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Theoretical Study on a Class of Organometallic Complexes Based on All-Metal Aromatic Ga_3^- Through Sandwiching Stabilization

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We report the theoretical study on a class of organometallic complexes containing the all-metal aromatic unit Ga_3^- on the basis of density functional theory calculations on a series of model sandwich-like compounds $[DM(Ga_3)]^{q-}$ as well as those of the saturated compounds $[DM_n(Ga_3)]$ [D = Ga_3^-, Cp^- ($C_5H_5^-$); M = Li, Na, K, Be, Mg, Ca] and extended compounds $(Cp^-)_m(Li^+)_n(Ga_3^-)_o$ (m, n, and o are integers). For the six metals, the all-metal aromatic Ga_3^- can only be assembled and stabilized in the "*heterodecked sandwich*" scheme (e.g. $[CpM(Ga_3)]^{q-}$) so as to avoid cluster fusion. Moreover, we designed a novel class of all-metal aromatic "metalloid" compounds. The ground state heterodecked sandwich species $(Cp)^-(M)^{q+}(Ga_3)^-$ (M = Li, Na, K, q = 1; M = Be, Mg, Ca, q = 2) and the extended sandwich species $(Cp^-)_m(Li^+)_n(Ga_3^-)_o$ are mainly ionic bonded, cluster-assembled "polyatomic molecule", grown from the combination of Cp^-, M atoms, and Ga_3^-. As a prototype for ionic bonding involving intact Ga_3^- subunits, $[CpM(Ga_3)]^{q-}$ may be a stepping stone toward forming ionic, cluster-assembled all-metal aromatic Ga_3-based bulk solids or materials. Additionally, our results for the first time showed that the electronic, structural, and aromatic properties of the all-metal aromatic Ga_3^- could be well retained during cluster assembly, which is indicative of "building block" character. Bearing the significant difference in bonding patterns between our designed metalloid compounds and the known metalloid species, synthesis of these novel species might present an attractive challenge to experimental chemists.

Introduction

Great interest has been focused in recent years on the study of the structure and electronic properties of small metal clusters[1] because they are often considered to be the bridges between isolated atoms and bulk matter, and they have fascinating chemical and physical properties. The group 13 elements are among the key building blocks for modern III–V semiconductor diode lasers. The Ga_n clusters are considerably important in thin-film deposition and for thin-layer growth in the deposition of multilayer structures.

In contrast, the recently discovered all-metal aromatic clusters[2] have triggered a revolution in the aromaticity and cluster realm. Because of their interesting chemical structures, bonding properties, and potential application in material science, it is no surprise that the all-metal aromatic species have received very extensive attention in various aspects.[2c,2d] The ultimate goal of the all-metal aromaticity studies may be to design novel 1D, 2D, and 3D cluster-assembled materials. In the all-metal aromatic family, aromatic gallium clusters have attracted special attention due to their fundamental importance and wide applications in material science and industry.

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Currently, in the study of molecular capsules, the stabilization of reactive species and reactions of encapsulated guests are areas of great interest as possible methods for drug delivery and for use as molecular reaction vessels.[3] Up to now, some experimental and theoretical efforts have been reported towards the synthesis and characterization of the ligand-stabilized organometallic gallium[4] complexes containing aromatic Ga_3^{2-}[4d,4e] and-Ga_4^{2-}[4h,4i] units.

However, we are aware that traditional organometallic gallium complexes (Ga_mR_n)[4] and metalloid gallium clusters (Ga_xL_y)[5] are usually stabilized by ligands that are connected to Ga atoms through M–L bonds. In such M–L bonds, the ligands provide unpaired electrons to form covalent bonds with Ga atoms or donate the lone pairs of electrons to Ga atoms to form donor–acceptor bonds. Moreover, the ligands constitute a protecting shell from the cluster cores. A key issue is that the structural and electronic properties of the naked cluster cores are perturbed by the connected ligands in Ga_xL_y and Ga_mR_n. Thus, the metalloid clusters are quite different from the naked clusters in the physical properties. There is no unequivocal and specific relationship between the naked cores and the corresponding metalloid clusters. So, it is difficult or even impossible to predict the properties of the metalloid clusters from the naked clusters. Inheriting good properties from parents to children is quite crucial during the Darwinian evolution process.[6] If the property-inheritable scheme

could be introduced into cluster assembly, interesting phenomena will be presented.

The all-metal aromatic Ga_3^-[2c,7] (D_{3h}) cluster forms the focus of our study due to its special particularity in the gallium cluster family. It is one of the simplest all-metal aromatic gallium clusters. Herein, we explore the bottom-up growth of relatively simple Ga_3^-, which is an ideal candidate and a nice example for novel organometallic molecular complexes and metalloid compounds due to its unique properties (i.e., high symmetry, aromaticity, three-membered ring, and simplicity). Here we considered an important strategy: "sandwiching", which is probably the most powerful one for assembly and growth of a stable unit [e.g., $C_5H_5^-$ (Cp^-)] into molecular materials and has led to rich chemistry of metallocene (CpMCp).[8] By investigating the structures and stabilities of a series of compounds $[DM(Ga_3)]^{q-}$ (D = Ga_3^-, Cp^-; M = Li, Na, K, Be, Mg, Ca) at the B3LYP/6-31+G(d) level, we found that Ga_3^- cannot be stabilized in the traditional "homodecked sandwich" form like $Ga_3MGa_3^{q-}$ both thermodynamically and kinetically. Instead, we applied the "heterodecked sandwich"[9] to assemble Ga_3^- in the form of $CpMGa_3^{q-}$ as well as the extended species –$CpMGa_3M$···Cp–. Moreover, we for the first time showed that when assisted by a rigid partner like Cp^-, the all-metal aromatic unit Ga_3^- possesses the building block feature. The already existent aromatic organometallic gallium complexes $M_2[(Mes_2C_6H_3)Ga]_3$ (M = Na, K; Mes = 2,4,6-$Me_3C_6H_2$),[4d,4e] $K_2[Ga_4R_2]$ [R = $C_6H_3(C_6H_2$-2,4,6-iPr$_3$)],[4h,4i] and aromatic cyclotrigermanium complex $R_3Ge_3^+$ [R = (EtBu$_3$)$_3$],[10a,10b] containing planar aromatic Ga_3, Ga_4, and Ge_3 rings, and the recent synthesis of the aluminum-based cycloallane $Na_2[(2,6\text{-}Mes_2C_6H_3)Al]_3$,[10c] featuring the aromatic Al_3 ring, provide hope that many more compounds with all-metal aromatic gallium building blocks may be synthesized in the future. It is thus very promising to realize the cluster-assembled compounds based on the all-metal aromatic Ga_3^-.

Computational Methods

Initially, we fully optimized the geometries of the $[DM(Ga_3)]^{q-}$ (D = Ga_3^-, Cp^-; M = Li, Na, K, Be, Mg, Ca) isomers and some related interconversion transition states at the B3LYP/6-31+G(d) level. The hybrid B3LYP[11] functional, as implemented in Gaussian 03,[12] includes a mixture of Hartree–Fock exchange with density functional exchange correlation. After geometrical optimization, harmonic vibrational frequencies[13] were calculated at the same level to check whether the obtained structure is a true minimum point with all real frequencies, a first-order saddle point (transition state) with only one imaginary frequency, or high-order saddle points with many imaginary frequencies. Despite its widespread use, aromaticity is more a concept rather than a directly measurable quantity. Consequently, measurements of aromaticity rely on many diverse criteria.[14] Among them, the nucleus-independent chemical shift (NICS),[15a] based on the "absolute magnetic shielding" taken at the center of a ring compound, is widely used and has been proven to be accurate for ordinary cyclic carbon compounds.[15] Recently, the method has also been successfully used for inorganic cyclic aromatic compounds,[16] including the characterization of the so-called d-orbital aromaticity.[17] Thus, the NICS values were calculated also at the B3LYP/6-31+G(d) level of theory. A positive value of the NICS indicates that the molecule is antiaromatic; a negative value indicates the aromaticity of the molecule. The NICS calculated at the center of the square [NICS(0)] describes the σ aromaticity, and the NICS above 1 Å out of the square plane [NICS(1)] describes the π aromaticity of the molecule. All the calculations were performed with the Gaussian-03 program.[12]

Theoretical Results and Discussions

The detailed discussions are organized as follows. First, we discuss the assembly of the all-metal aromatic Ga_3^- in both "homodecked" and "heterodecked" sandwich schemes. Second, we perform detailed stabilities and NBO and NICS analyses on our designed all-metal aromatic sandwich-type compounds. Third, we discuss how the all-metal aromatic Ga_3^- grows in the extended sandwich-like structures. Forth, we design a novel class of all-metal aromatic "metalloid" compounds, which can be achieved from the embellishment and functionalization all-metal aromatic cluster Ga_3^-. Fifth, we perform a comparison of the intrinsic difference between our designed cluster-assembly gallium compounds and traditional organometallic gallium complexes, metalloid gallium clusters, and the analogues of aluminum.

Cooperation of Metal Atoms with Organic Aromatic Deck Cp^-($C_5H_5^-$) Can Effectively Separate and Protect the All-Metal Aromatic Ga_3^-

With the inspiration and influence of the traditional metallocenes [e.g., $FeCp_2$ and $Cr(Bz)_2$, etc], we firstly consider the feasibility of the assembly and stabilization of the all-metal aromatic cluster Ga_3^- into cluster-assembled compounds; we found it is less likely due to the fusion tendency in the traditional "homodecked" sandwich scheme. This is consistent with the assembly and stabilization of a series of all-metal aromatic clusters, for example, Al_3^-,[9f] Al_4^{2-},[9g] and $SiAl_3^-$.[9h] Because of the limited space in the main text, we do not list the negative results of the "homodecked" sandwich section.

The above fact told us that the all-metal aromatic Ga_3^- still cannot grow solely assisted by metal atoms in the "homodecked sandwich" form. Additional assistance and other stabilization factors are necessary in the growth of Ga_3^-. Here we show that an isolation wall like the rigid and organic aromatic deck Cp^- can cooperate with the all-metal aromatic-numbered Ga_3^- to sandwich the metal atoms M by avoiding fusion in the growth process. Various isomeric forms for each of the six main-group elements (M = Li, Na,

K, Be, Mg, and Ca) are searched. For simplicity, only the lower-lying structures are shown in Figure 1. Others can be found in the Supporting Information. For all the six metals (M = Li, Na, K, Be, Mg, Ca), there are two kinds of sandwich forms $\mathbf{1}^{q-}$(f–f) and $\mathbf{1}^{q-}$(f–c), which are associated with the "face (Cp^-)–face (Ga_3^-)" (f–f) and "face (Cp^-)–corner (Ga_3^-)" (f–c) types, respectively. The scheme described here is called "heterodecked sandwich".[9] In this way, the all-metal aromatic units Ga_3^- can be effectively separated and protected. The designed species $[CpM(Ga_3)]^{q-}$ belong to a new class of sandwich-like compounds, which are intuitively of special interest because they contain both the classic organic aromatic unit Cp^- and the novel all-metal aromatic unit Ga_3^-. Moreover, the reported sandwich-like compounds containing the three-membered rings are usually very rare.

Interestingly, the rigid organic aromatic Cp^- plays a double role (both electronic and steric) in the cluster-assembly molecular compounds. From the view point of steric effects, the Cp rings are essentially spacer groups, which can effectively separate, isolate, and protect the exotic all-metal aromatic Ga_3^-, so as to avoid fusing of the Ga_3^- clusters during cluster assembly. We can vividly call the Cp ring a "rigid organic aromatic isolated wall". In contrast, Cp rings are electron acceptors and receive electrons donated from the metal atoms to form the close-shell anion Cp^-, which

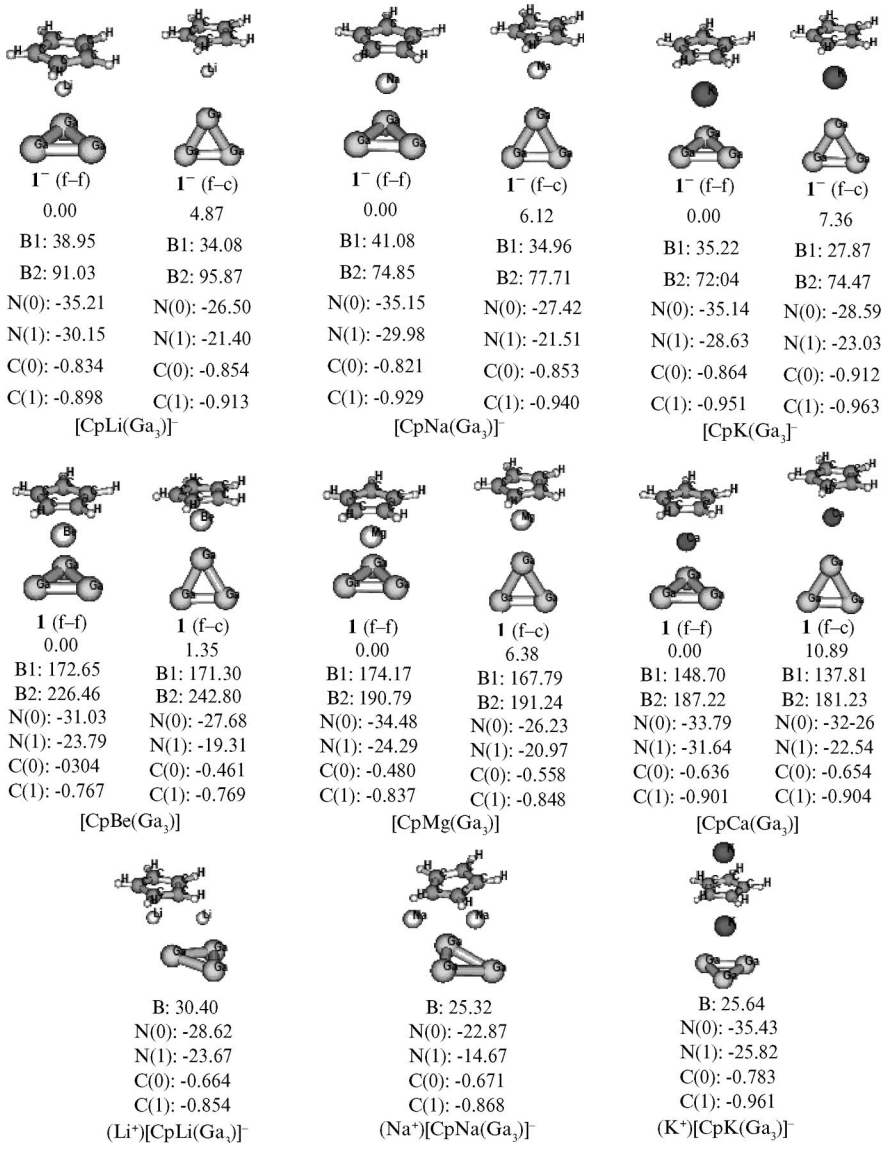
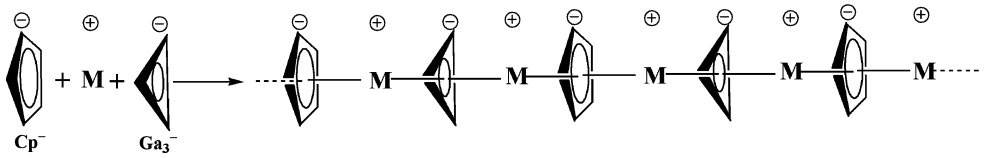


Figure 1. The low-lying sandwich forms of $[CpM(Ga_3)]^{q-}$ (M = Li, Na, K, q = 1; M = Be, Mg, Ca, q = 0) and the lowest-energy saturated sandwich forms of $(M^+)[CpM(Ga_3)]^-$ (M = Li, Na, K) obtained at the B3LYP/6-31+G(d) level. Energy values are in kcal mol^{-1}. "B(1)" denotes the binding energies between Ga_3^- and CpM^{q+}, "B(2)" denotes the binding energies between Cp^- and $M(Ga_3)^{q+}$ (M = Li, Na, K, q = 0; M = Be, Mg, Ca, q = 1). "N(0) and N(1)" denote the nucleus-independent chemical shift (NICS) at the ring center and 1 Å above the ring of Ga_3^-, respectively. "C(0)" and "C(1)" denote the natural charge distributions on the Ga_3 and Cp fragments, respectively. "B" denotes the binding energies between CpM and $M(Ga_3)$ in the saturated sandwich species (M = Li, Na, and K).



Scheme 1. The illustrative polymer structure of the heterodecked sandwich-type complexes with Ga_3^-, M atoms, and Cp^- in alternating positions in the array.

interacts with the metal atoms through electrostatic or ionic interactions. The fragments (Cp^-), (M^{q+}), and (Ga_3^-) form sandwich compounds $[CpM(Ga_3)]^{q-}$ by ionic interactions. Such interaction forms (Cp^-)–(M^{q+})–(Ga_3^-) (anions and cations alternate through electrostatic interaction) can develop into highly extended 3D sandwich-like species, for example, oligomers or polymers, which is a common phenomenon for the metallocenes of the main-group elements, especially for alkali and alkali-earth metallocenes a long time ago.[18]

Interestingly, among all the designed heterodecked sandwich species, the all-metal aromatic Ga_3^- generally prefers to use its face (Ga_3 plane) or corner (Ga atom) site to interact with the partner deck Cp^-. Moreover, among all the calculated $[CpM(Ga_3)]^{q-}$ systems, the planar Cp^- structure is well maintained, indicative of the unique "rigidity" of this organic unit. Fusion of the Cp^- and Ga_3^- decks to form new C–Ga or C–M bonds is energetically unfavorable. This indicates that Ga_3^- can be viewed as a building block. The Ga_3^- units can grow into dimers, trimers, oligomers, and even polymers by heterodecked packing through M atoms lying between Cp^- and Ga_3^-. The Ga_3^- units, M atoms and Cp^- moieties alternate positions in the array (Scheme 1), and this is an ideal arrangement that should be used in the design of more complex compounds based on the all-metal aromatic Ga_3^-. An illustrative structure is presented in Scheme 1.

Detailed Stabilities and NBO and NICS Analyses on Our Designed All-Metal Aromatic Sandwich-Type Compounds

From Figure 1, we can see that the strength of the Cp–$M(Ga_3)$ bonds (noted as "B2" in Figure 1) range from 72 to 243 kcal mol^{-1}, and the strength of the CpM–(Ga_3) bonds (noted as "B1" in Figure 1) range from 28 to 174 kcal mol^{-1} in the heterodecked sandwich-type complexes $[CpM(Ga_3)]^{q-}$. Thus, the binding energies of Cp ring to the metal atoms are larger than that of (Ga_3) ring to metal atoms; the Cp–$M(Ga_3)$ bonds are stronger than the CpM–(Ga_3) bonds in the heterodecked sandwich species. Such phenomena are mainly ascribed to the high stability and high aromaticity of the closed-shell organic Cp^- rigid deck, which leads to the fact that the stability of the $[Cp^- + M(Ga_3)^{q+}]$ dissociation fragments is higher than that of the (CpM^{q+} + Ga_3^-) dissociation fragments. In summary, the two kinds of ionic electrostatic interactions, [Cp–$M(Ga_3)$ and CpM–(Ga_3)], connect the two Cp^- and Ga_3^- decks by bridging metal atoms to form the heterodecked sandwich-type complexes Cp–M–(Ga_3).

In order to obtain insight into the interactions of our designed heterodecked sandwich-type complexes, we performed detailed NBO[19] analysis. The NBO analysis demonstrate that our designed sandwich-type compounds can be view as an ionic molecule comprising (Cp^-)(M^{q+})(Ga_3^-) (M = Li, Na, K, q = 1; M = Be, Mg, Ca, q = 2). In the Ga_3-based alkali-metal heterodecked sandwich-like compounds $CpM(Ga_3)^-$ (M = Li, Na, and K), the NPA charges located on the Ga_3 ring, Cp ring, and alkali metals range from –0.821 to –0.912 |e|, from –0.898 to –0.963 |e|, and from 0.731 to 0.876 |e|, respectively. Thus, they are quite consistent with the formal (Cp^-)(M^+)(Ga_3^-) formulation. For the Ga_3-based alkali-earth-metal heterodecked sandwich-type complexes, the NPA charges located on the Ga_3 ring, Cp ring, and alkali-earth metals (M = Be, Mg, and Ca) range from –0.304 to –0.654 |e|, from –0.767 to –0.904 |e|, and from 1.072 to 1.599 |e|, respectively. The NPA charges located on the Be, Mg, and Ca atoms range from 1.072 to 1.230 |e|, from 1.317 to 1.406 |e|, and from 1.537 to 1.599 |e|, respectively, in the heterodecked sandwich-like compounds $CpM(Ga_3)$ (M = Be, Mg, and Ca). The NPA charges located on Ga_3 rings are lower than the ionic limit of –1, especially for $CpBe(Ga_3)$. The NPA charges located on the alkali-earth metals (M = Be, Mg, and Ca) are lower than the ionic limit of +2, especially for M = Be. However, they are qualitatively consistent with the formal (Cp^-)(M^{2+})-(Ga_3^-) formation. Through two electrostatic interactions, the CpM^{q+} and Ga_3^- fragments and the Cp^- and MGa_3^{q+} fragments are held together to form sandwich-like complexes (Cp^-–M^{q+}–Ga_3^-).

Aromaticity is an interesting property in the sandwich-type complexes. We thus investigated the aromaticity of our designed heterodecked sandwich-like complexes through NICS(0) and NICS(1). From Figure 1, we can see that the aromaticity ["N(0) and N(1)" values in Figure 1] of the Ga_3^- units within the assembled compounds is nearly –32.67 [N(0)] and –25.65 [N(1)] ppm in comparison to that of free Ga_3^-, which is suggestive of good aromaticity conservation in the cluster assembly. Thus, Ga_3^- could act as a new type of building block or inorganic ligand in cluster-assembled molecular compounds. To the best of our knowledge, this is the first time that an all-metal aromatic gallium cluster has been considered as a building block or inorganic ligand.

All-Metal Aromatic Ga_3^- Grows into Extended Sandwich-Like Structures

Can all-metal aromatic Ga_3^- form extended sandwich compounds? From the preceding discussions, we have confi-

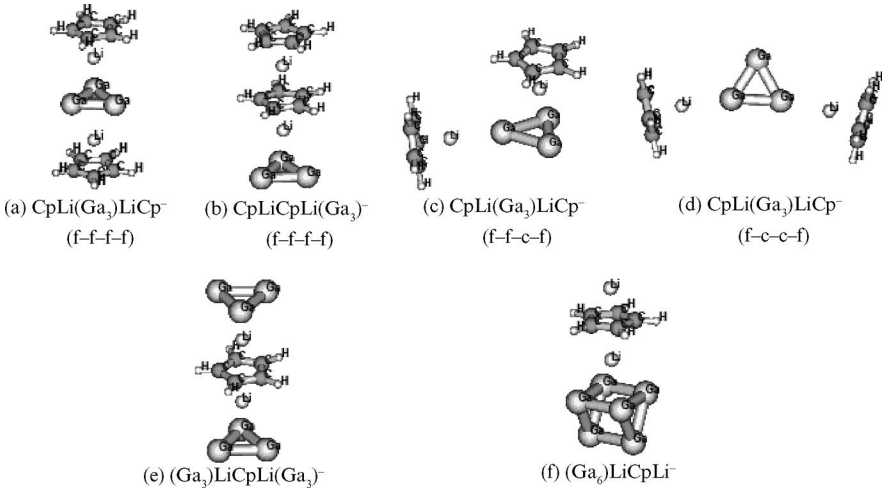


Figure 2. The illustrative structures of extended sandwich-type complexes $(CpLi)_2(Ga_3^-)$ and $(CpLi_2Ga_6)^-$ are obtained at the B3LYP/6-31+G(d) level. Energy values are in kcal mol^{-1}.

dence that the "heterodecked" sandwich scheme is an effective growth pattern for all-metal aromatic Ga_3^-. The high symmetry of Ga_3^- and the f–f and f–c interaction types render the "bottom-up" growth very promising! As an extension of the present study and to test for "bottom-up" growth, we designed Ga_3^--based extended systems containing more Cp^- and Ga_3^- units in various sandwich-like forms at the B3LYP/6-31+G(d) level. For simplicity, we use M = Li as an example, and only selected low-lying species are shown in Figure 2. Many other designed extended sandwich-like structures can be found in the Supporting Information. Firstly, $CpLiGa_3LiCp^-$ (Figure 2a) with a Cp^- terminus is more stable than its isomer $CpLiCpLiGa_3^-$ (Figure 2b) with a Ga_3^- terminus by 6.51 kcal mol^{-1}. The stability comes from the effective avoidance of fusion between the sandwiching decks due to the unique rigidity of Cp^-. Secondly, for compounds with one Cp^- and two Ga_3^- units, the fused structures $(Ga_6)MCpM^{q\pm}$ (Figure 2f) (M = Li, Na, K, q = –1; M = Be, Mg, Ca, q = +1) are energetically more stable than $(Ga_3)MCpM(Ga_3)^{q\pm}$ (Figure 2e) by 54.38, 52.43, 54.64, 43.30, 41.59, and 53.11 kcal mol^{-1}, for M = Li, Na, K, Be, Mg, and Ca, respectively. Moreover, in this type of $CpMGa_3MCp$ multiheterodecked sandwich form, the open–close process of the Ga_3^- deck should be greatly suppressed. We thus propose that the promising supermolecular chains are composed of $Cp(MGa_3MCp)_n$ units with a Cp^- terminus. In summary, we can easily see the atomic-level manipulation and assembly of all-metal aromatic Ga_3^-, as well as the isolation effects of Cp^-.

From Figures 1, 2, and 3, we can see that the structural and electronic integrity and the orbital features of the all-metal aromatic unit Ga_3^- are well maintained during the heterodecked sandwiching. Figure 3 illustrates the selected characteristic orbitals of double-decked sandwich-like compound $[CpLi(Ga_3)]^-$, triple-decked sandwich-like compound $[CpLi(Ga_3)LiCp]^-$, as well as the comparative species Ga_3^-. Figure 3 shows their two highest orbitals: the HOMO is a bonding σ orbital, which thus renders the σ aromaticity. The HOMO-1 is a bonding π orbital, which thus render the π aromaticity. From Figure 3 we can see that the shapes of the orbitals in (a) bare Ga_3^-, (b) double-decked sandwich-like compound $[CpLi(Ga_3)]^-$, and (c) triple-decked sandwich-like compound $[CpLi(Ga_3)LiCp]^-$ are generally the same. Thus, the all-metal aromatic unit Ga_3^- can maintain its electronic and structural integrity in sandwich forms. Also, the "double aromaticity" of Ga_3^- is well-conserved during cluster assembly. Therefore, Ga_3^- could be used as a robust building block to design cluster-assembled metalloaromatic organometallic molecular compounds.

A Novel Class of All-Metal Aromatic "Metalloid" Compounds Achieved from the Embellishment and Functionalization of All-metal Aromatic Cluster Ga_3^-

The above results call attention to the fundamental problem that effective isolation and sufficient protection are quite crucial in the assembly and stabilization of the all-

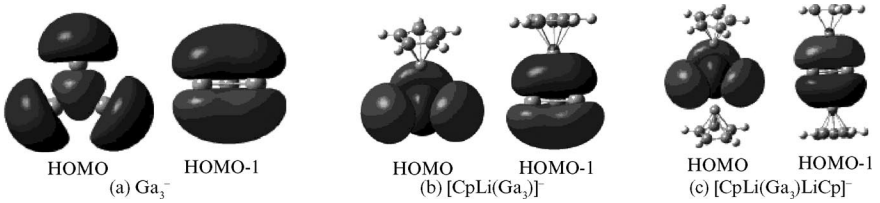


Figure 3. The characteristic orbitals of (a) Ga_3^-, (b) $[CpLi(Ga_3)]^-$, and (c) $[CpLi(Ga_3)LiCp]^-$ are obtained at the B3LYP/6-31+G(d) level.

metal aromatic clusters so as to avoid cluster fusion. From the prospective view of the potential applications, we discuss the isolation, protection, embellishment, and functionalization of all-metal aromatic Ga_3^- clusters. Generally, we considered two kinds of configurations of the all-metal aromatic "metalloid" compounds: the "rice-ball" and "cage" structures. Firstly, we designed the all-metal aromatic Ga_3^--based "metalloid" compounds at the B3LYP/6-31+G(d) level, and two representative structures are listed in Figure 4. Figure 4a is the "rice-ball" configuration $(Ga_3^-)(CpLi)_3$ with three dipoles LiCp [note that the NBO charges on the Li atom in LiCp is +0.909 |e| at the B3LYP/6-31+G(d) level; thus, LiCp could be viewed as a $^{\delta+}LiCp^{\delta-}$ dipole] connected to three corners of Ga_3^- in the three directions. If we added two LiCp dipoles in the directions of up and down of the Ga_3^- plane, then we could achieve a "cage" structure $(Ga_3^-)(CpLi)_5$ (Figure 4b), with five LiCp dipoles connected to five directions of Ga_3^-. If we want to more steric protections, we could change $Cp(C_5H_5)$ into $Cp^*(C_5Me_5)$, or use even more sterically hindered ligands. The binding energies between Ga_3^- and m(LiCp) are 84.01 and 138.56 kcal mol^{-1} for the rice-ball (m = 3) and cage (m = 5) structures, respectively. The average binding energy is about 28.00 kcal mol^{-1} for each LiCp unit. Such binding energies are indicative of sufficient and effective stability for the future synthesis of our designed all-metal aromatic "metalloid" compounds.

Figure 4. Illustrative structures of "metalloid" compounds $[(Ga_3^-)(LiCp)_m]$ (m = 3, 5) calculated at the B3LYP/6-31+G(d) level. Energy values are in kcal mol^{-1}.

Intrinsic Difference Between Our Designed Cluster-Assembly Gallium Compounds and Traditional Organometallic Gallium Complexes, Metalloid Gallium Clusters, and the Analogues of Aluminum

What is the difference between our designed "metalloid" compounds and the known organometallic complexes and metalloid clusters? How are the characteristics of our designed "metalloid" compounds distinguished from Robinson's cyclogallenes? In order to answer the above two questions and to obtain insight into the nature of our designed "metalloid" compounds, we made a detailed comparison of our designed "metalloid" compounds with the known metalloid clusters and organometallic complexes of group 13 (III).

We compare the designed all-metal aromatic Ga_3^--based "metalloid" compounds: $(Ga_3^-)(LiCp)_m$ (m = 1, 2, 3, 5) with their analogues: the aluminum-based cycloallane $Na_2[(2,6\text{-}Mes_2C_6H_3)Al]_3$ ($Na_2Al_3R_3$),[10c] the gallium-based cyclogallane $M_2[(Mes_2C_6H_3)Ga]_3$ ($M_2Ga_3R_3$) (M = Na, K; Mes = 2,4,6-$Me_3C_6H_2$),[4d,4e] $K_2[Ga_4R_2]$ [R = $C_6H_3(C_6H_2$-2,4,6-$iPr_3)$)],[4h] $Na_2[Ga_4R_4](thf)_2$ [R = Si(tBu)$_3$],[4g] $R_3Ge_3^+$ [R = (EtBu$_3$)$_3$].[10a,10b] The real differences between our designed all-metal aromatic "metalloid" compounds $(Ga_3^-)(LiCp)_m$ and the known metalloid clusters and organometallic complexes is that in $Ga_3R_3^{2-}$ there are two more occupied Ga–Ga σ-type orbitals than there are in Ga_3^-. Strictly speaking, the difference can be divided into the following aspects: (1) In metalloid organogallium compounds, the two alkali metals donate their two valence s electrons into the three empty gallium p orbitals to yield the Hückel-aromatic 2π-electron cyclogallene system. The cyclogallene rings in $M_2(Ga_3R_3)$ are valence isoelectronic to the cyclopropenium cation moiety in $(C_6H_5)_3C_3^+$, which is the smallest organic 2π-electron aromatic ring compound. Moreover, the known metalloid metal rings ($M_3R_3^{2-}$, $M_4R_2^{2-}$, and $M_4R_4^{2-}$, denoted $-M_3^{2-}-$ and $-M_4^{2-}-$) are stabilized by donation of electrons from the alkali-metal ions into the π orbital of the metal (aluminum/gallium) rings. (2) There are 2c–2e C–M (M = Al, Ga) covalent bonds formed in the metalloid clusters or organometallic complexes. However, there are mainly ionic interactions between the core Ga_3^- and the ligands LiCp in our designed "metalloid" compounds $(Ga_3^-)(LiCp)_m$. (3) The ligands are radicals with unpaired electrons located on the sp^2 hybrid carbon atoms in the benzene ring in the metalloid clusters or organometallic complexes. The ligands provide unpaired electrons in C atoms to pair with the unpaired electrons in M atoms to form covalent bonds. In stark contrast with this case, our ligands are closed-shell ionic dipole $^{\delta+}LiCp^{\delta-}$. The ligands and the cluster cores are connected by the ionic interactions rather than covalent interactions. (4) Generally, all-metal aromatic clusters are very reactive and their stabilization has to be gained through "steric stabilization" by using bulky substituents within the molecular skeleton [e.g., $-N(SiMe_3)_2$, $-C(SiMe_3)_3$, $-Si(SiMe_3)_3$, –Trip = 2,4,6-$iPr_3C_6H_2$, $-C_6H_3$-2,6 (C_6H_3-2,6-iPr_2)$_2$, $-C_6H_3$(2,4,6-$Me_3C_6H_2$)$_2$, etc]. Yet, their bulkiness might, in contrast, sterically block their further use as building units in cluster assembly. The present target core Ga_3^- is negatively charged throughout the entire all-metal aromatic clusters. The negative charges are evenly distributed over the peripheral three atoms, which suggests that each of the peripheral atoms is apt to react with outer reagents. Luckily, the "metalloid" scheme can effectively suppress the reactivity of the all-metal aromatic Ga_3^- core by introducing the LiCp ligands (Figures 1– 3). It is even possible that the reactivity of Ga_3^- can be completely suppressed by being fully "dressed" with five LiCp ligands (Figure 4b) in five directions. In this way, the all-metal aromatic Ga_3^- core is well captured into a "rice-ball" structure (Figure 4a) and a "cage" structure (Figure 4b). We call such an all-metal aromatic cluster-stabilization method as "metalloid-stabilization". The characteristics of the new method are: (1) the steric effect can easily be introduced by choosing suitable ligands/"dressers"

(e.g., change LiCp to LiCp* with all H-atoms substituted by methyl groups), (2) the neutral LiCp pairs can be facilely "undressed" by provide some additional energies under certain condition when we want to have Ga_3^- for further usage, and (3) the manipulation of aromaticity should be easy by simply capturing more all-metal aromatic core Ga_3^- units dressed with LiCp ligands.

Bearing the significant difference in bonding patterns between our designed metalloids and the known metalloid species, synthesis of these novel compounds might present an attractive challenge to experimental chemists. Yet, we are aware that various kinds of cluster-assembled compounds containing naked aromatic clusters have already been synthesized in crystals. The examples include $[Ti(P_5)]^{2-}$ with a naked aromatic P_5^- moiety,[20a] Na_8BaSn_6 and Na_8EuSn_6 with a Sn_5^{6-} moiety,[20b] $Li_{9-x}EuSn_{6+x}$, $Li_{9-x}CaSn_{6+x}$, $Li_5Ca_7Sn_{11}$, and $Li_6Eu_5Sn_9$ with a Sn_5^{6-} moiety,[20c] Na_4CaSn_6 with a Sn_6^{6-} moiety,[20d] Na_8BaPb_6 with a Pb_5^{6-} moiety,[20b] and $SrIn_4$ with an In_4^{2-} moiety.[20e] The recent solution synthesis of $Au_{20}(PPh_3)_8$[20f] even contains the huge aromatic tetrahedral Au_{20}.[20g] These compounds provide hope that many more compounds with aromatic building blocks may be synthesized in the future. Thus, we expect that our designed novel heterodecked sandwiching metalloid compounds might be synthesized through suitable synthetic technologies under appropriate conditions in future experiments.

Conclusions

The present study described an attempt to assemble and stabilize the all-metal aromatic unit Ga_3^- into assembled molecular systems in sandwich-like forms. Moreover, we designed a class of all-metal aromatic "metalloid" compounds, which is quite different from the traditional organometallic compounds and metalloid clusters of group 13 (III). The intrinsic difference between our designed cluster-assembled complexes with the traditional organometallic compounds and metalloid clusters were evaluated in detail. The growth pattern of all-metal aromatic Ga_3^- is apt to take the face–face (f–f) and face–corner (f–c) interaction forms, which are favorable in avoiding cluster fusion under the isolation effects. The designed species await future experimental verification (e.g., anion photoelectron spectroscopy and solution synthesis). Current studies suggest that it is possible to synthesize "cluster-salt crystals" of our predicted Ga_3^--based species. Such assembly procedures could also be applied to many other all-metal aromatic molecules [X_4^{2-} (X = Ga, In, Tl), X_3^- (X = In, Tl)] and other metal aromatic, mixed clusters, stable clusters [$AlSi_3B$, CAl_3Ge, CAl_3Ge^-, CSi_2X_2 (X = Al, Ga), and CGe_2Al_2]. In comparison to the traditional metallocenes with mere Cp^- decks, our designed complexes represent a new class of metallocene containing the all-metal aromatic Ga_3^- unit, among which Ga_3^- generally prefers to use its face (Ga_3 plane) or corner (Ga atom) to interact with the partner deck besides the traditional face–face interaction type for the known decks Cp^-, P_5^-, Al_4^{2-}, and N_4^{2-}. Moreover, the structural and electronic integrity of Ga_3^- are generally well kept during the heterodecked sandwiching. Thus, Ga_3^- could act as a new type of "building block". To the best of our knowledge, this is the first time that a metalloaromatic ring, that is, a ring solely composed of heavy main group metals, gallium cluster is proposed as a building block. Future studies on the building block and inorganic ligand chemistry of Ga_3^- are desired.

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