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Planar or quasi-planar octa- and ennea-coordinate aluminum and gallium in boron rings

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An *ab initio* theoretical investigation has been performed on planar or quasi-planar octa- and ennea-coordinate AI and Ga centered in X@B₈⁻ and X@B₉ (X=AI, Ga). These high symmetry molecular wheels all turned out to be true minima of the systems and σ + π double aromatic in nature, similar to the previously characterized D_{8h} B@B₈⁻ both electronically and geometrically. Adiabatic and vertical detachment energies of the anions and the ionization potentials of the neutrals have been calculated to aid their eventual experimental identification.

planar hyper-coordinate, aluminum, gallium, ab initio, geometry, electronic structure

1 Introduction

Boron clusters B_n and B_n^- in the size range of n=3-16have been confirmed to be planar or quasi-planar in a series of recent joint experimental and theoretical investigations $\frac{1-4}{2}$. The planarity of these clusters originates from their multiple aromaticity/antiaromaticity^[1,2]. B_n and their anions are expected to serve as a new class of inorganic ligands in chemistry. Quasi-planar hexa- coordinate B in B_7^- (C_{6v} B@B₆^{-)[3]} and planar hepta- and octacoordinate B in B₈⁻ (C_{2v} B@B₇⁻) and B₉⁻(D_{8h} B@ $B_{8}^{-})^{[4]}$ were characterized in combined photoelectron spectroscopy (PES) and *ab inito* investigations. Si@B₈^[5], $Ge(a)B_9^+$, and $Sn(a)B_{10}^{2+[6]}$ represented typical theoretical speculations of planar hyper-coordinate group 14 elements in boron rings. We recently investigated the possibility of the sandwich-typed $[\eta^6-B_6X]_2M$ (X=C, N; M=Mn, Fe, Co, Ni)^[7] and bowl- and tire-shaped $B_n M^{[8]}$ at density functional theory (DFT) level. We also presented a universal structural pattern for planar hyper-coordinate Si in B_nH_2Si series^[9]. Very recently, Luo proposed planar octa- and ennea-coordinate transition metals in M@B_n (M=Fe, Co; n=8, 9) at DFT^[10]. Bigger boron rings were even employed to host multiple planar

coordinate carbons^[11]. However, to the best of our knowledge, there have been no reports to date on planar hypercoordinate Al, Ga or other heavier group 13 elements.

To host a planar hyper-coordinate X center in a B_n ring stably, the central X atom and surrounding B_n ring must match both geometrically and electronically, the X center should have low electronegativity, and eventually, the complex as a whole possesses a right orbital energy order with the delocalized π molecular orbitals (MOs) lying generally higher in energy than their in-plane radial σ counterparts^[12–15]. Keeping this strategy in mind, we present in this work an *ab initio* investigation on planar or quasi-planar octa- and ennea-coordinate Al and Ga centered in $X@B_8^-$ and $X@B_9$ (X=Al and Ga) molecular wheels. These molecules all proved to possess three occupied delocalized π MOs and three occupied delocalized radial- σ MOs and therefore are $\sigma + \pi$ double aromatic in nature. This work and previous literature $\frac{[3,4]}{[3,4]}$ complete the series of planar or quasi-planar hyper-coordinate

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group 13 elements, including the nonmetal B, metallic Al, and semiconductor Ga, parallelizing the results obtained for planar hyper-coordinate group 14 elements^[5,6,12,13].

2 Theoretical procedure

Structural optimizations and frequency analyses were performed at the B3LYP^[16,17] and MP2(full)^[18,19] levels, using the basis of 6-311+G(3df) implemented in Gaussian 03 program^[20]. Adiabatic detachment energies (ADEs)

were calculated as the energy differences between the ground-states of the anions and the corresponding neutrals, while vertical detachment energies (VDEs) calculated as their energy difference at the anionic structures. The nucleus independent chemical shifts (NICS)^[21] were calculated with the ghost atom lying 1.0 A (NICS(1)) above the B_n planes. The calculated properties of X@B₈⁻, X@B₈⁺, and X@B₉ (X=Al and Ga) are summarized in Figure 1 and Table 1. Some of the low-lying isomers of AlB₉ neutral are depicted in Figure 2, with energies relative to D_{9h} Al@B₉ indicated at B3LYP.



Figure 1 Wheel-shaped structures of $C_{8v} X @B_8^-$, $D_{8h} X @B_8^-$, $D_{8h} X @B_8^+$, $C_{8v} X @B_8^+$, and $D_{9h} X @B_9$ (X=Al, Ga) with the bond lengths indicated in Å at B3LYP and [MP2] levels.

Table 1 Calculated HOMO-LUMO or SOMO-LUMO gaps ($\Delta E_{gap}/eV$), adiabatic and vertical detachment energies (ADE and VDE/eV), ionization potentials (IP/eV), natural atomic charges of the hyper-coordinate center X ($q_X/|e|$), total Wiberg bond indexes of X centers and the periphery B atoms (WBI_x and WBI_b), the lowest vibrational frequencies (v_{min}/cm^{-1}), and NICS(1) values of the concerned X@B_n complexes at the B3LYP/6-311+G(3df) level

$X@B_n^{a)}$	$\Delta E_{ m gap}$	ADE	VDE	q_X	WBI _X	WBI_B	$v_{\rm min}$	NICS(1)
1 . $C_{8v} Al@B_8^-(s)$	3.42	3.41	3.52	+1.5	2.5	3.8	+178	-19.2
2 . $D_{8h} Al@B_8^-(s)$	3.43			+1.5	2.5	3.8	-137	-23.1
3 . $D_{8h} Al@B_8^+(t)$	4.14			+1.1	2.9	3.3	-236	-19.6
4 . $C_{8v} Al@B_8^+(t)$	3.89			+1.3	2.7	3.3	+222	-18.0
5 . $C_{8v} Ga@B_8^-(s)$	3.55	3.23	3.32	+1.2	2.8	3.8	+139	-18.0
6 . $D_{8h} Ga@B_8^-(s)$	3.64			+1.2	2.9	3.8	-104	-25.9
7 . D_{8h} Ga@ $B_8^+(t)$	4.01			+0.8	3.2	3.3	-157	-23.3
8 . C_{8v} Ga@B ₈ ⁺ (t)	3.54			+1.0	2.9	3.3	+181	-17.5
9. $D_{9h} Al@B_9(s)$	3.26			+1.5	2.5	3.7	+139	-23.4
10 . $D_{9h} Ga@B_9(s)$	3.48			+1.3	2.8	3.6	+91	-25.4

a) s, Singlet state; t, triplet state.



Figure 2 Low-lying isomers of AlB₉ obtained at B3LYP with energies relative to D_{9h} Al@B₉(9) ($\Delta E/eV$) and the lowest vibrational frequencies (v_{min}/cm^{-1}) indicated.

3 Results and discussion

3.1 Geometrical structure

As group 13 elements, $Al(3s^23p^1)$ and $Ga(4s^24p^1)$ have similar electronic configurations with $B(2s^22p^1)$. Geometrical optimizations started from the previously reported $D_{8h} B@B_8^{-141}$ by replacing the B center with Al and Ga to produce the singlet $D_{8h} Al@B_8^{-1}$ (2) and $D_{8h} Ga@B_8^{-1}$ (6), respectively. However, these perfect planar structures all turned out to be transition states with one small imaginary frequency (a_{2u} mode) originating from the perpendicular vibrations of the planar octa-coordinate center X along the eighth-fold molecular axis.

Relaxation of structures 2 and 6 along the imaginary a_{2u} mode leads to the slightly more stable $C_{8v} Al@B_8^{-}(1)$ and C_{8v} Ga@B₈⁻ (5), respectively. However, the relaxation energies are very small. The relaxation energy for Al@ B_8^- from 2 to 1 is only 0.087 eV at DFT and 0.029 eV at MP2 with zero-point corrections included and 0.078 eV at CCSD(T). For Ga $(@B_8)^-$ from 6 to 5, the corresponding values are 0.151, 0.001, 0.204 eV, respectively. These relaxation energies proved to be smaller than the zero-point energies of the corresponding systems, suggesting that $D_{8h} X@B_8^-$ and $C_{8v} X@B_8^-$ be iso-energetic in experiments for X=Al and Ga. Besides, deviations of the Al center in 1 and Ga center in 5 from the B_8 plane are within 0.3-0.5 Å. Therefore, with zero-point vibrational motions considered, the vibrationally averaged structures of the quasi-planar 1 and 5 are eventually planar as 2 and 6, respectively.

Perfect planar hyper-coordinate Al and Ga can be achieved by employing a B_9 ring as ligand which is slightly bigger than B_8 in diameter. As shown in Figure 1 and Table 1, D_{9h} Al@B₉ (9) and D_{9h} Ga@B₉ (10) possess perfect enneagon structures without imaginary vibrational frequencies, indicating that both Al and Ga can stay comfortably and stably at the center of a B_9 ring. The diameters of the molecular wheels increase from 4.13 Å in D_{8h} Al@B₈⁻(2) to 4.45 Å in D_{9h} Al@B₉(9). A B₉ ring proves to provide a suitable cavity to host both Al and Ga at the center. Extensive searches produced no structures with energies lower than D_{9h} Al@B₉(9) and Ga@ B₉(10) which contain the first planar ennea-coordinate Al and Ga reported so far. As indicated in Figure 2, most of the low-lying isomers of AlB₉ can be derived either from C_{2h} B₁₀^[1] by replacing one B with an Al or from the nearly planar D_{2h} B₉^[1.4] by adding one Al along the molecular axis. The second lowest stable isomer (11) lies 0.27 eV above Al@B₉(9). Primary investigation indicates that a B_n ring with *n*>9 is required to host a In or Tl atom at its center.

3.2 Electronic structure

Orbital analyses indicate that $D_{8h} Al@B_8^-$ (2) has the valence electron configuration of $1a_{1g}^2 1e_{1u}^4 1e_{2g}^4 1e_{3u}^4$ $2a_{1g}^{2}1b_{2g}^{2}1a_{2u}^{2}2e_{1u}^{4}1e_{1g}^{4}$. The MOs of C_{8v} Al@B₈⁻(1) which lacks a symmetrical center prove to be similar to D_{8h} Al@B₈⁻ (2) in the same orbital energy order. As shown in Figure 3(a), among its valence MOs, D_{8h} Al@B₈⁻ (2) has three occupied delocalized π MOs with 6 electrons (the degenerate HOMO $(1e_{1g})$ and HOMO-2 (1a_{2u})), obeying the 4n+2 Huckel's rule for π aromaticity. It also contains three occupied delocalized σ -radial MOs with 6 electrons (the degenerate HOMO-1($2e_{1u}$) and HOMO-4($2a_{1g}$)), following the 4n+2 rule again and rendering σ aromaticity to the anion. D_{8h} Al@B₈⁻ is therefore $\sigma + \pi$ double aromatic in nature, similar to D_{8h} $B@B_8^{-[4]}$. But Al atom is instinctively a bit too big to be held stably at the center of a B_8 ring, making structure 2 a transition state. However, as discussed above and shown in Figure 3(b), the structural relaxation from the transition state 2 to the true minimum 1 is minor and both the three delocalized π MOs and three delocalized σ MOs have been well maintained in C_{8v} Al@B₈⁻ (1) though they are distorted in certain degree. Obviously, C_{8v} Al@B₈⁻ is σ + π double aromatic, too. Similar situation happens to C_{8v} Ga@B₈⁻ (5) and D_{8h} Ga@B₈⁻ (6).

Removing two electrons from $D_{8h} X@B_8^-$ produced the triplet $D_{8h} Al@B_8^+(3)$ and $D_{8h} Ga@B_8^+(7)$ which turned out to be transition states converted to the true minima of $C_{8v} Al@B_8^+(4)$ and $C_{8v} Ga@B_8^+(8)$ when relaxed along the imaginary mode. Both the triplet $Al@B_8^+$ and $Ga@B_8^+$ cations are $\sigma+\pi$ double aromatic, too: they follow the 4n Huckel's rule for triplet delocalized π systems and the 4n+2 rule for singlet delocalized σ systems. This judgment is well supported by the negative NICS(1) values calculated for these cations (Table 1).

As clearly shown in Figure 3(c), analogous to D_{8h} Al@B₈⁻ and D_{8h} Ga@B₈⁻, both the perfect planar D_{9h} Al@B₉ (9) and D_{9h} Ga@B₉ (10) neutrals also have three occupied delocalized π MOs (the degenerate HOMO and HOMO-2) and three delocalized σ MOs (the degenerate HOMO-1 and HOMO-4). These neutral molecules are therefore also $\sigma + \pi$ double aromatic in nature. D_{9h} X@B₉ contains one more B atom in comparison with D_{8h} $X@B_8^-$, generating a π electron in the HOMO of the neutral molecule to satisfy the 4n+2 Huckel's rule for aromaticity. Neutrals 9 and 10 follow the chemical intuition that delocalized π MOs lie generally higher in energy than their more effectively overlapped in-plane radial σ counterparts. The double aromaticity of D_{9h} $X@B_9$ (X=Al, Ga) provides extra stability to stabilize these unusual neutral molecules. As indicated in Table 1, the wheel-shaped anions, cations, and neutral molecules discussed in this work all possess negative NICS(1)^[19] vales in the range of -17-26 ppm, quantitatively confirming the overall aromaticity $(\sigma+\pi)$ of the systems,

which is in agreement with orbital analyses.

The calculated one-electron detachment energies of the anions turned out to be ADE=3.41 eV and VDE= 3.52 eV for **1** and ADE=3.23 eV and VDE= 3.32 eV for **5** at the B3LYP level. For planar ennea-coordinate neutrals, the calculated ionization potentials turned out to be IP=8.51 eV for **9** and IP=8.34 eV for **10**. The HOMO-LUMO(or SOMO-LUMO)energy gaps of these cluster isomers all turned out to be greater than 3.26 eV (Table 1), further supporting the electronic stability of the systems. These calculated values are expected to facilitate future spectroscopic experiments in identifying these clusters.

3.3 Natural bonding orbital (NBO) analyses

As shown in Table 1, the planar hyper-coordinate Al and Ga centers carry the positive charges of $q_x = +0.8 |e| -$ +1.5|e| and have the total Wiberg bond indexes of WBI_X=2.5-2.9, in consistent with the low electronegativities of Al and Ga atoms compared to B and their chemical valences of 3. The atomic electronic configurations of Al(3s^{0.34}3p_x^{0.36}3p_y^{0.36}3p_z^{0.39}) in 2 and Al (3s^{0.42} 3p_x^{0.34}3p_y^{0.34}3p_z^{0.34}) in 9 indicate that the charge transfer from the Al center to B₈ ligand mainly happens to Al 3s², while the Al sp² hybrids and Al 3p_z atomic orbitals partially participate in the delocalized σ and π MOs of the systems.

The periphery B atoms, on the other hand, possess the negative charges of $q_{\rm B}$ =-0.30|e|-0.35|e| and have the total bond orders of WBI_B=3.3-3.8. The atomic elec-



Figure 3 Delocalized MOs of D_{8h} Al@B $_8^-$ (a), C_{8v} Al@B $_8^-$ (b), and D_{9h} Al@B $_9$ (c).

tron configurations of $B(2s^{0.89}2p_x^{0.84}2p_y^{0.84}2p_z^{0.69})$ in **2** and $B(2s^{0.90}2p_x^{1.00}2p_y^{0.54}2p_z^{0.59})$ in **9** indicate that one B 2s electron has been promoted to B 2p atomic orbitals and B 2p_z orbitals mainly participate in the delocalized π MOs of the systems. The high bond orders between neighboring B atoms (WBI_{B-B} \approx 1.5) show that the periphery B-B interactions exhibit certain double bond character. It should be pointed out that though the calculated Wiberg bond order is 0.26–0.33 for each X–B interaction which is electron-deficient, eight or nine X-B bonds working together can effectively stabilize these octa- or ennea-coordinate X centers in X@B_n complexes. The planar hyper-coordinate X centers in these complexes mainly form covalent interactions with the surrounding B atoms, while the ionic bonding between the

- Alexandrova A N, Boldyrev A I, Zhai H J, Wang L S. All-boron aromatic clusters as potential new inorganic ligands and building blocks in chemistry. Coord Chem Rev, 2006, 250: 2811-2866[DOI]
- 2 Sergeeva A P, Zubarev D Y, Zhai H J, Boldyrev A I, Wang L S. A photoelectron spectroscopic and theoretical study of B_{16}^- and B_{16}^{2-} : an all-boron naphthalene. J Am Chem Soc, 2008, 130: 7244-7246[DOI]
- 3 Alexandrova A N, Boldyrev A I, Zhai H J, Wang L S. Electronic structure, isomerism, and chemical bonding in B₇⁻ and B₇. J Phys Chem A, 2004, 108(16): 3509-3517[DOI]
- 4 Zhai H J, Wang L S, Alexandrova A N, Boldyrev A I. Hepta- and octacoordinate boron in molecular wheels of eight- and nine-atom boron clusters: observation and confirmation. Angew Chem Int Ed, 2003, 42(48): 6004-6008[DOI]
- 5 Minyaev R M, Gribanova T N, Starikov A G, Minkin V I. Octacoordinated main-group element canters in a planar cyclic B8 environment: an *ab initio* study. Mendeleev Commun, 2001, 6: 1-2
- 6 Islas R, Heine T, Ito K, Schleyer P v R, Merino G. Boron rings enclosing planar hypercoordinate group 14 elements. J Am Chem Soc, 2007, 129(47): 14767-14774[DOI]
- 7 Li S D, Guo J C, Miao C Q, Ren G M. [(η⁶-B₆X)₂M] (X=C, N; M=Mn, Fe, Co, Ni): A new class of transition-metal sandwich-type complexes. Angew Chem Int Ed, 2005, 44(14): 2158-2161
- 8 Li S D, Miao C Q, Guo J C, Ren G M. Transition metal–boron complexes BnM: from bowls (*n*=8–14) to tires (*n* =14). J Comput Chem, 2006, 27: 1858–1865[DOI]
- 9 Li S D, Miao C Q, Guo J C, Ren G M. Planar tetra-, penta-, hexa-, hepta-, and octacoordinate silicons: a universal structural pattern. J Am Chem Soc, 2004, 126(49): 16227-16231[DOI]
- 10 Luo Q. Boron rings containing planar octa- and enneacoordinate cobalt, iron and nickel metal elements. Sci China Ser B-Chem, 2008, 51: 607-613[DOI]
- 11 Erhardt S, Frenking G, Chen Z F, Schleyer P V R. Aromatic boron wheels with more than one carbon atom in the center: C_2B_8 , $C_3B_9^{3+}$, and $C_5B_{11}^+$. Angew Chem Int Ed, 2005, 44: 1078–1082
- 12 Exner K, Schleyer P V R. Planar hexacoordinate carbon: A viable possibility. Science, 2000, 290: 1937-1940[DOI]
- 13 Wang Z X, Schleyer P V R. Construction principles of "Hyparenes": families of molecules with planar pentacoordinate carbons. Science,

positive X center and the negative B_n ring can not be neglected.

4 Summary

We have presented an *ab initio* investigation on planar or quasi-planar octa- and annea-coordinate Al and Ga in D_{8h} or $C_{8v} X@B_8^-$ and $D_{9h} X@B_9$ in this work. Similar to the previously characterized $B@B_8^-$, ^[4] these wheelshaped structures turned out to be $\sigma+\pi$ double aromatic in nature. As true minima on the potential surfaces of the concerned systems, they are expected to be stable thermodynamically and may be targeted in future experiments to expend the domain of planar hyper- coordinate elements to include metal Al and semiconductor Ga.

2001, 292: 2465-2469[DOI]

- 14 Wang L M, Huang W, Averkiev B B, Boldyrev A I, Wang L S. CB⁻₇: Experimental and theoretical evidence against hypercoordinate planar carbon. Angew Chem Int Ed, 2007, 46: 4550-4553[DOI]
- 15 Averkiev B B, Zubarev D Y, Wang L M, Huang W, Wang L S, Boldyrev A I. Carbon avoids hypercoordination in CB₆⁻, CB₆²⁻, and C2B5- planar carbon-boron clusters. J Am Chem Soc, 2008, 130: 9248-9250[DOI]
- 16 Beck A D. Density functional thermochemistry. III. The role of exact exchange. J Chem Phys, 1993, 98: 5648-5659 [DOI]
- Lee C, Yang W, Parr R G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys Rev B, 1988, 37: 785-791[DOI]
- 18 Head-Gordon M, Pople J A, Frisch M J. Mp2 energy evaluation by direct methods. Chem Phys Lett, 1988, 153: 503-506 [DOI]
- 19 Head-Gordon M, Head-Gordon T. Analytic Mp2 frequencies without fifth-order storage. Theory and application to bifurcated hydrogen bonds in the water hexamer. Chem Phys Lett, 1994, 220: 122-128[DOI]
- 20 Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Montgomery J A Jr, Vreven T, Kudin K N, Burant J C, Millam J M, Iyengar S S, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson G A, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox J E, Hratchian H P, Cross J B, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Ayala P Y, Morokuma K, Voth G A, Salvador P, Dannenberg J J, Zakrzewski V G, Dapprich S, Daniels A D, Strain M C, Farkas O, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Ortiz J V, Cui Q, Baboul A G, Clifford S, Cioslowski J, Stefanov B B, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin R L, Fox D J, Keith T, Al-Laham M A, Peng C Y, Nanayakkara A, Challacombe M, Gill P M W, Johnson B W, Chen M, Wong W, Gonzalez C, Pople J A. Gaussian 03, Revision A1. Pittsburgh: Gaussian Inc. 2003.
- 21 Schleyer P V R, Maerker C, Dransfeld A, Jiao H, van Eikema Hommes N J R. Nucleus-independent chemical shifts: a simple and efficient aromaticity probe. J Am Chem Soc, 1996, 118: 6317-6318[DOI]