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Designer Mg—Mg and Zn—Zn Single Bonds Facilitated by Double Aromaticity in the M₂B₇⁻ (M=Mg, Zn) Clusters†

Wei Wang, Jie Wang, Chu Gong, Chaonan Mu, Dongmei Zhang, Xinxing Zhang

Advanced Energy Materials Chemistry (Ministry of Education), Renewable Energy Conversion and Storage Center (ReCAST), College of Chemistry, Nankai University, Tianjin 300071, China

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The simple homodinuclear M—M single bonds for group II and XII elements are difficult to obtain as a result of the fulfilled s² electronic configurations, consequently, a dicaticionic prototype is often utilized to design the M⁺—M⁺ single bond. Existing studies generally use sterically bulky organic ligands L⁻ to synthesize the compounds in the L⁻—M⁺—M⁺—L⁻ manner. However, here we report the design of Mg—Mg and Zn—Zn single bonds in two ligandless clusters, Mg₂B₇⁻ and Zn₂B₇⁻, using density functional theory methods. The global minima of both of the clusters are in the form of M₂²⁺(B₇³⁻), where the M—M single bonds are positioned above a quasi-planar hexagonal B₇ moiety. Chemical bonding analyses further confirm the existence of Mg—Mg and Zn—Zn single bonds in these clusters, which are driven by the unusually stable B₇³⁻ moiety that is both σ and π aromatic. Vertical detachment energies of Mg₂B₇⁻ and Zn₂B₇⁻ are calculated to be 2.79 eV and 2.94 eV, respectively, for the future comparisons with experimental data.

Key words: Mg—Mg single bond, Zn—Zn single bond, Density functional theory, Double aromaticity, Cluster

I. INTRODUCTION

Due to the fulfilled s² electronic configurations, the simple homodinuclear M₂ (M=Group II and XII elements) molecule is not stable as a result of the filled σ bonding and σ* antibonding orbitals based on the molecular orbital (MO) interpretation (FIG. 1(a)). Consequently, even though the gas-phase Mg₂ and Zn₂ molecules have been experimentally produced and characterized [1, 2], they feature weak bond energies and long bond lengths (Table I). To strategically design a stable M—M single bond, the doubly charged M⁺—M⁺ ion should be able to play the role as the simplest model where the bond order is 1 (FIG. 1(b)). “Naked” dications such as Mg₂²⁺ and Zn₂²⁺ have been theoretically investigated [3, 4]. However, these M—M single bonds are presumably unstable or metastable due to the two positive charges confined in such a small molecule. Therefore, in order to design and synthesize a stable molecule, counter ions or ligands are often utilized to stabilize the M⁺—M⁺ core.

For the case of Mg₂ single bonds, Stasch et al. [5] synthesized the first Mg—Mg single bond in an L⁻—Mg⁺—Mg⁺—L⁻ manner, where ligands [(Ar)NC(NPr₂)N(Ar)]⁻ and {[(Ar)NC(Me)]₂CH}⁻ (Ar=2,6-diisopropylphenyl) were used. Later on, many more ligated Mg₂²⁺ molecules and their related reactions have been investigated [6–16]. Likewise, the first synthesis of a Zn—Zn single bond also utilized organic ligands in the form of L⁻—Zn⁺—Zn⁺—L⁻, where the ligand L⁻ is a cyclopentadienyl anion [17]. The syntheses of Zn—Zn single bonds with different ligands were then reported [18–21]. Sterically bulky ligands were used to stabilize and protect the Mg₂²⁺ and Zn₂²⁺ cores in all of these studies without any exceptions.

In the current study, we aim to design ligandless...
Mg−Mg and Zn−Zn single bonds in the form of cluster anions with density functional theory (DFT) methods. Anionic clusters, instead of neutral or cationic clusters, are calculated on purpose because we anticipate potential comparisons with future anion photoelectron spectroscopic studies, which have been proven to be a great experimental tool to interrogate the nature of chemical bonds in gas-phase clusters [22–32]. In the wish of constructing a M⁺−M⁺ single bond in a designer M₂²⁺(X³⁻) cluster anion, the X³⁻ kernel should better be highly stable even with three negative charges. A unique species B₇⁻ was previously reported in the Pr₂²⁺(B₇⁻) cluster [30], where the B₇ moiety is so inclined to maintain the −3 state that the Pr atom sacrificed its favorite +3 oxidation state for +2. Calculations and comparisons with anion photoelectron spectroscopy experiments reveal that the high stability of the B₇⁻ kernel is rationalized by its σ and π double aromaticity, which has been considered to be an important factor contributing to the stability of clusters [33]. The B₇⁻ cluster anion was also previously reported to have the double aromaticity [34]. In view of this, two designer clusters, Mg₂B₇⁻ and Zn₂B₇⁻ are carefully examined in this study with unbiased geometric search and chemical bonding analysis. Our results indicate that these clusters feature Mg−Mg and Zn−Zn single bonds in the form of M₂²⁺(B₇⁻), where the B₇⁻ kernel is doubly aromatic.

II. THEORETICAL METHODS

Unbiased global geometric searches using the coalescence kick (CK) program [35] were performed to locate the global minima (GM) of the M₂B₇⁻ (M=Mg and Zn) clusters. CK initially generates 10000 trial structures and optimizes them using the Gaussian 09 software [36] at the PBE0/6-31G(d) level of theory, subsequently the lowest structures are reoptimized with larger basis sets (SDD pseudopotentials [37, 38] for Zn and 6-311++G(3df,3pd) [39, 40] for other elements) at PBE0 and further ranked according to their relative energies. Structures of the six lowest isomers of Mg₂B₇⁻ and Zn₂B₇⁻ are presented in FIG. 2 and FIG. 4, respectively. The chemical bonding is analyzed using the adaptive natural density partitioning (AdNDP) method developed by Boldyrev et al. [41] at PBE0 level of theory (SDD for Zn and 6-311++G(3df,3pd) for other elements). To assess the aromaticity of the B₇⁻ moiety, the nucleus-independent chemical shift (NICS) [42, 43] calculations are also conducted for these two clusters. Vertical detachment energies, the energy difference between the ground state of the anion and the neutral with the same structure as the anion, are also calculated for the potential future comparisons with experimental data.

III. RESULTS AND DISCUSSION

The six lowest energy isomers of Mg₂B₇⁻ together with their relative energies are presented in FIG. 2 as iso 1 to iso 6. The Cartesian coordinates of all of these isomers are provided in the supplementary materials. The global minimum (GM), iso 1, has a C₂ᵥ structure where the two Mg atoms in the form of a Mg−Mg contact are positioned above a quasi-planar hexagonal B₇ moiety. The Mg−Mg bond length is 2.674 Å (Table I), much shorter than those in the “naked” Mg₂²⁺ dication [3] and the synthesized ligand protected L⁻⁻Mg⁺−Mg⁺−L⁻ molecule [5], suggesting that the B₇⁻ kernel provides a phenomenal stabilizing effect to the Mg₂B₇⁻ moiety. The other isomers are at least 0.19 eV higher in energy than the GM. Isomers with such a high energy difference can be easily identified in low-temperature gas-phase experiments [24], therefore, we anticipate a high viability for the potential future experimental observation of this particular GM cluster anion.

To further investigate the bonding situation, we have also performed the AdNDP analysis of the GM of the Mg₂B₇⁻ cluster (FIG. 3). There is clearly a Mg−Mg σ single bond with a occupation number (ON) of 1.98 [e], which is almost a classical two-center-two-electron (2c−2e) bond. The peripheral six boron atoms in the B₇ moiety form six 2c−2e σ single bonds, with ONs ranging from 1.87 [e] to 1.90 [e]. Of particular importance are the two sets of multi-center bonds: three in-plane seven-center two-electron (7c−2e) σ bonds (ON=2.0 [e])

![FIG. 2 Six lowest isomers and their relative energies of the Mg₂B₇⁻ cluster. Mg atoms are in yellow and B atoms are in pink.](image-url)
TABLE I  Bond length comparisons in different systems.

<table>
<thead>
<tr>
<th>System</th>
<th>M$_2$ cluster</th>
<th>M$_2$ $^{2+}$ dication</th>
<th>M$_2$L$_2$ molecule</th>
<th>work</th>
</tr>
</thead>
</table>

FIG. 3 AdNDP analyses of the chemical bonding in the GM of the Mg$_2$B$_7$– cluster at the PBE0/6-311++G(3df,3pd) level of theory.

<table>
<thead>
<tr>
<th>System</th>
<th>NICS(1)</th>
<th>NICS(1)$_{zz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_2$B$_7$–</td>
<td>−39.90</td>
<td>−56.59</td>
</tr>
<tr>
<td>Zn$_2$B$_7$–</td>
<td>−46.64</td>
<td>−60.68</td>
</tr>
</tbody>
</table>

FIG. 4 Six lowest isomers and their relative energies of the Zn$_2$B$_7$– cluster. Zn atoms are in blue and B atoms are in pink.

and three in-plane 7c–2e π bonds (ON=1.86–1.99 [e]), which represent the σ and π double aromaticity in the B$_7$– kernel. These two sets of bonds are reminiscent of the case in PrB$_7$– [30], both of which fulfill the Hückel 4n+2 rule with n=1. These almost fully occupied bonds on the B$_7$ moiety further confirm that it is in the −3 state. Nucleus-independent chemical shifts, NICS(1) and NICS(1)$_{zz}$ are calculated as an additional indicator for the aromaticity (Table II). The large negative values are consistent with the assessment of σ and π double aromaticity. Vertical detachment energy (VDE), the energy difference between the GM of the anionic Mg$_2$B$_7$– and the corresponding neutral with the same structure as the anion, is calculated to be 2.79 eV for future comparisons with the experimental data.

The six lowest energy isomers of Zn$_2$B$_7$– and the AdNDP analyses of the GM iso 1 are exhibited in FIG. 4 and FIG. 5 respectively. The Cartesian coordinates of all of these isomers are provided in the supplementary materials. The GM of Zn$_2$B$_7$– is structurally similar to that of Mg$_2$B$_7$–, and the AdNDP results also reveal a Zn–Zn single bond facilitated by the σ and π double aromaticity in the B$_7$– kernel. The Zn–Zn bond length is 2.363 Å (Table I), shorter than that in the “naked” Zn$_2$ $^{2+}$ dication [5], but slightly longer than the synthesized ligand protected L$^{-}$–Zn$^{+}$–Zn$^{+}$–L$^{-}$ molecule [17]. NICS(1) and NICS(1)$_{zz}$ again show large negative values (Table II), indicative of high aromaticity. The other isomers are at least 0.21 eV higher in energy than the GM. VDE of the GM of Zn$_2$B$_7$– is calculated to be 2.94 eV for future comparisons with the experimental data.

IV. CONCLUSION

To conclude, here we have reported a DFT study of the designer M$_2$B$_7$– (M=Mg, Zn) clusters where Mg–Mg and Zn–Zn single bonds are formed as a re-
result of the presence of the highly stable $B_7^{3-}$ moiety. We predicted that the global minima of the $M_2B_7^-$ (M=Mg, Zn) clusters have $C_{2v}$ structures where the $M-M$ bonds are positioned above a quasi-planar hexagonal $B_7$ moiety. AdNDP analyses reveal classical $M-M$ single bonds with occupation numbers that are almost 2.0, as well as the $\sigma$ and $\pi$ double aromaticity in $B_7^{3-}$, which is accountable for the unusually high stability of the clusters. NICS results also indicate high aromaticity of the $B_7^{3-}$ kernels in these two clusters. Based on the current study, we anticipate that the $B_7^{3-}$ kernel could potentially be used as a building block for the synthesis of other ionic compounds, and that the two exotic clusters can be experimentally synthesized and characterized spectroscopically in the gas phase in the near future.

Supplementary materials: The Cartesian coordinates of all of the six lowest energy isomers of Mg$_2$B$_7^-$ and Zn$_2$B$_7^-$ are available.

V. ACKNOWLEDGMENTS

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