarrow \text{Li}_3\text{Al}_4^- + \text{CpM}^{(1-q)+}$. (b) Extrusion of Cp^- : $[\text{CpM}(\text{Li}_3\text{Al}_4)]^{q-} \rightarrow \text{Cp}^- + \text{M}(\text{Li}_3\text{Al}_4)^{(1-q)+}$. Our considerations are based on the following facts. (1) The dissociation fragment Li_3Al_4^- has been experimentally observed, thus it should have sufficient stability to survive during the dissociation process. (2) The dissociation fragment Cp^- is the closed-shell organic rigid deck with highly stability and strong aromaticity. (3) The dissociation fragment alkali-metal-based half sandwich species CpM ($\text{M} = \text{Li}, \text{Na}, \text{K}$) and alkali-earth-metal-based sandwich species Cp_2M ($\text{M} = \text{Be}, \text{Mg}, \text{Ca}$) have been known for about half century. (4) We consider the fact that the metal-atoms connected closest to Cp should have larger possibility than other long-distance metal-atoms connected to Cp to form dissociation fragment CpM^{q+} in the dissociation channel (a).

From Fig. 1, we can see that the strength of the bonds $\text{Cp}-\text{M}(\text{Li}_3\text{Al}_4)$ (noted as “**B2**” in Fig. 1) ranges from 59.03 (58.78) to 157.76 (160.74) kcal mol^{−1}, and the strength of the bonds $\text{CpM}-\text{Li}_3\text{Al}_4$ (noted as “**B1**” in Fig. 1) range from 18.76 (19.55) to 162.49 (164.21) kcal mol^{−1} in $[\text{CpM}(\text{Li}_3\text{Al}_4)]^{q-}$. In general, the interaction energies of “**B2**” are larger than those of “**B1**”. Such phenomena are mainly ascribed to the high stability and strong aromaticity of Cp^- , which shows that the stability of the dissociation fragments ($\text{Cp}^- + \text{M}(\text{Li}_3\text{Al}_4)$) is higher than that of the dissociation fragments ($\text{CpM} + \text{Li}_3\text{Al}_4^-$). Thus, the strength of the bonds $\text{Cp}-\text{M}(\text{Li}_3\text{Al}_4)$ is stronger than that of $\text{CpM}-\text{Li}_3\text{Al}_4$. Note that the binding energies are very large for some alkali-earth metals, which can be mainly ascribed to the Coulomb interaction between the dissociation fragments Li_3Al_4^- and CpM^+ ($\text{M} = \text{Be}$ and Ca). Moreover, from Fig. 1, we can see that the two DFT results (B3LYP/BP86) agree well with each other. The above interaction energies are indicative of sufficient stabilities of our designed cluster-assembled complexes for future experimental syntheses or observations.

For some relevant species, e.g., $\text{CpLi}(\text{Li}_3\text{Al}_4)^-$, we used higher method CCSD(T) with basis sets 6-311+G(d) (in $[\]$) and 6-311++G(d, p) (in $\{ \}$) to test the reliability of the results obtained at the 6-311+G(d)–B3LYP/BP86 level. From Fig. 1, we can see that the higher CCSD(T) results generally agree with that of B3LYP/BP86. Additionally, the two CCSD(T) results generally agree with each other. Moreover, we found the binding energies at the higher CCSD(T) level are somewhat larger than those of the corresponding DFT results. The comparison of DFT and CCSD(T) led us to conclude that the DFT method is probably okay for

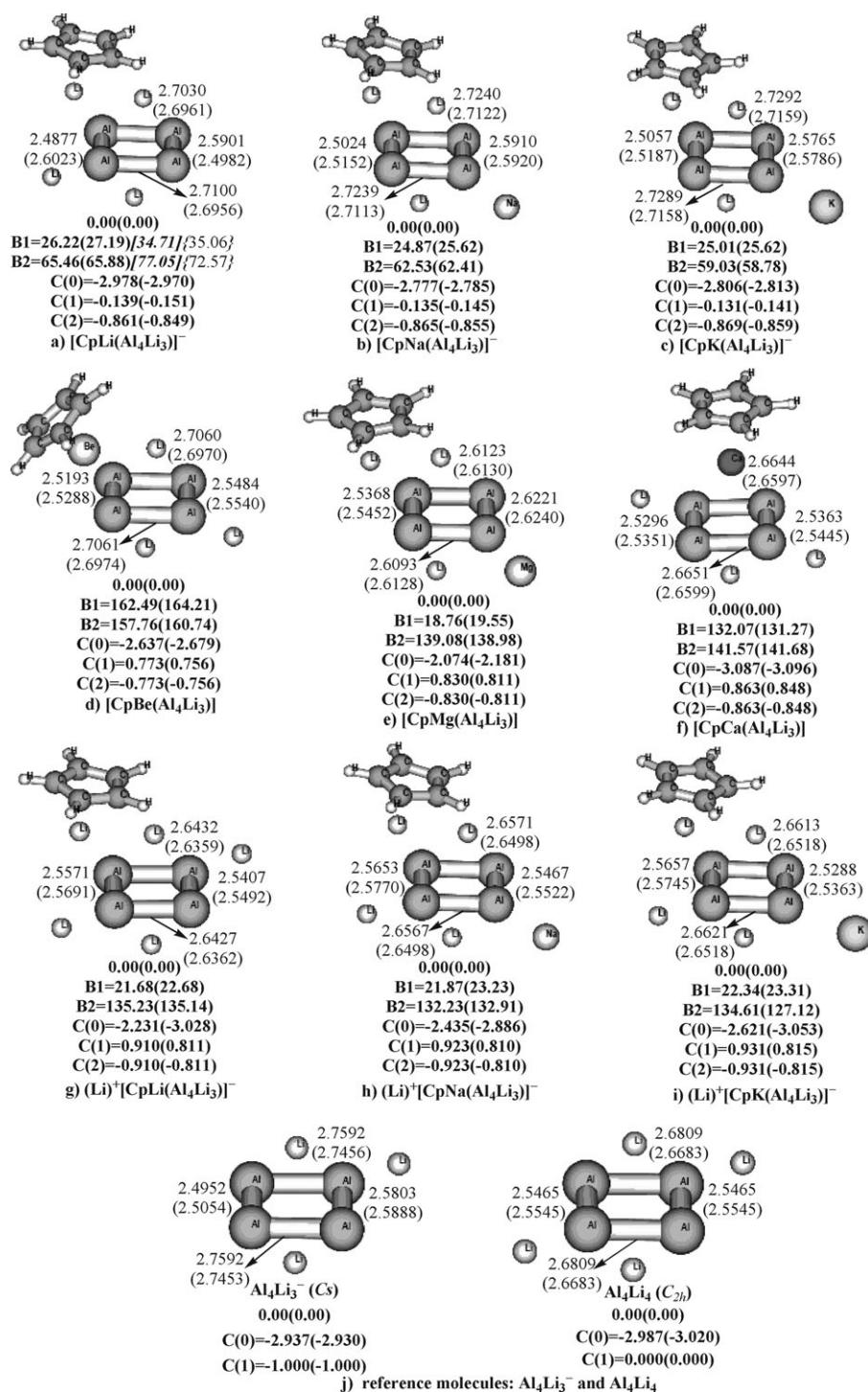


Fig. 1 The low-lying sandwich forms of [CpM(Li₃Al₄)]^{q-} (M = Li, Na, K, *q* = 1; M = Be, Mg, Ca, *q* = 0) and the lowest-energy saturated sandwich forms of (M⁺)[CpM(Li₃Al₄)]⁻ (M = Li, Na, K) obtained at the 6-311 + G(d)-B3LYP/BP86 level. Energy values are in kcal mol⁻¹. For some relevant species, The single points at the CCSD(T) with basis sets 6-311 + G(d) (in []) and 6-311 + + G(d, p) (in {}) level of calculations based on the B3LYP/6-311 + G(d) geometry are also given. “C(0)”, “C(1)” and “C(2)” denotes the natural charge distributions on the fragments Al₄, Al₄Li₃M^{q+} (M = Li, Na, K, *q* = 0; M = Be, Mg, Ca, *q* = 1) and Cp, respectively. The Al-Al bonds of Al₄-ring are listed in Å.

the systems treated. For the simplicity, only the 6-311 + G(d)-B3LYP/BP86 calculations are carried out for other systems due to the limited computational resources and extremely expensive CPU-cost CCSD(T) calculations for such large systems.

Let us consider the possible synthetic reactions $\text{CpM} + \text{Li}_3\text{Al}_4^- \rightarrow [\text{CpM}(\text{Li}_3\text{Al}_4)]^-$, which have sufficient exothermicity for alkali-metals, *i.e.*, 26.22 (27.19), 24.87 (25.62) and 25.01 (25.62) kcal mol⁻¹ for Li, Na and K, respectively. So these reactions are thermodynamically feasible for alkali-

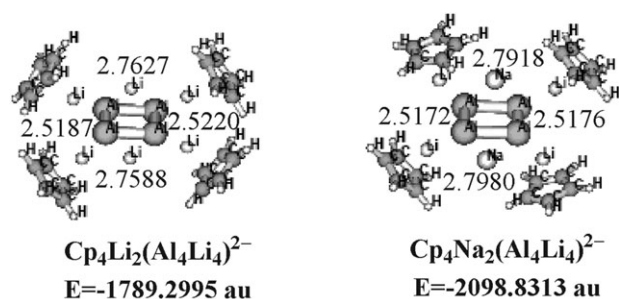


Fig. 2 Illustrative structures of $[\text{Cp}_4(\text{Al}_4\text{Li}_4)\text{M}_2]^{2-}$ ($\text{M} = \text{Li}$ and Na) obtained at the B3LYP/6-31 + G(d) level. For clarity, the Al–Al bond lengths of Al_4 -ring are presented in blue color.

metals. Here, we propose a possible synthetic route for our designed hetero-decked sandwich-type compounds, *i.e.*, add some reagents half-sandwich alkali-metal metallocenes CpM into the laser vaporization supersonic cluster source (that used to prepare Li_3Al_4^- cluster, then detected by photoelectron spectroscopy) for co-vaporization by direct laser ablation. Experimentalists can study the produced examples with a tandem (time-of-flight) TOF mass spectrometer experiment.

The BP86/6-311 + G(d) results (in ()) are comparable with those of B3LYP/6-311 + G(d), thus, for the simplicity and clarity, we only use the B3LYP results to discuss various properties (*e.g.*, geometry parameters, NBO charges, *etc.*) in the following sections.

As an extension of the present investigation, we also study the possibility of the extended antiaromatic compounds at the B3LYP/6-31 + G(d) level. Two illustrative low-lying structures are shown in Fig. 2.

From the geometrical parameters of Al_4 -ring in Fig. 1 and 2, we can see that the planarity and rectangular shape are well-retained in the cluster-assembled compounds. The short Al–Al

bonds range from 2.4779 to 2.6734 Å, the long Al–Al bonds range from 2.5937 to 2.7997 Å in the rectangular Al_4 -ring (see Fig. 1 and 2). The bond lengths of Al–Al bonds in the Al_4 -rings in the cluster-assembled compounds (see Fig. 1a–i) are comparable to that of the free clusters Li_3Al_4^- and Li_4Al_4 (see Fig. 1j).

Additionally, we perform detailed NBO¹⁰ analysis. The NPA charges of Al_4 -ring range from -2.010 to $-3.087|e|$ in $[\text{CpM}(\text{Li}_3\text{Al}_4)]^{q-}$ as that of Al_4 -ring in the free Li_3Al_4^- and Al_4Li_4 . (The NPA charges of Al_4 -ring range from $-2.987|e|$ in Al_4Li_4 (C_{2h}) to $-2.937|e|$ in Li_3Al_4^- (C_s)). The NPA charges on the metal M range from $+0.715$ to $+0.830|e|$, from $+0.727$ to $+0.859|e|$, from $+0.777$ to $+0.931|e|$, from $+0.651$ to $+1.108|e|$, from $+0.981$ to $+1.384|e|$, from $+1.352$ to $+1.668|e|$ in $[\text{CpM}(\text{Li}_3\text{Al}_4)]^{q-}$ for $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Be}, \text{Mg}, \text{Ca}$, respectively. The NPA charges of alkali/alkali-earth metal atoms are slightly lower than ionic limit of $+1$ and $+2$, respectively. The NPA charges on the Cp-fragment range from -0.773 to $-0.962|e|$, which is slightly lower than ionic limit of -1 . But those are qualitatively consistent with the formal charges. For $\text{M} = \text{Be}$, the departure is slightly larger due to its large covalent property. The NPA charges on the fragments $\text{M}(\text{Li}_3\text{Al}_4)$ (see “C(1)” in Fig. 1a–f) range from -0.118 to $-0.139|e|$, from -0.070 to $-0.135|e|$, from -0.038 to $-0.131|e|$, from 0.773 to $0.832|e|$, from 0.798 to $0.849|e|$, from 0.820 to $0.864|e|$ in model $[\text{CpM}(\text{Li}_3\text{Al}_4)]^{q-}$ for $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Be}, \text{Mg}, \text{Ca}$, respectively. For the saturated $(\text{Li}^+)[\text{CpM}(\text{Li}_3\text{Al}_4)]^-$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$), the NPA charges on the fragments $\text{M}(\text{Li}_3\text{Al}_4)$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) (see “C(1)” in Fig. 1g–i) are 0.910 , 0.923 and $0.931|e|$, for $\text{M} = \text{Li}, \text{Na}$ and K , respectively. We can see that the counterions alkali-metals saturated $\text{Li}_3\text{Al}_4\text{M}$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) bear almost no charges or slightly negative charges, and the alkali-earth metals saturated $\text{Li}_3\text{Al}_4\text{M}$ ($\text{M} = \text{Be}, \text{Mg}, \text{Ca}$) bear about one positive charges.

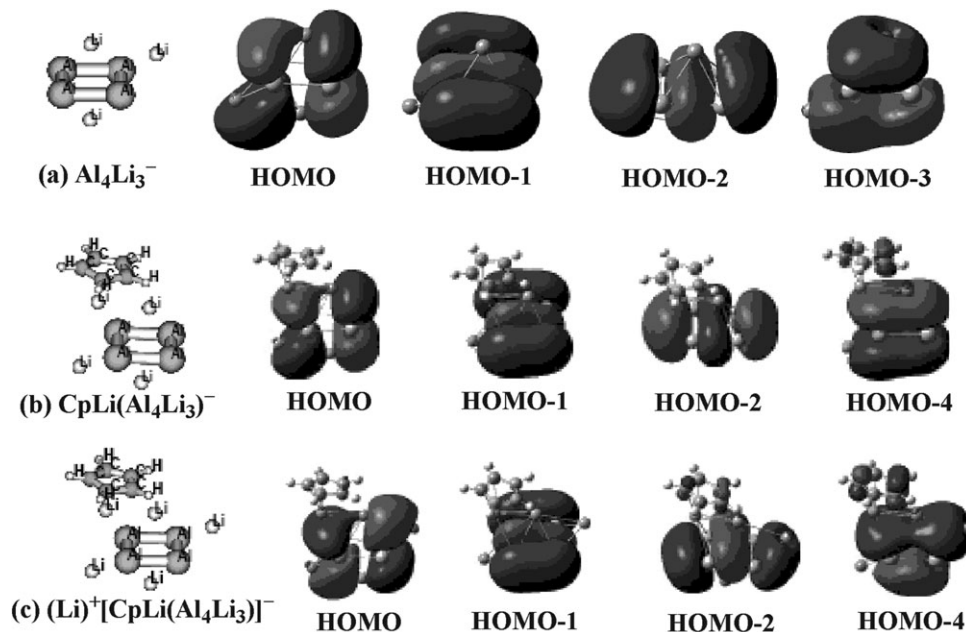


Fig. 3 Characteristic orbitals of (a) Li_3Al_4^- ; (b) the model compound $\text{CpLi}(\text{Li}_3\text{Al}_4)^-$; (c) the lowest-lying saturated cluster-assembled compound $(\text{Li}^+)[\text{CpLi}(\text{Li}_3\text{Al}_4)]^-$ obtained at B3LYP/6-311 + G(d) level.

Such phenomena are consistent with the formal charges and atomic number. In summary, the NBO analysis demonstrated that the positive and negative charges are dominant position at the M-atom and Cp unit, respectively, indicative of the major molecular formula $(\text{Cp}^-)\text{M}^{q+}(\text{Li}_3\text{Al}_4^-)$. Note that the departure to the formula $(\text{Cp}^-)\text{M}^{q+}(\text{Li}_3\text{Al}_4^-)$ is slightly larger for $\text{M} = \text{Be}$ due to its large covalent property.

In general, the characteristic orbitals¹¹ of the all-metal antiaromatic unit Li_3Al_4^- are well maintained during cluster assembly, for example, the model and saturated hetero-decked sandwich forms $[\text{CpLi}(\text{Li}_3\text{Al}_4)]^-$ and $(\text{Li}^+)[\text{CpLi}(\text{Li}_3\text{Al}_4)]^-$. Fig. 3 illustrates the selected characteristic orbitals of $[\text{CpLi}(\text{Li}_3\text{Al}_4)]^-$ and $(\text{Li}^+)[\text{CpLi}(\text{Li}_3\text{Al}_4)]^-$ as well as the comparative free clusters Li_3Al_4^- . The two delocalized σ -bonding MOs (HOMO-1 and HOMO-2) in Al_4^{4-} also give it characteristic of σ -aromaticity. The π HOMO of Al_4^{4-} is bonding within the two shorter Al–Al bonds but is antibonding between the two pairs of Al atoms, resulting in the rectangular shape and antiaromatic character of Al_4^{4-} . The HOMO-3 (in naked Al_4Li_3^-) and HOMO-4 (in cluster-assembled $\text{CpLi}(\text{Al}_4\text{Li}_3)^-$ and $(\text{Li}^+)[\text{CpLi}(\text{Al}_4\text{Li}_3)]^-$) are the completely delocalized π molecular orbital. From Fig. 3, we can see that the four characteristic orbitals in the free Li_3Al_4^- are well retained in the cluster-assembled compounds.

From the above analyses and discussions, the all-metal antiaromatic Li_3Al_4^- could indeed act as a new type of building block and inorganic ligand in the cluster-assembled molecular compounds. To our knowledge, this is the first time to **realize** the all-metal antiaromatic Li_3Al_4^- as a building block or inorganic ligand with **almost intact antiaromaticity** in the cluster-assembled compounds.

4. Conclusions

In summary, we have predicted by DFT a new class of all-metal antiaromatic cluster-assembled complexes $[\text{CpM}(\text{Li}_3\text{Al}_4)]^{q-}$, in which the antiaromaticity of Li_3Al_4^- is well retained as that of the naked Li_3Al_4^- . The results could be applicable to other gas-phase antiaromatic or conflicting aromatic units $\text{Na}^+\text{Pn}_4^{2-}$ ($\text{Pn} = \text{P}, \text{As}, \text{Sb}$), $\text{M}_x\text{Al}_4^{q-}$ ($\text{M} = \text{Na}, \text{K}, q = 0, x = 4; q = 1, x = 3$), $\text{B}_5^-, \text{B}_6^-, \text{B}_{14}, \text{B}_{15}, \text{AlSi}_2^-, \text{AlSiGe}^-, \text{AlGe}_2^-$ and other main-group metals, *e.g.*, higher alkali- (Rb, Cs), alkali-earth (Sr, Ba) by the effective and powerful “hetero-decked sandwich” scheme. Compared to the traditional metallocenes with all-organic aromatic Cp^- decks, our designed $\text{CpM}(\text{Li}_3\text{Al}_4)^{q-}$ represents a new class of metallocenes containing the all-metal antiaromatic Li_3Al_4^- units. Moreover, during the hetero-decked sandwiching process, the electronic, structural, and antiaromatic properties of Li_3Al_4^- are well kept. This indicates that when assisted by a rigid partner like Cp^- , the all-metal antiaromatic Li_3Al_4^- unit might be a new example of building block and inorganic ligand as the numerous aromatic units. Realization of the all-metal antiaromatic Li_3Al_4^- -incorporated compounds is very promising. The $\text{CpM}(\text{Li}_3\text{Al}_4)^{q-}$ complex series proposed in this work are expected to be synthesized in gaseous phases in future experiments (*e.g.*, photoelectron spectroscopy, *etc*) to open a new branch of chemistry on the all-metal antiaromatic complexes. Hopefully, this work should improve the insight

and cognition on the nature and origin of the chemistry of all-metal antiaromaticity. Such information is also important in designing and understanding various hitherto unknown assembled antiaromatic compounds. A large body of hitherto unknown chemistry of antiaromaticity/conflicting aromaticity will be foreseen.

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