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# The unique sandwich $K_6Be_2B_6H_6$ cluster with a real borozene $B_6H_6$ core†

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Theoretical evidence is reported for a boron-based  $K_6Be_2B_6H_6$  sandwich cluster, showing a perfectly  $D_{6h}$   $B_6H_6$  ring, being capped by two tetrahedral  $K_3Be$  ligands. Due to the comfortable charge transfer, the sandwich is viable in  $[K_3Be]^{3+}[B_6H_6]^{6-}[BeK_3]^{3+}$  ionic complex in nature. The  $[B_6H_6]^{6-}$  core with  $6\pi$  aromaticity vividly imitates the benzene ( $C_6H_6$ ), occurring as a real borozene. In contrast, the tetrahedral  $[K_3Be]^{3+}$  ligand is  $2\sigma$  three-dimensional aromatic, acting as the simple superatom. Thus, this complex possesses a collectively three-fold  $2\sigma/6\pi/2\sigma$  aromaticity. The interlaminar interaction is governed by the robust electrostatic attraction. The unique chemical bonding gives rise to interesting dynamic fluxionality.

## 1. Introduction

The electron-deficiency of boron leads to unconventional structures in its allotropes and compounds,<sup>1–11</sup> which is quite different from its neighbour carbon. The pure boron clusters favor the (quasi-)planar geometries over a wide range of sizes. Most of the planar boron clusters are controlled by the double ( $\sigma + \pi$ ) aromaticity, especially, their  $\pi$  frameworks are analogous to those in benzene<sup>1,12,13</sup> or polycyclic aromatic hydrocarbons (PAHs).<sup>14–17</sup> The planar  $B_7^{3-}$ ,  $B_8^{2-}$ , and  $B_9^-$  clusters<sup>12,18–22</sup> are representative, possessing the identical  $6\pi$  aromaticity to  $C_5H_5^-$ ,  $C_6H_6$ , and  $C_7H_7^+$ . Thus, they are endowed a relevant name of “borozene” by L. S. Wang, albeit that they are  $6\sigma$  aromatic as well.<sup>23</sup> The “borozene” was first proposed for the planar  $B_{12}H_6$  cluster by N. G. Szwacki.<sup>24</sup> Moreover, the metal-doped boron molecular wheels<sup>25–30</sup> and various inorganic benzene analogues<sup>31,32</sup> with double aromaticity are also widely investigated.

Strictly speaking, the real “borozene” is corresponding to the planar and aromatic  $B_6H_6^{6-}$  ring, assuming as a derivative of  $C_6H_6$  by replacing the C atom with  $B^-$ , just like the  $CH_4$  and  $BH_4^-$  anion. However, the boron hydrides and their dianion species like forming the three-dimensional (3D) geometries, the latter are extremely stable with the 3D aromaticity.<sup>33</sup> Thus, it is more challenging to flatten the boron hydrides in chemistry. Additionally, the repulsion in highly charged  $B_6H_6^{6-}$  is drastic, need to neutralize with the counter-cations. In 2003, A. I.

Boldyrev computationally investigated the  $Li_6B_6H_6$  cluster in the spirit of  $C_6H_6$ , providing a theoretical proof for existence of aromatic  $B_6H_6^{6-}$  motif, albeit with a somewhat low  $D_{2h}$  symmetry.<sup>34,35</sup> The chemists have paid a lot of efforts into designing the transition metal centred  $M@B_6H_6$  molecular wheels. Unfortunately, none of  $B_6H_6$  motifs can be recognized as real “borozene” in view of the strong covalent interaction between the central metal atom and  $B_6H_6$  ring, and abnormal charge distribution.<sup>36–39</sup> Last year, the author computationally reported a “Big Mac” sandwich of  $Rb_6Be_2B_6$  cluster, consisting of a hexagonal  $B_6$  ring and two tetrahedral  $Rb_3Be$  ligands, which skilfully mimics the style of ferrocene. The hexagonal  $B_6$  core exists in the  $B_6^{6-}$  charge state with double  $6\pi/6\sigma$  aromaticity, being sufficiently stable in the cationic field provided by two  $[Rb_3Be]^{3+}$  ligands.<sup>40</sup> The bare planar  $B_6$  ring as a structural motif has been found in the crystal structure of a solid state phase ( $Ti_7Rh_4Ir_2B_8$ ),<sup>41</sup> and be discovered in some inverse sandwich clusters.<sup>28,42,43</sup> One interesting question arises, whether the planar  $[B_6H_6]^{6-}$  ring can be stabilized in the similar field of counter-cation? If it is feasible, the real “borozene” will be achieved.

The target of present work lies in probing the viability of aromatic  $[B_6H_6]^{6-}$  in  $K_6Be_2B_6H_6$  cluster, which is consist of a perfectly planar  $B_6H_6$  ring and two tetrahedral  $K_3Be$  ligands. The natural charge analyses show that  $K_6Be_2B_6H_6$  cluster is a typical ionic complex, can be described by  $[K_3Be]^{3+}[B_6H_6]^{6-}[BeK_3]^{3+}$  formula. The perfectly planar  $[B_6H_6]^{6-}$  ring possesses the  $6\pi$  aromaticity merely, occurring as a real “borozene”. In contrast, the tetrahedral  $[K_3Be]^{3+}$  ligand with  $2\sigma$  delocalized electrons has the 3D aromaticity (or spherical aromaticity), serving as the superatom. Thus, this sandwich cluster has a collectively three-fold  $2\sigma/6\pi/2\sigma$  aromaticity, whose three components are hold together *via* the robust electrostatic attraction. We believe that the stabilization of  $[B_6H_6]^{6-}$

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borozene in  $K_6Be_2B_6H_6$  complex is not an individual case. The planar aromatic  $[B_5H_5]^{6-}$  and  $[B_7H_7]^{6-}$  ring might be viable in such sandwich complexes.

## 2. Methods

We have theoretically designed a quaternary  $K_6Be_2B_6H_6$  sandwich cluster basing on the concept of charge transfer and multi-fold aromaticity. The potential energy surface scan for  $K_6Be_2B_6H_6$  cluster was performed using the Coalescence Kick (CK) algorithm<sup>44,45</sup> at the B3LYP/6-31G level, aiding with the manual constructions. Various possible initial structures were explored and fully reoptimized at the PBE0/6-311+G(d,p) level.<sup>46</sup> Vibrational frequencies were checked at the same level to guarantee that all presented isomers are true minima. The accurate energies of top five low-lying isomers at the PBE0/6-311+G(d,p) level were further estimated at the single-point CCSD(T)/6-311+G(d,p)//PBE0/6-311+G(d,p) level.<sup>47</sup> The transition state (TS) structures were searched using the QST2 method, and verified by intrinsic reaction coordinate (IRC) calculations.

For interpreting the stabilization of  $K_6Be_2B_6H_6$  cluster, we have performed the Wiberg bond indices (WBIs) and natural atomic charges calculation using the NBO 6.0 program<sup>48</sup> at the PBE0/6-311+G(d,p) level. Chemical bonding was elucidated using the canonical molecular orbital (CMO), electron localization functions (ELFs),<sup>49,50</sup> and adaptive natural density partitioning (AdNDP) methods.<sup>51</sup> The AdNDP calculations were performed at the PBE0/6-31G level due to the low sensitivity to the theoretical level. The ELFs and AdNDP data were visualized using Molekel 5.4.0.8.<sup>52</sup> The nucleus-independent chemical shifts (NICSS)<sup>53</sup> were calculated at the PBE0/6-311+G(d,p) level. Born–Oppenheimer molecular dynamics (BOMD) simulations were performed at the PBE0/6-31G\* level at the temperature of 300 and 600 K.<sup>54</sup> All electronic structure calculations and BOMD simulation were done using the Gaussian 09 package.<sup>55</sup>

## 3. Results and discussion

### 3.1. Geometric structures

Extensive structural searches and density functional theory calculations at the PBE0/6-311+G(d,p) level suggest that the  $K_6Be_2B_6H_6$  cluster possesses two almost degenerated isomers (Fig. 1), the global minimum (GM) ( $D_{3d}$ ,  $^1A_{1g}$ ) and the closest low-lying isomer (LM) ( $D_{3h}$ ,  $^1A'_1$ ). Both isomers adopt the

fascinating sandwich architectures, featuring a perfectly  $D_{6h}$   $B_6H_6$  ring being jammed by two tetrahedral  $K_3Be$  ligands. As a whole, two isomers are ingeniously assembled on the basis of the hierarchy of electronegativity. They are discrepant in assembling style of  $K_3Be$  ligands, a staggered fashion for GM and eclipsed one for LM. Their cartesian coordinates are given in Table S1 (ESI†). At the PBE0/6-311+G(d,p) level,  $D_{3d}$  ( $^1A_{1g}$ ) GM is marginally more stable by 0.04 eV than  $D_{3h}$  ( $^1A'_1$ ) LM with the zero-point energy (ZPE) corrections. Noted the dispersion corrections are not sensitive for present system according to the results at the PBE0-D3/6-311+G(d,p) level. The relative energies of two degenerated isomers were further refined at the CCSD(T)/6-311+G(d,p)//PBE0/6-311+G(d,p) level, which gives an energy distinction of 0.05 eV merely. The  $T_1$  diagnostic factors of CCSD(T) for the GM and LM are 0.019, indicating the reliable CCSD(T) data. The other low-lying isomers (see Fig. S1, ESI†) are highly unstable, being at least 0.34 eV above the GM at the CCSD(T) level. Frankly, given the extremely complicated potential energy surface, we cannot completely ensure the true global minimum of the quaternary system. We have performed the minima hopping (MH)<sup>56</sup> search for this system (about 500 stationary points) as well, and did not find more stable isomers than the  $D_{3d}$  ( $^1A_{1g}$ ) GM structure.

### 3.2. The bond distances, Wiberg bond indices and natural atomic charges

The bond distances for  $D_{3d}$  ( $^1A_{1g}$ ) GM and  $D_{3h}$  ( $^1A'_1$ ) LM at the PBE0 level are shown in Fig. 1. Two structures have almost identical bond distances, all of them are within 0.01 Å, apart from the K–K bonds (0.04 Å). Specifically, the B–B distances are 1.67 Å in the GM and 1.68/1.67 Å in the LM, respectively, being slightly shorter than the standard B–B single bond (1.70 Å).<sup>57</sup> The B–H bond distances are 1.23 Å. The B–Be/Be–K/K–K bond distances are distinctly longer than their referenced single bonds, suggesting the weak covalent interaction of them.

The WBIs for GM and LM structures are in accordance with the bond distances. The B–B bonds have the WBIs of 1.34 for the  $D_{3d}$  ( $^1A_{1g}$ ) GM (Fig. S2(a), ESI†) and 1.35/1.33 for  $D_{3h}$  ( $^1A'_1$ ) LM (Fig. S2(c), ESI†), being intermediate between the single and double bonds. Thus, they are dominated by the delocalized bonds apart from the two-center two-electron (2c–2e)  $\sigma$  bond. The WBIs of B–H bonds is 0.93, representing the normal single bond. The Be–K/K–K bonds with the nonnegligible WBIs of

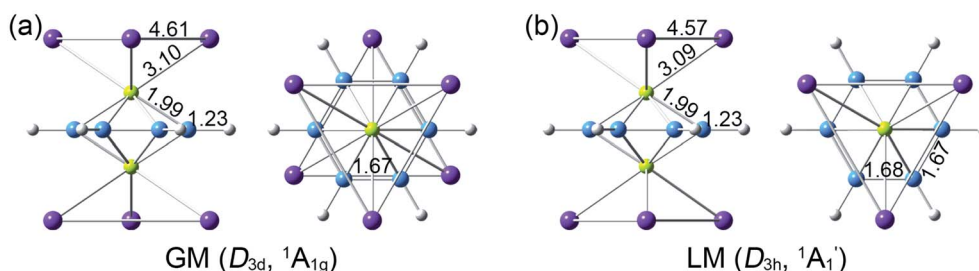


Fig. 1 Optimized geometries for (a)  $D_{3d}$  ( $^1A_{1g}$ ) global-minimum (GM) and (b)  $D_{3h}$  ( $^1A'_1$ ) low-lying isomer (LM) of  $K_6Be_2B_6H_6$  cluster at the PBE0/6-311+G(d,p) level, along with the bond distances (in Å). Both side- and top-views are presented.



0.21/0.13 have somewhat strong covalent interaction than B–Be bonds, the WBIs of latter is negligible (only 0.07), which leads to an integrally tetrahedral  $K_3Be$  ligands in two isomers. Furthermore, the Be–K and K–K bonds in  $K_3Be$  ligand have a collective WBIs of 1.02, being in line with one four-center two-electron ( $4c-2e$ ) bond.

As for the natural atomic charges, the  $D_{6h}$   $B_6H_6$  rings in  $D_{3d}$  ( $^1A_{1g}$ ) GM and  $D_{3h}$  ( $^1A'_1$ ) LM have the same charge distribution ( $-0.91|e|$  for B and  $-0.02|e|$  for H, see Fig. S2(b and d), ESI†). Thus, the  $B_6H_6$  rings exist in the  $[B_6H_6]^{6-}$  charged state, being isoelectronic with  $C_6H_6$ . The Be and K atom carries a positive charge of  $+0.94|e|$  and  $+0.63/0.62|e|$ , respectively. The tetrahedral  $K_3Be$  ligand has a collectively positive charge of  $+2.83/2.80|e|$ , being in line with  $[K_3Be]^{3+}$  species. Thus, both GM and LM could be viewed as the  $[K_3Be]^{3+}[B_6H_6]^{6-}[BeK_3]^{3+}$  ionic complexes, in which the electron-deficiency of  $B_6H_6$  is reasonably compensated by two tetrahedral  $K_3Be$  ligands.

### 3.3. Chemical bonding

In order to interpret the unique geometries and stability of the  $D_{3d}$  GM ( $^1A_{1g}$ ) and  $D_{3h}$  ( $^1A'_1$ ) LM sandwiches, we performed the systematic chemical bonding analyses for them. The  $D_{3d}$  GM ( $^1A_{1g}$ ) has 34 valence electrons in total, occupying 17 CMOs (Fig. 2). According to their constituent atomic orbitals (AOs), these occupied CMOs are reasonably sorted into four subsets. In subset (a), there are six  $\sigma$  CMOs composed by the B  $2s/2p$  AOs, which can be directly recombined as six Lewis  $2c-2e$  B–B  $\sigma$  bonds. The six CMOs in subset (b) originated from the radical B  $2p$  AOs and H  $1s$  AOs are shown one-to-one correspondence with those in subset (a), which describes the six Lewis  $2c-2e$  B–H  $\sigma$  bonds in nature. The subset (c) exhibits a perfectly  $\pi$  sextet on the  $D_{6h}$   $B_6H_6$  ring, faithfully mimicking that in organic

benzene, although the degenerated HOMO–3/HOMO–3'  $\pi$  CMOs have slight hybridization with the HOMO–2/HOMO–2'  $\sigma$  CMOs in subset (b). Thus, the  $B_6H_6$  ring possesses  $6\pi$  aromaticity according to the  $(4n + 2)$  Hückel rule. These 15 CMOs in subsets (a–c) with 30 occupying electrons are located on the  $B_6H_6$  motif, supporting the assertion of  $[B_6H_6]^{6-}$  charge state of NBO results. Two CMOs in subset (d) are clearly located on the two tetrahedral  $K_3Be$  ligands, which can be directly recombined into two  $4c-2e$   $\sigma$  bonds, one on each  $K_3Be$  tetrahedron. Thus, the tetrahedral  $K_3Be$  ligand has the  $2\sigma$  3D aromaticity according to  $2(n + 1)^2$  electron counting rule.<sup>58</sup> It can also be viewed as a superatom.<sup>59,60</sup>

On the whole, the CMOs in subsets (a) and (b) describe the interactions of B–B and B–H of  $B_6H_6$  ring, being in line with its six localized B–B and B–H  $\sigma$  bonds. The CMOs in subsets (c) and (d) represent the delocalized frameworks, including of the  $6\pi$  aromaticity on  $B_6H_6$  ring and  $2\sigma$  aromaticity on two  $K_3Be$  tetrahedrons, which collectively renders the three-fold ( $2\sigma/6\pi/2\sigma$ ) aromaticity for the  $[K_3Be]^{3+}[B_6H_6]^{6-}[BeK_3]^{3+}$  complex. The three-fold aromaticity underlies the stability of the GM structure. Moreover, the orbital component analysis suggests that HOMO–5 has a 14.2% Be  $2s$  AOs contribution, in which two Be  $2s$  AOs pretends to be the “ $p_z$ ” style, taking part in the globally delocalized  $\pi$  bonding. As for the degenerated HOMO–3/HOMO–3', there is a 12.0% Be  $2p_x/2p_y$  AOs contribution, being bonding to the B  $2p_z$  AOs of  $B_6H_6$  ring. The minimal contribution of Be  $2s/2p_x/2p_y$  AOs to three  $\pi$  CMOs is responsible for the extremely weak covalent interaction of B–Be bonds. The CMOs pattern of  $D_{3h}$  ( $^1A'_1$ ) LM is similar to that in  $D_{3d}$  ( $^1A_{1g}$ ) GM, and its degenerated  $\pi$  CMOs with less hybridization are more elegant (Fig. S3, ESI†).

The above CMOs bonding images of  $D_{3d}$  ( $^1A_{1g}$ ) GM and  $D_{3h}$  ( $^1A'_1$ ) LM are fully supported by the AdNDP analyses. As

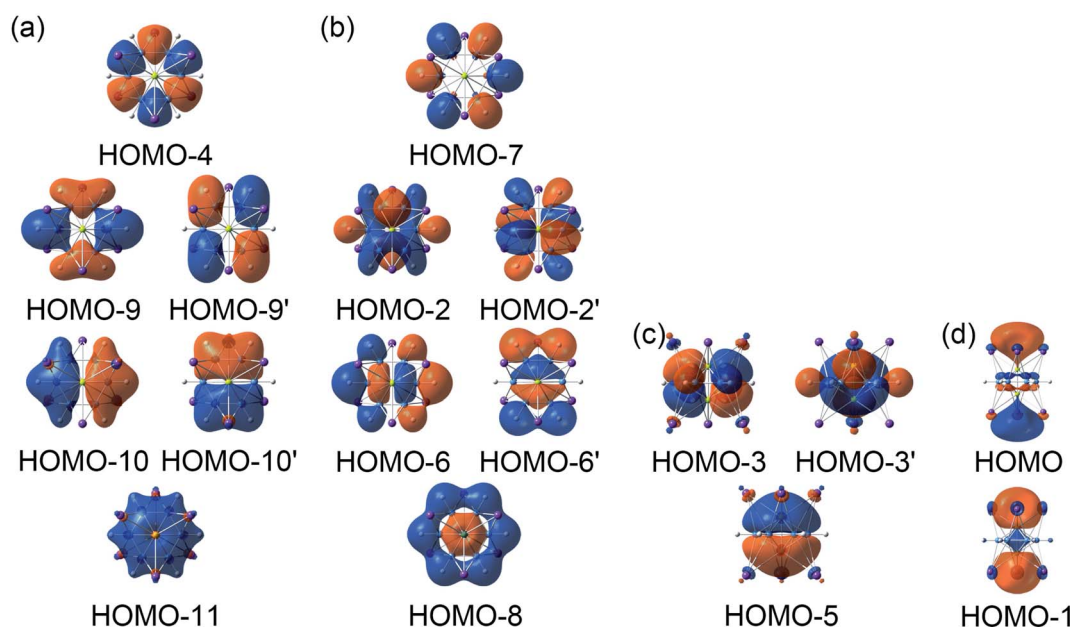


Fig. 2 Occupied canonical molecular orbitals (CMOs) of  $D_{3d}$  ( $^1A_{1g}$ ) GM for  $K_6Be_2B_6H_6$  cluster. (a) Six  $\sigma$  CMOs for six B–B  $\sigma$  bonds. (b) Six  $\sigma$  CMOs for six B–H  $\sigma$  bonds. (c) Three delocalized  $\pi$  CMOs on  $B_6H_6$  ring. (d) Two  $\sigma$  CMOs over two tetrahedral  $K_3Be$  ligands.



shown in Fig. 3, the AdNDP result for the  $D_{3d}$  ( $^1A_{1g}$ ) GM clearly reproduces six localized 2c–2e B–B and B–H  $\sigma$  bonds, as well as two delocalized 4c–2e  $\sigma$  bonds on tetrahedral  $K_3Be$  ligands and three delocalized six-center two-electron (6c–2e)  $\pi$  bonds on  $B_6H_6$  ring. All the occupation numbers (ONs) are ideal. The delocalized  $\sigma$  and  $\pi$  frameworks further confirm the three-fold ( $2\sigma/6\pi/2\sigma$ ) aromaticity of the system. Note that the scheme of 4c–2e  $\sigma$  bond in  $K_3Be$  tetrahedron is more rational than the alternative three-center two-electron (3c–2e)  $\sigma$  bond on  $K_3$  triangle, the latter gives rise to a rather low ON of 1.48|e|. It means that Be atom has a remarkable 20.4% contribution to the 4c–2e  $\sigma$  bond, being close to K atom (26.5%).<sup>40</sup> The identical AdNDP bonding pattern is observed in the  $D_{3h}$  ( $^1A'_1$ ) LM (Fig. S4†).

### 3.4. Interaction between $B_6H_6$ ring and tetrahedral $K_3Be$ ligands

As mentioned above, the  $B_6H_6$  ring and two tetrahedral  $K_3Be$  ligands are viable in hexavalent anion  $[B_6H_6]^{6-}$  and trivalent cation  $[K_3Be]^{3+}$ , respectively. The interaction between the  $B_6H_6$  ring and tetrahedral  $K_3Be$  ligands should be mainly dominated by the robust electrostatic attraction. We qualitatively estimate the ionic interaction by manually expanding the distances of two Be atoms to 10 Å, and subsequently performing a single-point calculation at the same level of theory. In this case, the energy difference with respect to the ground state structure is mainly attributed to the electrostatic attraction. The calculated ionic interaction energies are as high as 18.35 eV for the  $D_{3d}$

( $^1A_{1g}$ ) GM and  $D_{3h}$  ( $^1A'_1$ ) LM. Thus, the sandwiches are quite stable against dissociation. Alternatively, we also estimated the electrostatic attraction between the  $Be_2B_6H_6$  inverse sandwich and the two  $K_3$  rings by separating the  $K_3$  rings to 10 Å distance, which are 5.09 eV for the GM and 5.01 eV for LM, respectively.

Furthermore, we calculated the dissociation energy of  $[K_3Be]^{3+}$  units in  $K_6Be_2B_6H_6$  cluster according to the following formula,  $[K_3Be]^{3+}[B_6H_6]^{6-}[BeK_3]^{3+}$  ( $D_{3d}$ ,  $^1A_{1g}$ ) =  $[K_3Be]^{3+}[B_6H_6]^{6-}[BeK_2]^{2+}$  ( $C_s$ ,  $^1A'$ ) +  $K^+$ . The  $[K_3Be]^{3+}[B_6H_6]^{6-}[BeK_2]^{2+}$  ( $C_s$ ,  $^1A'$ ) is obtained from the GM structure by removing a K atom, and performing a fully optimization using its anion state at the same level. Such calculation can be used to evaluate quantitatively the energetics of the combination of  $[K_2Be]^{2+}$  and  $K^+$  with respect to the tetrahedral  $[K_3Be]^{3+}$  ligands in  $K_6Be_2B_6H_6$  cluster. The result suggests that the dissociation energy of tetrahedral  $[K_3Be]^{3+}$  is as high as 4.90 eV, hinting the tetrahedral  $[K_3Be]^{3+}$  ligands is enough stable, and against disintegrating into the  $[BeK_2]^{2+}$  and  $K^+$  components.

### 3.5. The $B_6H_6$ ring in $K_6Be_2B_6H_6$ complex: a real borozene

The real “borozene” should accurately imitate the  $C_6H_6$  in both molecular structure and chemical bonding. Bonding analyses indicate that the  $K_6Be_2B_6H_6$  cluster can be described as  $[K_3Be]^{3+}[B_6H_6]^{6-}[BeK_3]^{3+}$  complex. Here, the  $D_{6h}$   $[B_6H_6]^{6-}$  ring is isoelectronic with  $C_6H_6$ , possessing the identical  $\pi$  sextet and Lewis B–B/B–H  $\sigma$  bond skeletons with the  $C_6H_6$  (Fig. 2(c) and 3). Actually, it is an example of electronic transmutation, the boron

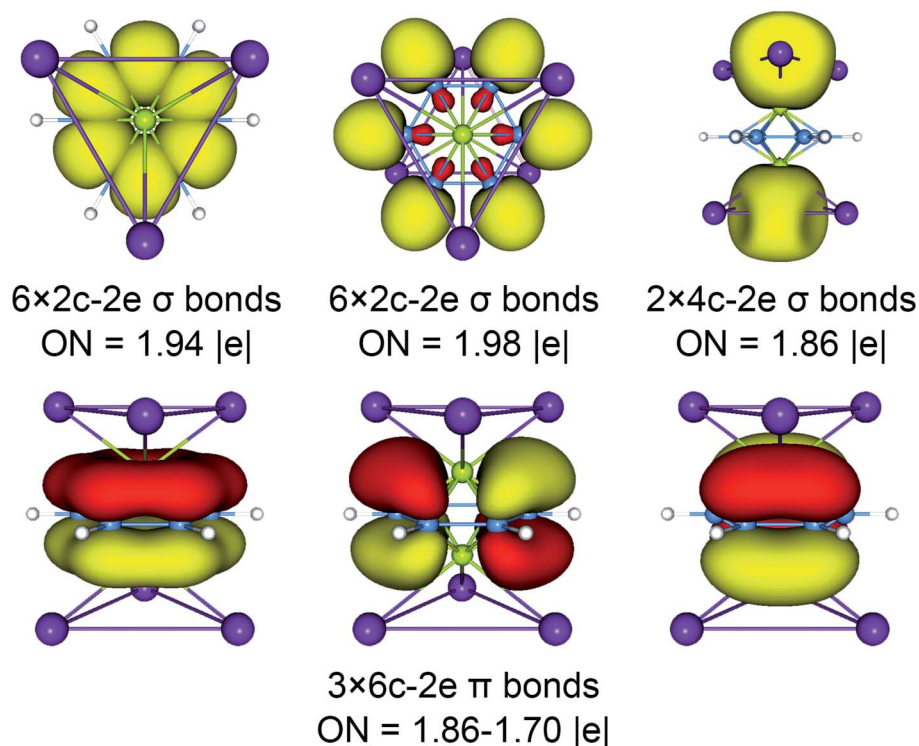


Fig. 3 Adaptive natural density partitioning (AdNDP) bonding pattern of  $D_{3d}$  ( $^1A_{1g}$ ) GM for  $K_6Be_2B_6H_6$  cluster. Occupation numbers (ONs) are indicated.





atom acquiring an extra electron is transmuted into the carbon.<sup>64</sup> Therefore, it truly occurs as a “borozene”. The ELF data provide the further theoretical proof. As shown in Fig. 4, the  $D_{6h}$   $[B_6H_6]^{6-}$  ring in the  $D_{3d}$  ( $^1A_{1g}$ ) GM and  $D_{3h}$  ( $^1A'_1$ ) LM exhibit the identical bonding patterns (ELF $_{\sigma}$  and ELF $_{\pi}$ ) with the  $C_6H_6$ , despite the bifurcation value of ELF $_{\pi}$  for the  $[B_6H_6]^{6-}$  ring in  $D_{3d}$  ( $^1A_{1g}$ ) GM is somewhat lower (0.58) (Fig. 4(a)), which is mainly attributed to the weak hybridization of  $\pi$  CMOs (as indicated above). Interestingly, the  $[B_6H_6]^{6-}$  ring in  $D_{3h}$  ( $^1A'_1$ ) LM presents an ideal bifurcation value (Fig. 4(b)), which positively confirms the  $6\pi$  aromaticity of  $[B_6H_6]^{6-}$  ring. Compared with the  $C_6H_6$  (Fig. 4(c)), the  $D_{3d}$  ( $^1A_{1g}$ ) GM and  $D_{3h}$  ( $^1A'_1$ ) LM have two additional 4c–2e  $\sigma$  bonds on tetrahedral  $[K_3Be]^{3+}$  ligands, being in line with their three-fold ( $2\sigma/6\pi/2\sigma$ ) aromaticity, which are responsible for the stabilization for  $B_6H_6$  and  $K_3Be$  components. The three-fold ( $2\sigma/6\pi/2\sigma$ ) aromaticity in  $D_{3d}$  ( $^1A_{1g}$ ) GM cluster is confirmed independently by the NICS calculation at the PBE0/6-311+G(d,p) level. The calculated NICS and NICS $_{zz}$  values are enough negative:  $-19.8$  and  $-25.4$  ppm for the center of  $K_3Be$  ligand, and  $-16.0$  and  $-22.8$  ppm for  $0.5$  Å above the center of  $B_6H_6$  ring.

### 3.6. The dynamic fluxionality

The three-fold ( $2\sigma/6\pi/2\sigma$ ) aromaticity and robust electrostatic attraction in the  $[K_3Be]^{3+}[B_6H_6]^{6-}[BeK_3]^{3+}$  complex would facilitate interesting dynamic fluxionality of the cluster.<sup>62–64</sup> We obtained two TS structures (Fig. 5),  $D_{3d}$  ( $^1A_{1g}$ ) TS $_1$  and  $D_{3h}$  ( $^1A'_1$ ) TS $_2$ , along with the displacement vectors for two soft vibrational modes of  $46.2$  and  $24.7$   $cm^{-1}$  of the GM (Fig. S5(a)†). The TS $_1$  and TS $_2$  can be located from the GM by an independent rotation of  $30^\circ$  for  $B_6H_6$  ring or an opposite rotation of  $30^\circ$  for each tetrahedral  $BeK_3$  ligand with the  $B_6H_6$  ring fixation, respectively. Alternatively, they also can be located from the LM by the similar operation. The LM structure has two soft vibrational modes of  $58.8$  and  $8.9$   $cm^{-1}$  (Fig. S5(b)†), relating to the intramolecular rotations. At the PBE0/6-311+G(d,p) level, the TS $_1$  and TS $_2$  structures are  $0.10$  and  $0.18$  eV above the GM with the ZPE corrections, which are refined to  $0.14$  and  $0.23$  eV at the single point CCSD(T) level. The small energy barriers imply that the clusters are dynamically fluxional at room temperature. The structural evolution process is illustrated in Fig. 5. Two pathways are demonstrated for the rotation of  $B_6H_6$  ring (blue line) and the

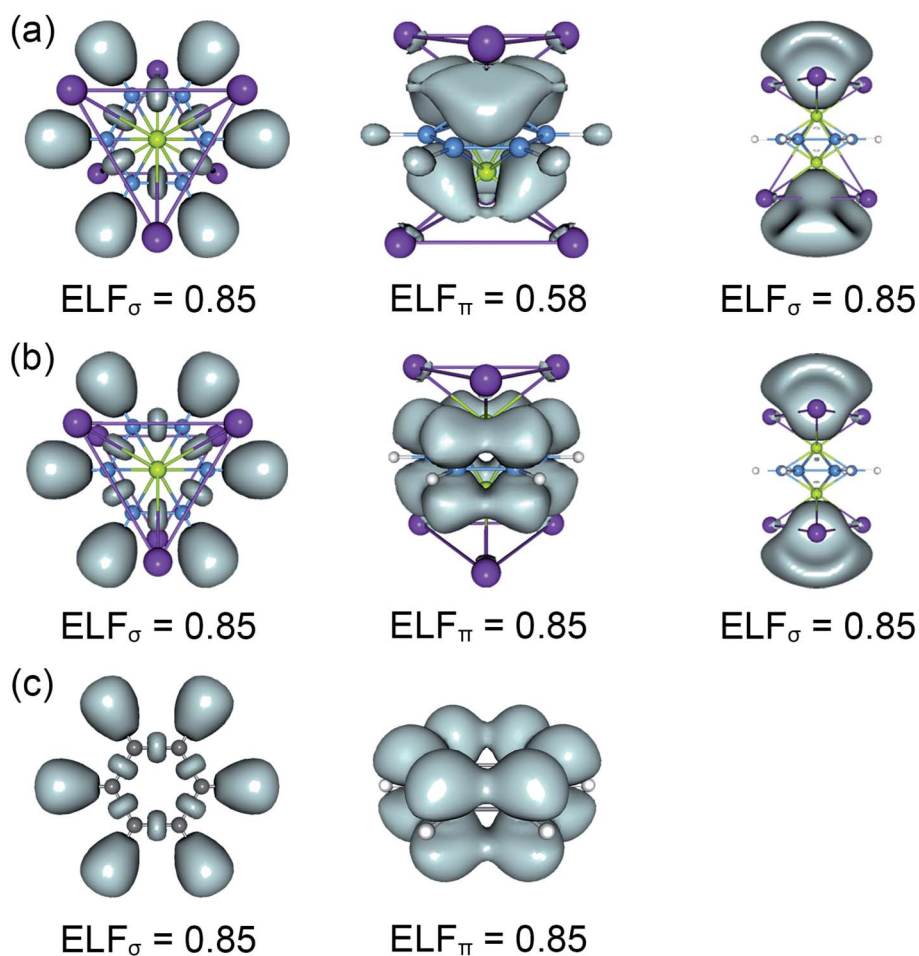


Fig. 4 Electron localization functions (ELFs) of (a)  $D_{3d}$  ( $^1A_{1g}$ ) GM and (b)  $D_{3h}$  ( $^1A'_1$ ) LM for  $K_6Be_2B_6H_6$  cluster, and (c)  $D_{6h}$  ( $^1A_{1g}$ )  $C_6H_6$ . The images support the three-fold ( $2\sigma/6\pi/2\sigma$ ) aromaticity of  $K_6Be_2B_6H_6$  cluster and the assertion of borozene for  $B_6H_6$  ring.



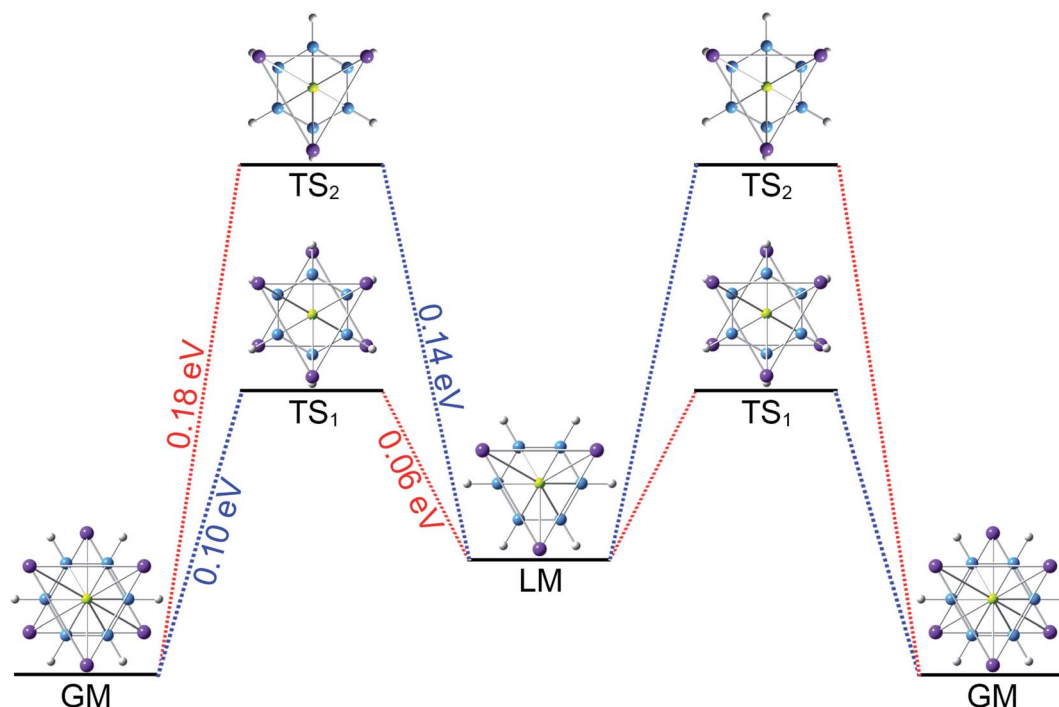


Fig. 5 Structural evolution of  $K_6Be_2B_6H_6$  cluster during dynamic rotations. Two pathways are demonstrated for the rotation of  $B_6H_6$  ring (blue curve) and the opposite rotation of two tetrahedral  $K_3Be$  ligands (red curve). The energy barriers of two transition state (TS) structures are 0.10 eV for  $TS_1$  and 0.18 eV for  $TS_2$  at the PBE0/6-311+G(d,p) level.

opposite rotation of two tetrahedral  $K_3Be$  ligands (red line). The BOMD simulation performed at the temperature of 300 K at the PBE0/6-31G\* level faithfully confirm the above assessment (see the video in the ESI†), vividly demonstrating the fascinating dynamic structural fluxionality of the system. It should be noted that the structural integrity of  $K_6Be_2B_6H_6$  cluster is maintained consistently even at the higher temperature of 600 K.

## 4. Conclusions

We have computationally designed a boron-based  $K_6Be_2B_6H_6$  sandwich cluster, featuring a  $B_6H_6$  ring being sandwiched by two tetrahedral  $K_3Be$  ligands. There is significant charge transfer from the  $K_3Be$  tetrahedrons to  $B_6H_6$  ring (three electrons for each  $K_3Be$ ), yielding the  $[K_3Be]^{3+}[B_6H_6]^{6-}[BeK_3]^{3+}$  complex. The  $[B_6H_6]^{6-}$  ring (with  $6\pi$  delocalized electrons) precisely mimics the benzene in both geometry and chemical bonding, occurring as a real borozene. The tetrahedral  $[K_3Be]^{3+}$  ligand with  $2\sigma$  delocalized electrons possesses the three-dimensional aromaticity, serving as a superatom in essence. Overall, the sandwich cluster is a three-fold  $2\sigma/6\pi/2\sigma$  aromatic system. The multi-fold aromaticity and robust electrostatic attraction among three motifs facilitates interesting dynamic fluxionality.

## Conflicts of interest

There are no conflicts to declare.

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