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How can carbon favor the planar multi-coordination in boron-based clusters? Global structures of $CB_xE_y^{2-}$ (E=Al, Ga, x+y=4)

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Abstract: With the high preference in forming multi-center bonding, boron has been a miracle ligand in constructing diverse planar multi-coordinate (tetra/hyper) (pM) species. Unfortunately, the boron ligand usually dislikes to encompass a pM carbon (pMC) due to the high competition of pM boron (pMB), which makes the realization of boron-based pMC very difficult and quite challenging. Here we propose a strategy that by means of the cooperative doping and charge-compensation, we can successfully improve and tune the stability of pMC relative to pMB for CB_4^{2-}. In the free $CB_xE_y^{2-}$ (E=Al/Ga) species, ptC is thermodynamically less stable than the global ptB in mono- and di-substituted systems, in agreement with the results of Boldyrev and Wang. Yet, the thermodynamic preference of the pMC increases along with the Al/Ga-doping. The pMC species can be further stabilized by the introduction of the alkaline-earth counterion (Mg^{2+}). The CB_2E_2Mg (E=Al, Ga) designed in the present work represents the first successful design of the boron-based planar pentacoordinate carbon (ppC) structures as the global minima. The strategy proposed in this work should be useful in the manipulation of the competition between the exotic pMC and pMB in B-based systems.

Keywords: planar carbon, thermodynamic stability, boron, computational chemistry, global minimum

1. Introduction

Boron and carbon, which are the neighbors in the same row of the periodic table, are two important elements in the field of two-dimensional (2D) materials and planar science. Recent combined experimental and theoretical studies on planar and quasi-planar boron cluster of B_{30}^{-}, B_{32}^{-}, B_{35}, B_{36} and B_{40}^{-} have pushed the limits of the number of boron atoms and further exhibited the capability of planar multi-coordinate (tetra/hyper) (pM) bonding of boron arising from its nature of electron deficiency.[1-6] Being able to form both the strongly localized bonding and the delocalized σ/π bonding, boron is intrinsically suitable for constructing a rich family of ring systems encompassing one or more multi-coordinate centers, including transition metal,[7] heavier group,[8] alkaline earth metal[9] and boron itself.[10] Notably, $Co@B_8^{-}$,[11] $M@B_9^{-}$ (M=Ru, Rh, Ir)[12] and $M@B_{10}^{-}$ (M=Nb, Ta)[13] have been found to be the *global minima* and have been experimentally characterized.

To date plenty of works have been devoted to the design and characterization of novel planar multi-coordinate carbon (pMC) clusters, nanostructure and extended systems containing the pMC centers[14] ever since the first proposal of the anti-van't Hoff and LeBel concept.[15] Most of these species contain the boron rings. Despite their structural beauty, they have constantly broadened the coordinative capability of carbon and greatly widened human being's imagination in molecular architecture.[16] Yet, somewhat awkwardly, these species generally do not constitute the global minima on the corresponding potential energy surface, which is disadvantageous for the gas-phase experimental characterization. In fact, only two boron-related examples CB_4^{+} and $CBAl_3^{2-}$ possess the global planar tetracoordinate carbon.[17, 18] The reason that carbon disfavors the planar central position in the boron-based species could be interpreted that carbon with higher electronegativity than boron prefers to participate in localized 2c-2e σ-bonding.[16]

Can we diminish the pMB competition relative to pMC in boron-based clusters? We are aware that in Al-based clusters, the ptC structure can easily be achieved and retained, e.g., CAl_4^{2-}, CAl_4^{-}, $CSiAl_3^{-}$, $CGeAl_3^{-}$, $Na^+CAl_4^{2-}$)[19], planar pentacoordinate carbon (ppC) (CAl_5^{+}, CAl_4Be, $CAl_2Be_3^{2-}$)[20], double ptC (C_2Al_4)[21] and star-like species $C_5Al_5^{-}$.[22] Moreover, a single Al-substitution can promote the non-planarity→planarity change (i.e., $B_7^{-}/B_{12}^{-} \rightarrow AlB_6^{-}/AlB_{11}^{-}$) by slightly expanding the size of the outer boron rings to minimize the non-planarity factor (mechanical).[23] Therefore, it is our expectation that Al-doping in boron-based clusters can help promote the thermodynamic preference of pMC over pMB. In this work, we present a theoretical investigation on tuning the "pMC vs pMB competition" by the Al/Ga doping to CB_4^{2-}, whose ptC structure satisfies the "18-electron" count.[24] In the target $CB_xE_y^{2-}$ (E=Al, Ga; x+y=4), the thermodynamic competition of pMC relative to pMB can be significantly promoted to even be the global minimum along with the Al/Ga-doping. Further inclusion of the alkali-earth counterions stabilizes the pMC structure, and gratifyingly, prompts not only the coordination of planar carbon center to enlarge from four to five, but also a set of ppCs is characterized as global minima in mono- and di-substituted $CB_xE_y^{2-}$ species, i.e., CB_3EMg and CB_2E_2Mg. The high stability of these salt-stabilized global ppCs was further confirmed by the Born-Oppenheimer molecular dynamics (BOMD) simulations, showing their high accessibility in future experimental study.

2. Computational Methods

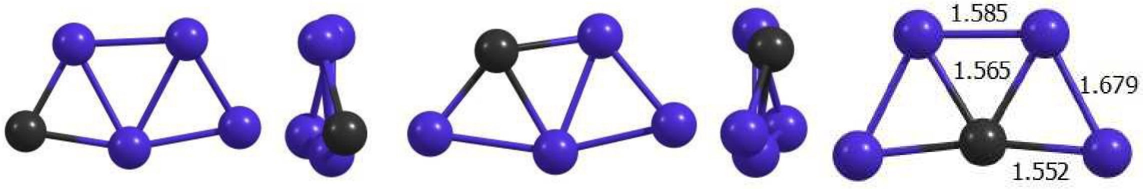
In order to explore systematically the potential energy surfaces (PESs) of the free and salt-stabilized $CB_xAl_y^{2-}$ and $CB_xGa_y^{2-}$ species, the grid-based comprehensive isomeric search strategies were initially calculated at the B3LYP/6-31G(d) level.[25] All isomers were refined with followup frequency calculations at the B3LYP[26]/6-311+G(d) level. For low-lying isomers, we employed the B3LYP/aug-cc-pVTZ basis set for better geometrical and frequency prediction. Using these geometries, the final single-point energies of the low-lying isomers were calculated at the CCSD(T)[27]/aug-cc-pVTZ level. The T1 values were computed to check the accuracy of the mono-determinantal B3LYP and CCSD(T).[28] We found that T1 values are in a range of 0.017 to 0.030 for the low-lying isomers of all the free and salt-stabilized systems except for CB_4^{2-} (above 0.05, see Table S1). The unrestricted B3LYP based on the broken-symmetry (BS) approach[29] was performed for CB_4^{2-} to get geometries, and their energies were corrected by the MCQDPT2 method[30] using the converged CASSCF(18e,13o) wavefunctions with 18 active electrons and 13 active orbitals, where full valence space of carbon and boron atoms and four virtual orbitals were chosen in the active space (4 electrons per C atom and 3 electron per B atom). The conventional intruder-state avoidance technique (ISA) was used with a shift of 0.02 au in these calculations. All calculations above were carried out with GAUSSIAN09 program packages[31] except for the multi-reference calculations carried out with Firefly program suite (version 8.1.0).[32]

3. Results and Discussions

Numerous isomers were obtained by the grid-based comprehensive isomeric search strategies. The structures of low-lying isomers (within around 10 kcal/mol relative to global minimum) were refined at the B3LYP/aug-cc-pVTZ level. In our discussions, "**y-Al-m**" and "**y-Ga-m**" refer to the isomer **m** for the free system $CB_xAl_y^{2-}$ and $CB_xGa_y^{2-}$, respectively, while "**y-AlM-m** and **y-GaM-m**" refer to the isomer **m** for the fully saturated $CB_xAl_y^{2-}$ and $CB_xGa_y^{2-}$ by the counterions Mg^{2+} (y is the number of Al/Ga atoms). Fully optimized low-lying geometries were provided in the Supporting Information (SI). We used the single-point CCSD(T)//B3LYP/aug-cc-pVTZ+ΔZPE_{B3LYP} level (including the zero-point energy (ZPE) corrections) energies for further discussion. Since the triplet isomer of the free and salt-stabilized $CB_xAl_y^{2-}$ and $CB_xGa_y^{2-}$ species are less stable than the corresponding singlet ones, the triplet structures will not be discussed here.

3.1 Parent CB_4^{2-}

To maintain a perfect planar multi-coordinate (pM) structure, there should be a nice matching between the "electronic" and "mechanical" factors. For small clusters, a useful electron-counting rule, i.e., "18 electron rule", have been established for stabilization of pMC structures.[24] One well-known molecule of this series is CAl_4^{2-} and its salt-stabilized CAl_4Na^{-}.[19d] To our surprise, though also belonging to the 18e system, the binary CB_4^{2-} species has not received previous attention. We found that for CB_4^{2-}, the ptC structure **0-3**$^{2-}$ with C_{2v} symmetry was a genuine minimum, yet it bears the multi-reference character. Using the UB3LYP/aug-cc-pVTZ geometry obtained via the broken-symmetry strategy, the multi-reference MCQDPT2/CAS(18e,13o)/aug-cc-pVTZ calculations showed that **0-3**$^{2-}$ lies 22.4 and 2.3 kcal/mol above the di-coordinate carbon **0-1**$^{2-}$ and tri-coordinate carbon **0-2**$^{2-}$ isomers, respectively (see Figure 1). Thus, in the parent CB_4^{2-}, ptC is not the global isomer and quasi-ptB is energetically superior to ptC. This is well consistent with the results of Boldyrev and Wang on a series of C-B systems (i.e., CB_6^-, $C_2B_5^-$, CB_7^-, and CB_8^-)^{16} that the higher electronegativity of carbon compared to boron disfavors the planar central coordination. Note that the low-lying **0-1**$^{2-}$ and **0-2**$^{2-}$ are nonplanar with a central B atom, in contract to the perfect planar structure of **0-3**$^{2-}$.



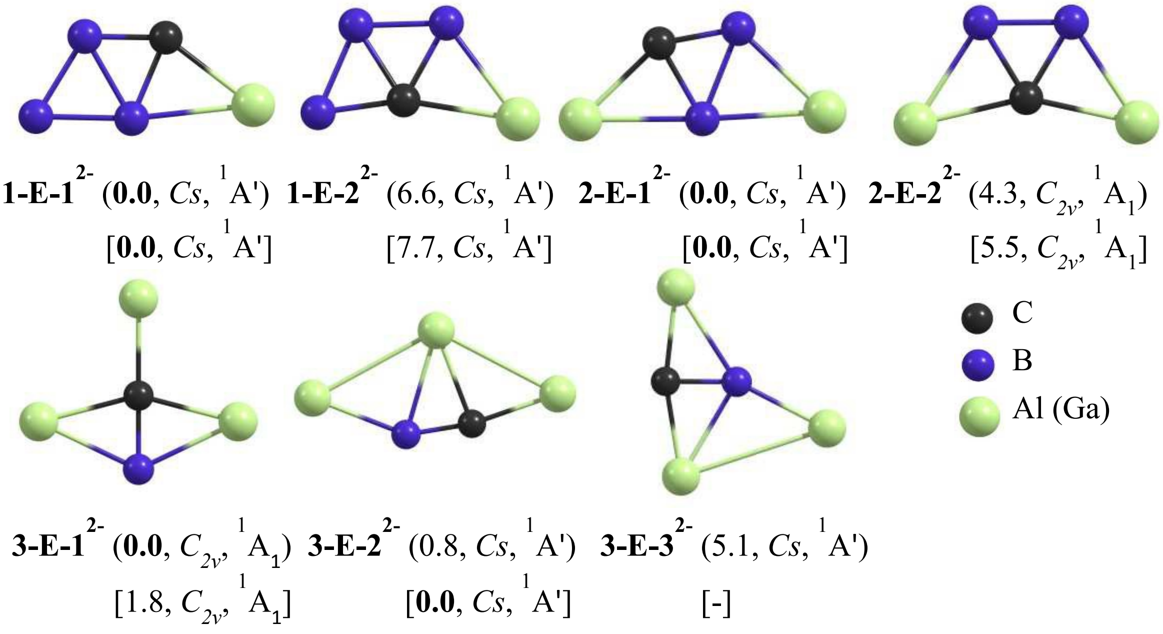
0-1^{2-} (0.0, C_1, ^1A) **0-2**$^{2-}$ (20.1, C_1, ^1A) **0-3**$^{2-}$ (22.4, C_{2v}, $^1A_1$)

Figure 1. Optimized geometries of the low-lying structures of parent CB_4^{2-} species at the broken-symmetry UB3LYP/aug-cc-pVTZ level. The relative energies of isomers are calculated at the MCQDPT2/CAS(18e,13o)/aug-cc-pVTZ level. Symmetries and spectroscopic states are given in the parentheses. Bond lengths are in angstroms. The energy values are in kcal/mol.

3.2 Al and Ga-substitution effect

When B atom is substituted by the Al, Ga-atom, which is less electronegative, yet has larger atomic radius, the geometrical and energetic situation of the multi-coordinate carbon and boron structure gradually changes. As shown in Figure 2, the tetracoordinate boron was located as the minimum having a prefect planar arrangement in $CB_xE_y^{2-}$ (y=1, 2, 3; E=Al, Ga) compared to the nonplanar tetracoordinate boron in CB_4^{2-} (**0-1**$^{2-}$ and **0-2**$^{2-}$

), indicating that Al and Ga substitution of the peripheral B atom in CB_4^{2-} induces planarization by slightly expanding the outer ring. In energy, the lowest and second lowest isomers are ptB (**y-E-1^{2-}**) and ptC (**y-E-2^{2-}**) (y=1,2) for mono- and di-substituted species, respectively. Notably, ptC (**3-Al-1^{2-}**)[17] and planar tricoordinate C/B (**3-Ga-2^{2-}**) were predicted to be a global minimum in the tri-substituted CBE_3^{2-} system, indicating that the thermodynamic stability of ptC is significantly improved along with the increasing of the number of Al and Ga substituted atoms. To further evaluate the energetic competition of ptB and ptC, we plot the energy difference between ptC and global minimum as a function of the number of Al and Ga-substituted atoms (ptB is the global minimum for most systems). We can see from Figure 3 that the thermodynamic stability of ptC is significantly increased on increasing the number of Al and Ga substituted atoms, most importantly, the energy order is even reversed at the tri-substituted system, in which the global ptC (**3-Al-1^{2-}**) of $CBAl_3^{2-}$ is more stable than ptB (**3-Al-3^{2-}**) by 5.1 kcal/mol and ptB is not found in the $CBGa_3^{2-}$ system (see Figure 2). This indicates that in addition to the geometrical effect on ptC, the Al- and Ga-substitution can significantly affect the thermodynamic stability of ptC. Note that the full substitution of all B atoms in CB_4^{2-} by Al and Ga (4 at horizontal axis) leads to the global ptC, as reported previously.[33] Yet, with no B-atom, both systems surely fall out of the scope of the present study, i.e., pMC vs pMB competition.



1-E-1^{2-} (**0.0**, Cs, ^{1}A') [**0.0**, Cs, ^{1}A']

1-E-2^{2-} (6.6, Cs, ^{1}A') [7.7, Cs, ^{1}A']

2-E-1^{2-} (**0.0**, Cs, ^{1}A') [**0.0**, Cs, ^{1}A']

2-E-2^{2-} (4.3, C_{2v}, ^{1}A$_1$) [5.5, C_{2v}, ^{1}A$_1$]

3-E-1^{2-} (**0.0**, C_{2v}, ^{1}A$_1$) [1.8, C_{2v}, ^{1}A$_1$]

3-E-2^{2-} (0.8, Cs, ^{1}A') [**0.0**, Cs, ^{1}A']

3-E-3^{2-} (5.1, Cs, ^{1}A') [-]

Figure 2. Optimized geometries of the low-lying structures of $CB_xE_y^{2-}$ (E=Al, Ga) species at the B3LYP/aug-cc-pVTZ level. The relative energies of isomers are calculated at the CCSD(T)/aug-cc-pVTZ level. The values in square brackets refer to Ga-based species. Symmetries and spectroscopic states are given in the parentheses. The energy values are in kcal/mol. "–" means the structure is not available.

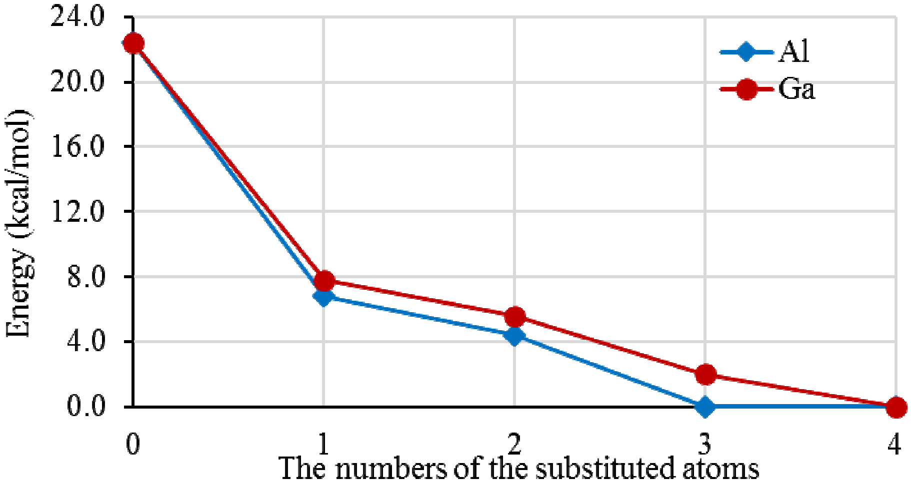
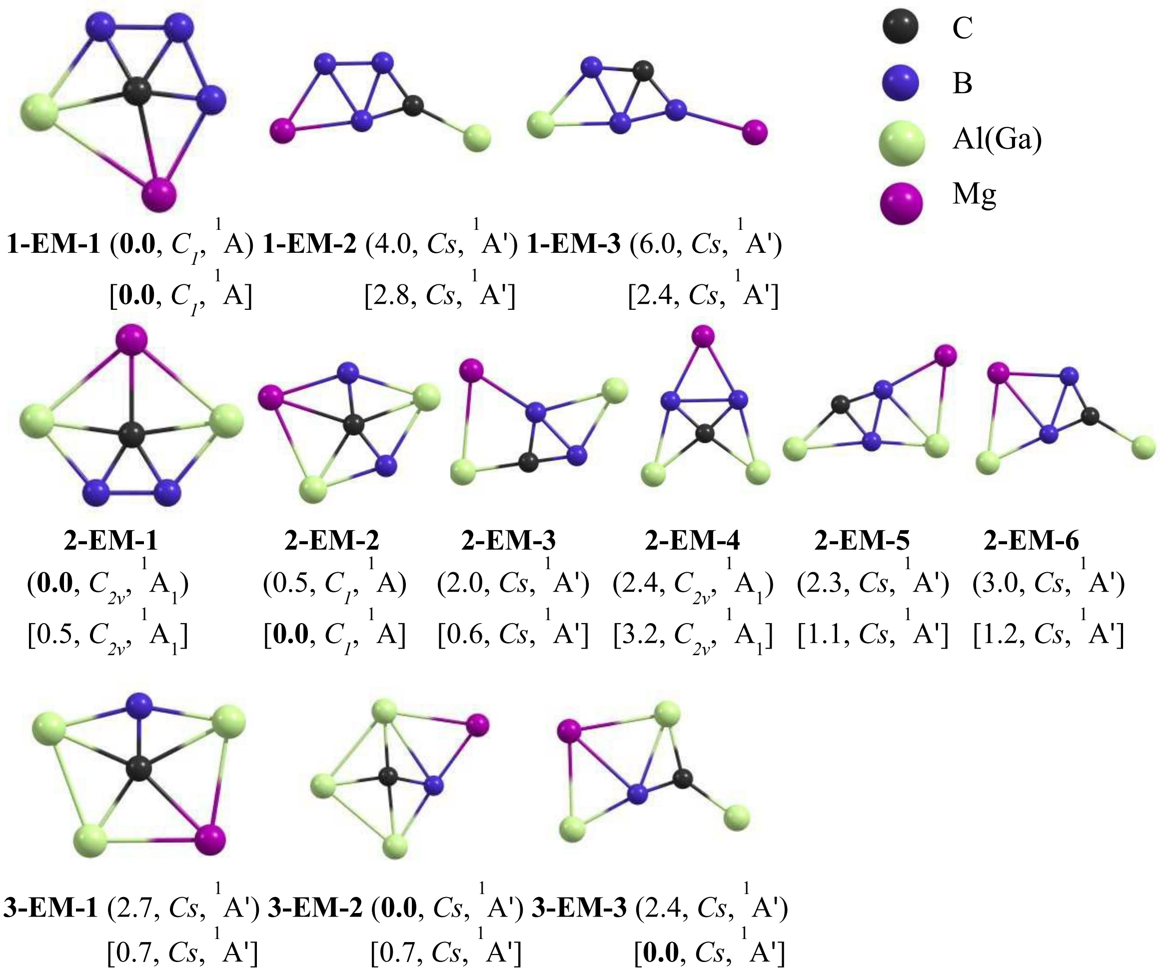


Figure 3. The energy difference between ptC and ground state as a function of the number of the Al and Ga substituted atoms without counterions.

3.3 Counterion effect

To remove the strong Coulomb repulsion in the multiply negatively charged anions, we further investigated the salt-stabilized species by using the alkali-earth counterions Mg^{2+}, i.e., $[CB_xE_y{}^{2-}]M^{2+}$ (E=Al, Ga; M=Mg). For the parent $[CB_4]Mg$, the penta-coordinated carbon structure is of C_{2v} symmetry with a central C atom significantly out of plane, which lies 6.4 kcal/mol less stable than the corresponding ground states, indicating that the outer ring composed of B and counterions Mg are too small to host the carbon in perfect planar arrangement. However, in $[CB_xE_y]Mg$ (E=Al, Ga; y>0), the introduction of Al and Ga slightly expand the outer ring, which enables the peripheral ring to host the central C atom in a perfect planar arrangement (see Figure 4). Additionally, $CB_xE_y{}^{2-}$ possesses the trapezoidal structure that facilitates Mg to interact with the planar tetracoordinate center resulting in penta-coordinate configuration. Indeed, planar penta-coordinate carbon (ppC, **y-EM-1**) can be generally formed as shown in Figure 4. Note that the **1-EM-1** having quasi-ppC is predicted to be ground state that lies 4.0 and 2.8 kcal/mol more stable than the nearest low-lying pMB isomer **1-EM-2** in CB_3AlMg and CB_3GaMg, respectively. For the di-substituted systems CB_2Al_2Mg and CB_2Ga_2Mg, the lowest-energy structure is pMC in the ppC form, i.e., **2-EM-1** or **2-EM-2** (E=Al, Ga), while pMB in the ptB form (i.e., **2-EM-3**) is somewhat higher in energy. For the tri-substituted systems, the ground structure **3-EM-2** for E=Al contains both pMC and pMB, and for E=Ga, the pMC **3-EM-1 and 3-EM-2** lies by 0.7 kcal/mol above the pMB **3-**

EM-3. Note that the stability of pMC relative to pMB in the tri-substituted system is still increased by 1.1 kcal/mol compared to the naked $CBGa_3^{2-}$. It is clear that for the 18e system CB_4^{2-}, the Al/Ga-substitution and the counterions can improve the stabilization of the planar carbon central coordination, and the cooperation of the two effects can lead to the realization of a global ppC minimum. In addition, Figure 5 presents the geometric comparison based on the M06-2X and B3LYP methods with aug-cc-pVTZ basis set, and the similar structures predicted by these two methods indicate that the designed planar multi-coordinate species in this work are well predicted by B3LYP method (see Figure S1).

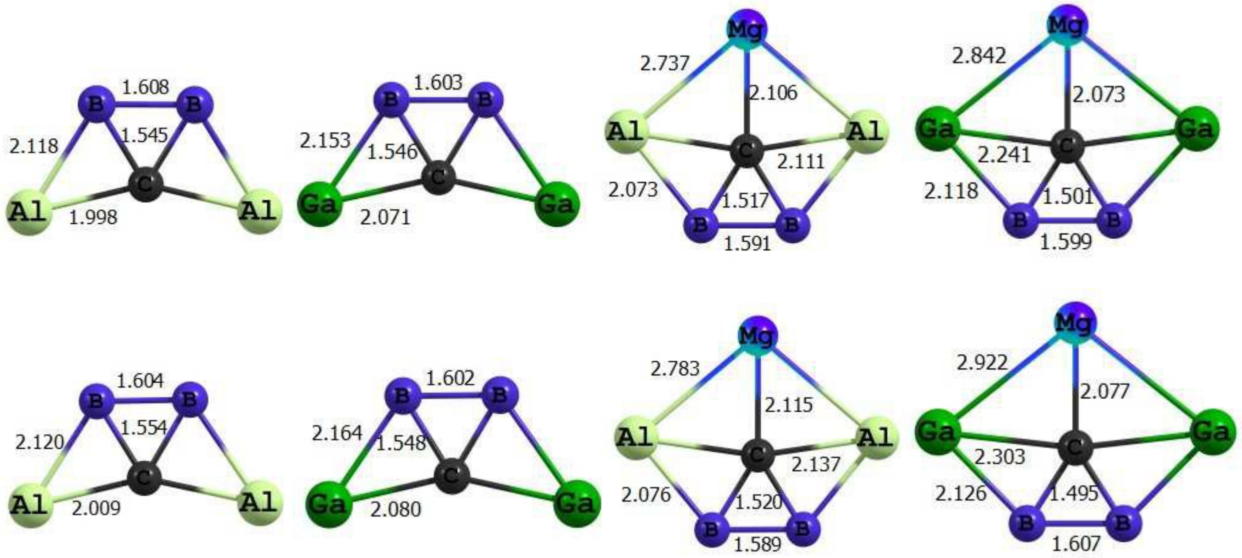


1-EM-1 (**0.0**, C_1, ^{1}A) [**0.0**, C_1, ^{1}A]
1-EM-2 (4.0, Cs, ^{1}A') [2.8, Cs, ^{1}A']
1-EM-3 (6.0, Cs, ^{1}A') [2.4, Cs, ^{1}A']

2-EM-1 (**0.0**, C_{2v}, $^1A_1$) [0.5, C_{2v}, $^1A_1$]
2-EM-2 (0.5, C_1, ^{1}A) [**0.0**, C_1, ^{1}A]
2-EM-3 (2.0, Cs, ^{1}A') [0.6, Cs, ^{1}A']
2-EM-4 (2.4, C_{2v}, $^1A_1$) [3.2, C_{2v}, $^1A_1$]
2-EM-5 (2.3, Cs, ^{1}A') [1.1, Cs, ^{1}A']
2-EM-6 (3.0, Cs, ^{1}A') [1.2, Cs, ^{1}A']

3-EM-1 (2.7, Cs, ^{1}A') [0.7, Cs, ^{1}A']
3-EM-2 (**0.0**, Cs, ^{1}A') [0.7, Cs, ^{1}A']
3-EM-3 (2.4, Cs, ^{1}A') [**0.0**, Cs, ^{1}A']

Figure 4. Optimized geometries of the low-lying structures of the salt-stabilized $[CB_xE_y^{2-}]Mg^{2+}$ (E=Al, Ga) species at the B3LYP/aug-cc-pVTZ level. The relative energies of isomers are calculated at the CCSD(T)/aug-cc-pVTZ level. The values in square brackets refer to Ga-based species. Symmetries and spectroscopic states are given in the parentheses. The energy values are in kcal/mol.



$2\text{-}Al\text{-}2^{2-}$ **$2\text{-}Ga\text{-}2^{2-}$** **2-AlM-1** **2-GaM-1**

Figure 5. Geometric comparison between M06-2X (top) and B3LYP (bottom) with aug-cc-pVTZ basis set.

3.4 Bonding feature

From the above discussion, the novel class of ppCs have been obtained by means of the cooperation of the substitution and counterion effects. In this section, we further investigate the bonding nature of two kinds of prefect ppCs, i.e., **2-EM-1** and **3-EM-1**. Generally, Al- and Ga-based ppCs are quite similar from the natural bonding orbital

(NBO) analysis. We take CB_2Al_2Mg (**2-AlM-1**) and $CBAl_3Mg$ (**3-AlM-1**) as example for the further analysis. As shown in Figure 6, similar to previously reported ppCs,[20] a significant contribution of the perpendicular $2p_z$ orbital of the central carbon atom to the π-orbital was found (HOMO-4), in agreement with the electronic stabilization mechanism proposed by Hoffmann et al.[15] The rest includes three radial orbitals (HOMO, HOMO-1 and HOMO-5) and other five σ-orbitals, in which the bonding between M and peripheral Al is present. The valence population of the central carbon of ppCs are shown in Table 1. For all ppCs, the relatively higher $2p_x$ and $2p_y$ occupancies and lower occupancies in $2p_z$ orbitals are manifestations of the back-donation. Note that the central carbon of pMC acts as a σ-acceptor/π-donator. The large HOMO–LUMO gap (2.2~2.9 eV) indicates that the new class of ppCs have a high electronic stability. Moreover, the Natural Population Analysis (NPA) charges on M and ppC atom are strongly positive and negative, respectively, indicating that the interaction between counterions M and CB_xE_y fragment is mostly ionic.

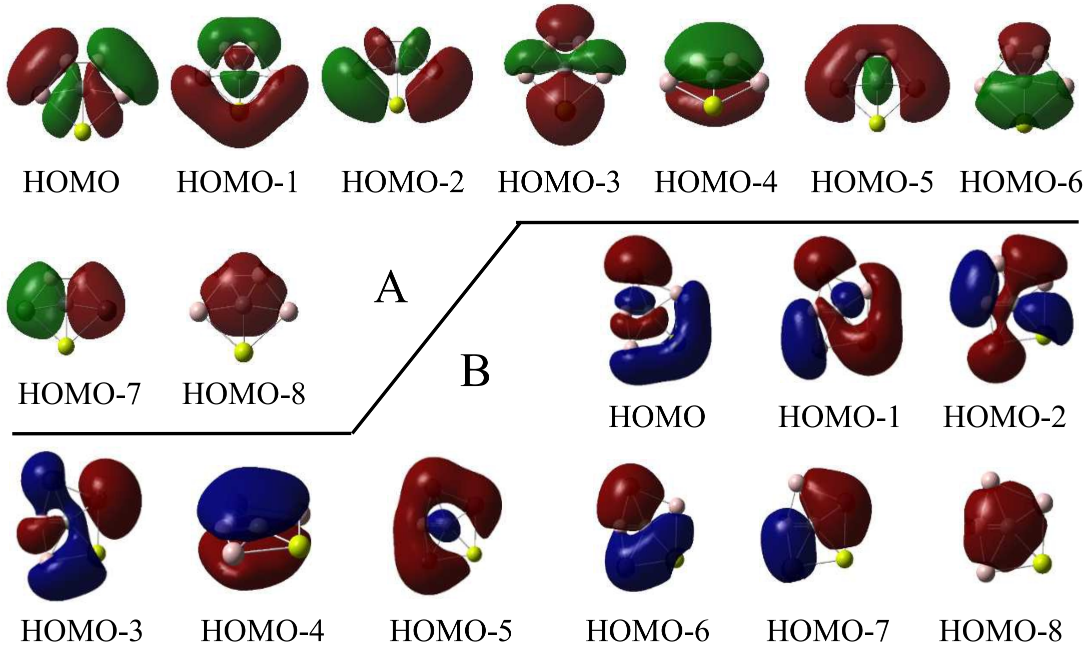


Figure 6. Characteristic orbitals of ppC of **2-AlM-1** (A) and **3-AlM-1** (B) at the B3LYP/aug-cc-pVTZ level.

Table 1 The Lowest Vibrational Frequencies ($V_{min,}$ cm^{-1}), Bond Distances (R, Å), Wiberg Bond Indices, NBO Charges (Q, |e|), Carbon Valence Population (VP) and HOMO–LUMO gaps (Gap, eV) of ppCs of the CB_xE_yMg and CAl_5^+ species. All values have been computed at the B3LYP/aug-cc-pVTZ level. The values in parenthesis refer to Ga-based system. "–" means that the value is not available.

Species	V_{min}	R_{Mg-C}	WBI_{Mg-C}	Q(C)	Q(M)	VP(C)	Gap
2-AlM-1	93.7	2.115	0.15	-1.77	0.79	$2s^{1.38}2p_x^{1.51}2p_y^{1.53}2p_z^{1.23}$	2.4
2-GaM-1	47.3	2.077	0.20	-1.62	0.83	$2s^{1.36}2p_x^{1.45}2p_y^{1.51}2p_z^{1.21}$	2.2
3-AlM-1	90.6	2.303	0.16	-2.01	0.62	$2s^{1.46}2p_x^{1.52}2p_y^{1.58}2p_z^{1.35}$	2.9
3-GaM-1	51.6	2.240	0.19	-1.86	0.62	$2s^{1.46}2p_x^{1.57}2p_y^{1.42}2p_z^{1.33}$	2.8
CAl_5^+	68.0	–	–	-2.80	–	$2s^{1.66}2p_x^{1.75}2p_y^{1.75}2p_z^{1.48}$	2.8

3.5 Kinetic stability of ppC

The good stability can find support from the Born-Oppenheimer molecular dynamic (BOMD) simulations,[34] for which we only take Al-based system as examples. At the B3LYP/6-31G(d) level, we employed the BOMD simulations at 373 K for **y-AlM-1** (2, 3). The root-mean-square deviations (RMSD) structure evolutions are shown in Figure 7. The small RMSD fluctuations indicate that ppC has reasonable kinetic stability at least for 27 ps. Clearly, the considerable thermodynamic and kinetic stability suggest that all the ppCs have promise to be experimentally realized. In the present penta-atomic $CB_xE_y^{2-}$ systems, planarization of the ligand rings is not a problem. In fact, even the fully Al, Ga-doped CAl_4^{2-} and CGa_4^{2-} is a planar structure. The importance of Al- and Ga-doping lies in their ability in tuning the relative competition between the C-in vs C-out arrangements, the latter of which usually predominates in C-B systems.

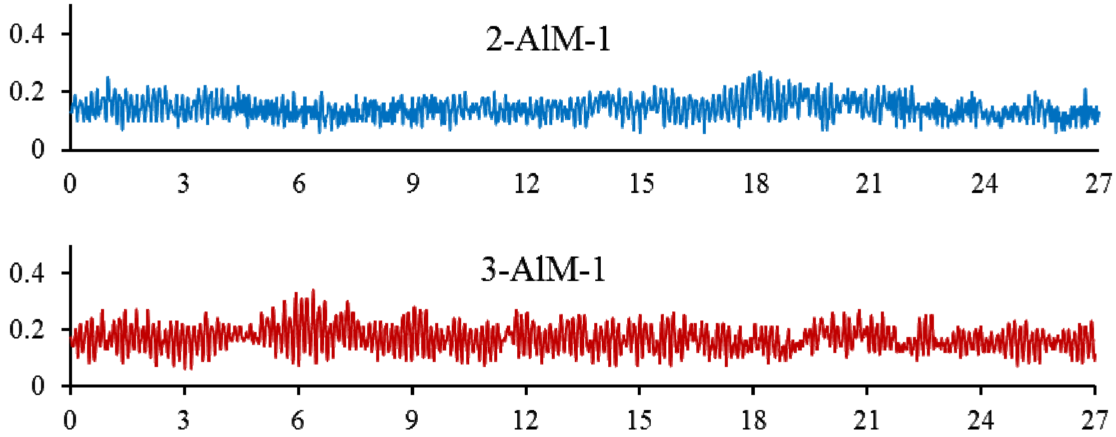


Figure 7. The structural evolutions of the ppC described by RMSD during 27 ps at 373 K at the B3LYP/6-31G(d) level.

Conclusions

We present in this work a systematic theoretical investigation on the competition of pMB and pMC in the free and salt-stabilized $CB_xE_y^{2-}$ (E=Al, Ga; x+y=4) systems. The parent CB_4^{2-} does have a ptC structure, yet it is thermodynamically less stable than the global ptB. This is in agreement with the results of Boldyrev and Wang that the higher electronegativity of carbon compared to boron clearly disfavors the tetracoordinate center form. For $CB_xE_y^{2-}$, the thermodynamic stability of ptC compared to ptB can be significantly improved along with increasing the number of Al/Ga-doping atoms, and importantly the relative energy order of ptC and ptB can be reversed, i.e., ptC is energetically superior to ptB. Further, the counterion Mg^{2+} has great potential to stabilize the ptC structures via the interaction between counterions and the central carbon, forming ppCs. The novel ppCs represent the first successful design of the C-B related ppC structures as the global minima. By means of the BOMD simulations analysis, the newly found global ppCs have good kinetic stability and wait for experimental realization.

Acknowledgments

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Supporting Information Available: Full citations for reference 31; the low-lying structures of the free and salt-stabilized $CB_xE_y^{2-}$ (E=Al, Ga; x+y=4).

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TOC graphic

Tuning the pMC vs. pMB preference