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Title: Unconventional charge distribution in the planar wheel-type $\text{M@B}_6\text{H}_6^{\text{-/0/+}}$ ($\text{M} = \text{Mn, Fe and Co}$): central M with negative charges and peripheral boron ring with positive charges

This work reports planar wheel-type $D_{6h}\text{M@B}_6\text{H}_6^{\text{-/0/+}}$ ($\text{M} = \text{Mn, Fe and Co}$ for anion, neutral and cation, respectively) clusters designed and investigated by density functional theory. The detailed calculations suggest that the charges of transition between the M atom and boron ring lead to an unconventional charge distribution, i.e. the M atom is negatively charged, while the boron ring is positively charged. This study may open a new area in coordination chemistry for planar hexacoordinate transition metals and awaits experimental verification. In addition, I very gratefully acknowledge financial support from Professor Jingwen Lv.
Unconventional charge distribution in the planar wheel-type $M \bigcirc \!B_6H_6^{-7/0/+}$ ($M = \text{Mn}, \text{Fe} \text{ and Co}$): central $M$ with negative charges and peripheral boron ring with positive charges

Jianhua Hou,$^{a,b}$ Qian Duan,$^{a,b}$ Jieming Qin,$^{a,b,c}$ Xiande Shen,$^{a,b}$ Jianxun Zhao,$^{a,b}$ Qingcheng Liang,$^{a,b}$ Dayong Jiang$^{a,b}$ and Shang Gao$^{a,b}$

Planar wheel-type $D_{6h}$, $M \bigcirc \!B_6H_6^{-7/0/+}$ ($M = \text{Mn}, \text{Fe} \text{ and Co}$ for anion, neutral and cation, respectively) clusters with a planar hexacoordinate transition-metal at the center of the boron ring were designed and investigated by density functional theory. These planar clusters are chemically stable as a result of their large binding energy, vertical ionization potential, and vertical electron affinity. The detailed natural population and molecular orbital analyses suggest that not only does the $M$ atom donate electrons to the boron ring for participation in the $\pi$-delocalized bonding, but also the boron ring donates electrons back to the $M$ atom for the formation of the $\sigma$-delocalized bonding, which leads to a strong aromaticity and unconventional charge distribution, i.e., the $M$ atom is negatively charged, while the boron ring is positively charged. This study may open a new area in coordination chemistry for planar hexacoordinate transition metals and we expect further experimental exploration of their synthesis and potential applications.

1. Introduction

The planar tetracoordinate carbon proposed by Hoffmann et al.$^1$ has been observed in $D_{4h}$ Al$_4$C$^2$ and $C_{2v}$ Al$_2$XC ($X = \text{Si, Ge}$).$^3$ Since then, planar tetra-, penta-, hexa-, hepta- and octa-coordinate main group elements have been extensively investigated.$^{4-10}$ Generally, special planar clusters contain two types of delocalized bonding, i.e., in-plane $\sigma$ bonding and out-of-plane $\pi$ bonding, which can enhance their stability. However, these extreme violations of classical bonding principles are not limited to main group elements. Numerous planar wheel-type clusters with a central hypercoordinate transition-metal (M) encircled by different ligands, such as planar $n$-membered metal rings ($n = 5$ to $7$)$^{11-14}$ and planar $n$-membered boron rings ($n = 7$ to $10$)$^{15-21}$ have been studied experimentally and computationally. The studies from $M \bigcirc \!B_n$ $^{15-21}$ (The $\bigcirc$ sign proposed by Wang and Boldyrev$^{17}$ to designate the planar $n$-membered boron ring with a central $M$ atom distinguishes the $\bigcirc$ sign used for a 3D cage cluster with an endohedral atom.) demonstrate that transition metal atoms are better suited for the central position in the boron ring because they prefer to participate in delocalized bonding with the boron ring. To achieve the design of $M \bigcirc \!B_n$ $^\circ$, Wang and Boldyrev also developed a chemical bonding model in which to satisfy the peripheral B-B bonding and the delocalized $\sigma$ and $\pi$ bonding, and the required valence for the central transition-metal atom $M$, is $12 - n - k$.$^{16-18}$ Compared to pure boron clusters, hydrogenated small boron clusters favor the adoption of 3D aromatic structures.$^{22-25}$ Thus, it is challenging to obtain planar hypercoordinate elements with BH ligands. In 2009, Yu and co-workers$^{26}$ reported a planar wheel-type $D_{3h}$, $B_5\bigcirc \!B_3H_5^+$ cluster, which is the global minimum according to their calculation. In 2013, Cheng$^{27,28}$ presented some $B_nH_n$ ($n = 5$ to $8$) clusters doped with Be, V, Cr and Mn. However, they are not planar structures except for $D_{2h}$ $V \bigcirc \!B_2H_2^+$, which is a planar local minimum. To date, the planar wheel-type $M \bigcirc \!B_nH_n$ clusters are paid less attention compared to the planar wheel-type $M \bigcirc \!B_n$ clusters. Herein, we applied density functional theory (DFT) to investigate the geometrical and electronic structures of planar wheel-type $D_{6h}$, $M \bigcirc \!B_6H_6^{-7/0/+}$ ($M = \text{Mn}, \text{Fe} \text{ and Co for anion, neutral and cation, respectively}$) clusters. The results show that the planar clusters containing a central hexacoordinate $M$ atom with six BH ligands are theoretically validated to be favorable in energy, exhibit strong aromaticity and unconventional charge distribution, and they may be targeted in future experiments to open a new area of coordination chemistry.

$^a$ School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, People’s Republic of China. E-mail: houjh163@163.com
$^b$ Engineering Research Center of Optoelectronic Functional Materials, Ministry of Education, People’s Republic of China
$^c$ Inner Mongolia University for the Nationalities, People’s Republic of China
2. Computational details

For the calculation methods, potential energy surface scans of MB₆H₆⁻/₀/⁺ clusters were performed using the Saunders’ “Kick” method²⁸ to search the global minimum. Various initial structures obtained at the BP86/6-311G(3df,p) level were optimized at the BP86/6-311+G(3df,p) level, and imaginary frequencies were checked at the same level. Natural population analysis (NPA)³³ charge computations and Wiberg bond indices (WBI)³⁴ were computed at the same level using the natural bond orbital (NBO)³⁵ to gain insight into their bonding pattern. In order to assess the aromatic character of MC₆B₆H₆⁻/₀/⁺, nucleus-independent chemical shifts (NICS),³⁶ supposing by Schleyer and co-workers, were calculated with the ghost atom lying d Å (NICS(d) = 1.0–5.0 Å) above the M atom. The NICS(d) values were obtained at the BP86/6-311+G(3df,p) level with the gauge including the atomic orbital (GIAO)³⁷ method. The binding energy (E₀) between M⁻/₀/⁺ and B₆H₆ is defined as E₀ = E(M₆B₆H₆⁻/₀/⁺) − E(M⁻/₀/⁺) − E(B₆H₆). The vertical electron affinity (VEA) and vertical ionization potential (VIP) of M₆B₆H₆⁻/₀/⁺ are defined as the total energy difference between M₆B₆H₆⁻/₀/⁺ ± e (+ for VEA and − for VIP) and M₆B₆H₆⁻/₀/⁺ clusters at the optimized geometry of M₆B₆H₆⁻/₀/⁺. All the calculations were performed using the GAUSSIAN 09 program packages. The dimensional plots of the molecular configurations and orbitals were generated with the GaussView program.³⁹

3. Results and discussion

3.1 Geometry structure and WBIs

The optimized geometries of M₆B₆H₆⁻/₀/⁺ are a perfect planar hexagonal boron ring with a planar hexacoordinate M atom, possessing the highest D₆h symmetry, as shown in Fig. 1. Fig. 2 shows the eight low-energy isomers of MB₆H₆⁻/₀/⁺ performed at the BP86/6-311+G(3df,p) level. The planar wheel-type D₆h Mn₆C₆B₆H₆⁻ and Fe₆C₆B₆H₆⁻ are the global minimum structures, and are 9.77 and 12.27 kcal mol⁻¹ lower in energy than the second-lowest energy isomers, respectively. However, the planar wheel-type D₆h Co₆C₆B₆H₆⁻ is not the global minimum, and it is 4.09 kcal mol⁻¹ higher in energy than the lowest energy isomer.

Table 1 tabulates the calculated bond angles and bond lengths of the D₆h, M₆C₆B₆H₆⁻/₀/⁺, B–M–B angles are 60° and the B–H bond lengths are about 1.20 Å. All the B–B bond lengths are equal to the M–B bond lengths in M₆C₆B₆H₆⁻/₀/⁺ and they are 1.851, 1.832 and 1.833 Å for M = Mn, Fe and Co, respectively. Although these B–B bond lengths are significantly longer than the typical B–B bond distances (1.593 Å) reported for CB₆⁻,⁴⁰ they are still in the single-bond range of 1.706 to 1.859,⁴¹ which shows that the B–B interactions are very weak. However, the M–B bond distances are notably shorter by 0.379, 0.328 and 0.267 Å, compared with the M–B covalent radii sums of 2.23, 2.16 and 2.10 Å (ref. 42) for M = Mn, Fe and Co, respectively. This suggests the existence of robust interactions between the peripheral boron ring and central M atom. In order to evaluate the precision of the calculated M–B bond lengths, the geometry of Fe₆C₆B₆H₆⁻ was also optimized at the B3LYP/6-311+G(3df,p)⁴³,⁴⁴ and LC-wPBE/6-311+G(3df,p)⁴⁵ levels, and the same computational levels, as well as BP86/6-311+G(3df,p) were used for the geometry of Cp*Fe(CO)₂BCl₂.⁴⁶ The B3LYP and LC-wPBE lengths of the Fe–B bond in Fe₆C₆B₆H₆⁻ are 1.825 and 1.806 Å, respectively, and are similar to the BP86 length. In addition, for Cp*Fe(CO)₂BCl₂, the BP86, B3LYP and LC-wPBE lengths of the Fe–B bond are 1.982, 1.986 and 1.950 Å and they are also similar. Moreover, they agree well with the experimental value (1.942(3) Å),⁴⁶ indicating that the calculated bond length of the M–B in M₆C₆B₆H₆⁻/₀/⁺ is convincing.

![Fig. 1](image-url) Optimized geometries of D₆h, M₆C₆B₆H₆⁻/₀/⁺ (H atoms are white and B atoms are pink) at BP86/6-311+G(3df,p). Bond distances are in angstroms and bond angles are in degrees.

![Fig. 2](image-url) The optimized geometries and the relative energies of the eight lowest energy minima of MnB₆H₆⁻ (1), FeB₆H₆⁻ (2) and CoB₆H₆⁻ (3) at BP86/6-311+G(3df,p). The relative energies (E_rel in kcal mol⁻¹) are based on the global minima.
Concerning the thermodynamic stability of M@B$_6$H$_6$–, the energy changes of the following processes B$_6$H$_6$ ($C_{2v}$, $A_1$) + M –– M@B$_6$H$_6$– ($D_{6h}$, $A_1g$) were calculated. With zero-point corrections included, we find that the reactions are highly exothermic ($\Delta E = -70.3$, $-52.5$ and $-25.1$ kcal mol$^{-1}$ for M = Mn, Fe and Co, respectively), indicating that the desired products are favored in thermodynamics and are therefore viable in experiments.

The smallest harmonic vibration frequencies ($v_{\text{min}}$), HOMO–LUMO energy gap ($\Delta$H–L), $E_{\text{b}}$, VIP and VEA of M@B$_6$H$_6$– are also listed in Table 1. The $D_{6h}$ M@B$_6$H$_6$– have no imaginary frequencies. Moreover, the $v_{\text{min}}$ (96.7–184.1 cm$^{-1}$) are reasonably large. Although AH–L (0.90–1.90 eV) are rather small, $E_{\text{b}}$, VIP and VEA in our systems are fairly large and they are similar to those included, we find that the reactions are highly exothermic ($\Delta E = -70.3$, $-52.5$ and $-25.1$ kcal mol$^{-1}$ for M = Mn, Fe and Co, respectively), indicating that the desired products are favored in thermodynamics and are therefore viable in experiments.

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### Table 1: Calculated B–M–B bond angle ($\angle$ BMB/degree), bond distances ($R_{\text{M-B}}$, $R_{\text{B-B}}$ and $R_{\text{B-H}}$/Å), Wiberg bond indices of M–B and B–B bonds (WBIM$_{\text{M-B}}$, WBIM$_{\text{B-B}}$) and total Wiberg bond indices of the M and B atoms (WBIB$_{\text{M}}$, WBIB$_{\text{B}}$), and the harmonic vibration frequencies ($\nu_{\text{min}}$), HOMO–LUMO energy gap ($\Delta$H–L/eV), vertical binding energy ($E_b$/eV), vertical ionization potential (VIP/eV) and vertical electron affinity (VEA/eV) of B$_6$H$_6$, M@B$_6$H$_6$–/0/+ at BP86/6-311+G(3df,p) level

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<th>$R_{\text{B-B}}$</th>
<th>$R_{\text{B-H}}$</th>
<th>WBIM$_{\text{M-B}}$</th>
<th>WBIM$_{\text{B-B}}$</th>
<th>WBIB$_{\text{M}}$</th>
<th>WBIB$_{\text{B}}$</th>
<th>$\nu_{\text{min}}$</th>
<th>$\Delta$H–L</th>
<th>$E_b$</th>
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<th>VEA</th>
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### Table 2: Calculated natural atomic charges of the M and B atoms ($Q_M$ and $Q_B$) for $D_{6h}$ M@B$_6$H$_6$–/0/+ V@B$_6$H$_6$– and Be@B$_6$H$_6$ employed by the BP86 method with six different basis sets: 6-311+G(d), 6-311+G(3df,p), 6-311+G(3df,3p), 6-311G(d), 6-311G(3df,p) and 6-311G(3df,3p)

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<th>$Q_M$</th>
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Table 3 Calculated Hirschfeld, ADCH, Becke and APT charges of the M and B atoms (Q_M and Q_B/|e|) for D_{6h} M@C_6B_{2}H_{6}^{−10/4}, as compared with the NPA method.

<table>
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<th>Method</th>
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<th>Fe@C_6B_{2}H_{6}</th>
<th>Co@C_6B_{2}H_{6}^{+}</th>
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<tr>
<td>APT</td>
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</table>

Table 4 Calculated natural atomic electronic configuration of the B atom (2s 2p_x 2p_y and 2p_z/|e|) for D_{6h} M@C_6B_{2}H_{6}^{−10/4} and numbers of electron transfer (Q_M−B) donation of π-electrons from M to B, Q_M−B ring: donation of σ-electrons from M to B and Q_M−B ring: back-donation of σ-electrons from the boron ring to M/|e| for D_{6v}, M@C_6B_{2}H_{6}^{−10/4} at the BP86/6-311+G(3df,p) level.

<table>
<thead>
<tr>
<th>Method</th>
<th>Mn@C_6B_{2}H_{6}^{−}</th>
<th>Fe@C_6B_{2}H_{6}</th>
<th>Co@C_6B_{2}H_{6}^{+}</th>
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3.4 Aromaticity and molecular orbital

According to the perfect planar structure and considerable electron transfer between the central M atom and the boron ring, we can propose that M@C_6B_{2}H_{6}^{−10/4} should possess aromaticity. NICS is a simple and efficient criterion to characterize aromatic nature. A large negative NICS above the molecular plane indicate the presence of diamagnetic ring currents. Fig. 3 plots the NICS(d) (d = 1.0−5.0 Å) of M@C_6B_{2}H_{6}^{−10/4} and C_6H_{6}. As shown in Fig. 3, the NICS values of M@C_6B_{2}H_{6}^{−10/4} are all negative, and have the same tendency as C_6H_{6}, which can prove that the diamagnetic ring current effect, which is characteristic for aromaticity, exists in M@C_6B_{2}H_{6}^{−10/4}. Especially, we can find that Mn@C_6B_{2}H_{6}^{−} and Fe@C_6B_{2}H_{6}^{−} have very strong aromatic character because their NICS(1) = −25.2 and −15.3 are more negative than −10.0 for C_6H_{6}.

Fig. 3 NICS scans of D_{6h} M@C_6B_{2}H_{6}^{−10/4} compared with those of C_6H_{6} with the NICS values in ppm and the distances (d) above the central M atom in Å.
shown in Fig. 4. The MOs of the other clusters are very similar, and therefore are not shown. The HOMO – 1 and the degenerate HOMO – 3 are delocalized π MOs, which exhibits the typical pattern of the aromatic molecule, benzene. Thus, Fe@C₆B₆H₁₂ with six π electrons is considered to be aromatic, conforming to the (4n + 2) Hückel rule. The others clusters are also aromatic as well as Fe@C₆B₆H₁₂. It is the π aromaticity that is responsible for the perfect planar molecular structure. The HOMO – 1 and the degenerate HOMO – 3 consist of 3dₓ² and 3dₓ²–y² orbitals of the Fe atom and 2pₓ orbitals of the B atoms. These π-electrons MOs are responsible for the πFe→π. Moreover, the HOMO – 7 and degenerate HOMO – 5 and HOMO – 8 are comprised of in-plane B 2pₓ and 2pᵧ orbitals that point to the central Fe atom and effectively overlap with the 3dₓ and 3dₓ²–y² orbitals of the Fe atom, showing remarkably delocalized σ MOs character. Thus, a part of the σ-electrons of the B atom diffuses to the orbitals of the Fe atom and forms the σFe→σ bonds.

4. Conclusion

In summary, we theoretically predicted the planar wheel-type D₆h, M@C₆B₆H₁₂⁻/⁺ (M = Mn, Fe and Co for anion, neutral and cation, respectively.) clusters at the B3LYP/6-311+G(3df,p) level. Their chemical stability may facilitate their experimental observation and synthesis. Moreover, strong aromaticity exists in M@C₆B₆H₁₂⁻/⁺ as well as the other planar wheel-type clusters.11–21 It is remarkable that the central transition-metal M atom is negatively charged while the boron ring is positively charged. The natural population and molecular orbital analyses reveal that the unconventional charge distribution is due to the electron transfer between M and the boron ring. These predictions deserve experimental confirmation because they would open a new area in coordination chemistry for planar hexacoordinate transition metals.

Acknowledgements

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