I. INTRODUCTION

The discovery in 1951 of the transition metal π-complex, ferrocene (Fe(C5H5)2), gave rise to great interest being shown in the possible structures of such compounds and in the nature of the metal-ring bonding. Subsequently, the sandwich type structures had been proposed. Among these, Fe(C5H5)2 (Refs. 4–14) and dibenzenechromium Cr(C6H6)2 (Refs. 10, 11, and 15–27) as two typical sandwich compounds have been studied extensively. For Fe(C5H5)2, a cyclopentadienyl anion (C5H5−) contributes six π electrons as π-bonding ligand and the Fe2+ (3d6) contributes six electrons, which follows the 18-electron principle. Similarly, for Cr(C6H6)2, a benzene molecule (C6H6) contributes six π electrons as π-bonding ligand and the Cr3+ (3d4) contributes six electrons, which also meets the 18-electron principle. With more studies on sandwich compounds, the ligands are various and include not only hydrocarbons, e.g., borane, CO, PH3, boron clusters, etc. The spectroscopic and theoretical studies have shown that boron clusters have planar geometries and exhibit aromatic and antiaromatic electronic properties analogous to hydrocarbons, so they are predicted to be promising molecules for coordination chemistry as potential new ligands and for materials science as new building blocks. A series of small carbone molecules containing multiple aromatic B3 and B4 units have been reported by Berndt and co-workers. Up to now, some theoretical confirmations have been reported to design potential sandwich-like complexes based on the pure boron units B3−31, B6−32,33, B7−34, B8−35, and B6−14. In particular, Zhai and co-workers have demonstrated that B12 can be viewed to be analogous to C6H6. Later, Alexandra and co-workers indicated that B12 can represent a better candidate to be a new inorganic ligand and building block of solids because of its closed shell structure with σ and π aromaticity.

Therefore, we design a new sandwich compound Cr(B12)2 based on B12 ligand. In this paper, we investigate the structural stability and electronic properties of staggered Cr(B12)2 by using density functional theory (DFT). We show that: (i) B12 unit can be a stable ligand in the sandwich Cr(B12)2 (D3d); (ii) the sandwich Cr(B12)2 (D3d) is very stable, following the 18-electron principle, as well as Fe(C5H5)2 and Cr(C6H6)2.

II. COMPUTATIONAL METHODS

Initially, we optimized the geometries of Fe(C5H5)2, Cr(C6H6)2, and Cr(B12)2 (D3d and D3h) by using the TPSSh functional. In the optimization procedure, the 6-31G* and lanl2dz basis sets are employed for ligands and metals, respectively. The calculations of the energies and HOMO-LUMO gaps are performed at the TPSSh/6-311+G* level. Ligands (including hydrocarbon/boron) are also studied at the TPSSh functional for these systems. The calculations of vertical ionization potential and vertical electron affinity (vertical optimized at the TPSSh/6-31G* level. Then, the IP = E(M+) − E(M) and EA = E(M) − E(M−) values are the vertical ionization potential and vertical electron affinity, respectively. In order to justify the use of TPSSh functional for these sandwich compounds, a benchmark calculation (Table I) on Fe(C5H5)2 compound is completed by B3LYP, M06, PBE0, and TPSSh functional with 6-311+G* basis set, and the high-level MP2 method with aug-cc-pvtz basis set. The results of the benchmark calculation and experimental data verify the reliability of the TPSSh functional for these systems. The calculations of vibrational frequencies and ultraviolet-visible (UV-vis) absorption spectra and natural bond orbital (NBO) analysis were
performed by TPSSh functional (ligands at 6-31G* and metals at lanl2dz levels). All calculations are carried out using the GAUSSIAN 09 package.  

### III. RESULTS AND DISCUSSION

#### A. Energies and stability

The optimized geometries of B\(_{12}\), Cr(B\(_{12}\))\(_{2}\) (\(D_{5d}\) and \(D_{3h}\)), Cr(C\(_{6}H_{6}\))\(_{2}\), and Fe(C\(_{5}H_{5}\))\(_{2}\) are shown in Figure 1. The XYZ coordinates of the Cr(B\(_{12}\))\(_{2}\) (\(D_{5d}\) and \(D_{3h}\)) compound can be found in the supplementary material.  

<table>
<thead>
<tr>
<th>Method(^a)</th>
<th>(E_b) (eV)(^b)</th>
<th>(\Delta\text{E}_{\text{HL}}) (eV)(^c)</th>
<th>VEA (eV)(^d)</th>
<th>VIP (eV)(^e)</th>
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</thead>
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<td>B3LYP</td>
<td>5.98</td>
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<tr>
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<td>7.06</td>
</tr>
<tr>
<td>TPSSh</td>
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<td>4.26</td>
<td>0.34</td>
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</tr>
<tr>
<td>MP2</td>
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<td>4.26</td>
<td>0.33</td>
<td>6.26</td>
</tr>
<tr>
<td>Expt.</td>
<td>-6.37(^f)</td>
<td>-0.51</td>
<td>7.05(^g)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Method: the basis set of DFT is 6-311+G*. \(^b\)\(E_b\) is binding energy. \(^c\)\(\Delta\text{E}_{\text{HL}}\) is HOMO-LUMO gap. \(^d\)VEA is vertical electron affinity. \(^e\)VIP is vertical ionization potential. \(^f\)-6.37 eV is the experimental \(E_b\) of Fe(C\(_{6}H_{6}\))\(_{2}\) (Ref. 56). \(^g\)7.05 eV is the experimental VIP of Fe(C\(_{6}H_{6}\))\(_{2}\) (Ref. 15).

The binding energies (\(E_b\)\(^h\)), HOMO-LUMO gaps, vertical electron affinities (VEAs), and vertical ionization potentials (VIPS) of sandwich compounds Fe(C\(_{5}H_{5}\))\(_{2}\), Cr(C\(_{6}H_{6}\))\(_{2}\), and Cr(B\(_{12}\))\(_{2}\) (\(D_{3h}\) and \(D_{5d}\)) are listed in Table II. Comparing with the stable compounds Fe(C\(_{5}H_{5}\))\(_{2}\) and Cr(C\(_{6}H_{6}\))\(_{2}\), we find that the staggered Cr(B\(_{12}\))\(_{2}\) is also very stable. The calculated vibrational frequencies of B\(_{12}\) · Cr · B\(_{12}\) (staggered and eclipsed) compound are shown in Figure 2. The vibrational frequencies of staggered Cr(B\(_{12}\))\(_{2}\) are verified to be all positive, so it is indeed a local minimum. But there is a small imaginary vibrational frequency for eclipsed Cr(B\(_{12}\))\(_{2}\) at 105 cm\(^{-1}\), as labeled by arrow, so the eclipsed Cr(B\(_{12}\))\(_{2}\) is a saddle point on the potential surface, which is the transition state for the rotation of the two B\(_{12}\) moieties with respect to each and is 0.51 eV higher in energy. For Fe(C\(_{5}H_{5}\))\(_{2}\), the staggered \(D_{5d}\) form is the transition state and the barrier to rotation from \(D_{3h}\) to \(D_{5d}\) is 0.04 eV (0.9 kcal/mol). For Cr(C\(_{6}H_{6}\))\(_{2}\), the barrier to rotation from \(D_{5d}\) to \(D_{3h}\) is 0.03 eV (0.75 kcal/mol). Therefore, the sandwich Cr(B\(_{12}\))\(_{2}\) is analogous to Fe(C\(_{5}H_{5}\))\(_{2}\) and Cr(C\(_{6}H_{6}\))\(_{2}\).

The calculated \(E_b\) of Fe(C\(_{5}H_{5}\))\(_{2}\) is -7.66 eV, which is consistent with experimental \(E_b\) = -6.37 eV (-147 kcal/mol). The \(E_b\) of Cr(B\(_{12}\))\(_{2}\) (\(D_{5d}\)) is -5.93 eV, smaller than Fe(C\(_{5}H_{5}\))\(_{2}\) (-7.66 eV), but larger than Cr(C\(_{6}H_{6}\))\(_{2}\) (-2.83 eV). Moreover, the HOMO-LUMO gaps of Fe(C\(_{5}H_{5}\))\(_{2}\) and Cr(C\(_{6}H_{6}\))\(_{2}\) are 4.26 eV and 3.30 eV, respectively, and the HOMO-LUMO gap of Cr(B\(_{12}\))\(_{2}\) (\(D_{5d}\)) is also very large (2.37 eV). The optical band-edge of UV-vis absorption spectra (Figure S1 in the supplementary material) is 2.29 eV, which is consistent with the computed HOMO-LUMO gap (2.37 eV). In addition, the calculated VIPS of Fe(C\(_{5}H_{5}\))\(_{2}\) and Cr(C\(_{6}H_{6}\))\(_{2}\) are 7.14 eV and 5.40 eV, which are in agreement with the experimental VIPS (Fe(C\(_{5}H_{5}\))\(_{2}\): 7.05 eV, Cr(C\(_{6}H_{6}\))\(_{2}\): 6.90 eV). To further verify the reliability of the TPSSh functional for these systems, the VEA and VIP of Fe(C\(_{5}H_{5}\))\(_{2}\) are calculated by the high-level MP2 method with aug-cc-pvtz basis set and ab initio results (VEA = -0.33 eV and VIP = 6.26 eV) conform to the TPSSh results (VEA = -0.34 eV and VIP = 7.14 eV). Besides, the energy difference between VIP and VEA of Cr(B\(_{12}\))\(_{2}\) (\(D_{5d}\)) is 5.41 eV (7.72 - 2.31), smaller than Fe(C\(_{5}H_{5}\))\(_{2}\) (7.14 + 0.34 = 7.48 eV), but near to Cr(C\(_{6}H_{6}\))\(_{2}\) (5.40 + 0.27 = 5.67 eV). In summary, the sandwich Cr(B\(_{12}\))\(_{2}\) (\(D_{5d}\)) is indeed a very stable compound.

#### B. Orbital analysis

To study the chemical bonding of these sandwich compounds Fe(C\(_{5}H_{5}\))\(_{2}\), Cr(C\(_{6}H_{6}\))\(_{2}\), and Cr(B\(_{12}\))\(_{2}\) (\(D_{5d}\)) and ligands, molecular orbital (MO) analysis was given.
Here we first make detailed orbital analysis for each ligand as follows. From the MO diagrams (Figure S2 in the supplementary material), the three delocalized \( \pi \) orbitals can be identified easily (MO = 21, 27, and 28 in Figure 3), but it is difficult to identify the delocalized \( \sigma \) orbitals. It is reported that \( \text{B}_{12} \) is triply aromatic, i.e., \( \pi \) aromatic and double \( \sigma \) aromatic.\(^{59}\) In order to gain insight into the nature of the bonding in \( \text{B}_{12} \), we apply a new tool named adaptive natural density partitioning (AdNDP) to obtain patterns of chemical bonding. The method was recently developed by Zubarev and Boldyrev.\(^{60–62}\) AdNDP is based on the concept of the electron pair as the main element of chemical bonding models, which recovers both Lewis bonding elements (1c–2e and 2c–2e objects) and delocalized bonding elements (nc–2e). In addition, we compare the results of AdNDP analysis of \( \text{B}_{12} \) with the ones of hydrocarbon ligands (including \( \text{C}_5\text{H}_5^- \) and \( \text{C}_6\text{H}_6 \)). The results of AdNDP analysis are displayed in Figure 4. According to the results of AdNDP analysis, \( \text{C}_5\text{H}_5^- \) (Figure 4(a)) has five peripheral 2c–2e C–C \( \sigma \) bonds with occupation numbers ON = 1.98 \( \text{lel} \) (superimposed on the single molecular framework), five 2c–2e C–H \( \sigma \) bonds with ON = 1.99 \( \text{lel} \) (superimposed on the single molecular framework), and three 5c–2e delocalized \( \pi \) bonds with ON = 2.00 \( \text{lel} \) responsible for the \( \pi \) aromaticity of \( \text{C}_6\text{H}_6 \). The quasi-planar \( \text{B}_{12} \) (Figure 4(c)) has nine peripheral 2c–2e \( \sigma \) bonds (three \( \sigma \) bonds with ON = 1.93 \( \text{lel} \) and six \( \sigma \) bonds with ON = 1.89 \( \text{lel} \)), three 4c–2e \( \sigma \) bonds (ON = 1.96 \( \text{lel} \)) delocalized mainly over the internal three-atomic cycle, which is responsible for \( \sigma \) aromaticity satisfying Hückel’s 4\( n \)+2 rule, three 5c–2e \( \sigma \) bonds with ON = 1.93 \( \text{lel} \) responsible for the \( \sigma \) aromaticity, and three 7c–2e \( \pi \) bonds (ON = 1.97 \( \text{lel} \)) binding the inner \( \text{B}_3 \) and the outer \( \text{B}_9 \) rings, which is responsible for the \( \pi \) aromaticity of \( \text{B}_{12} \). The above three distinct aromatic sextets (4\( n \)+2) of \( \text{B}_{12} \) are shown clearly in Figure 4(c), which is in agreement with the previous study.\(^{59}\) The delocalized 6\( \pi \)-electron \( \text{B}_{12} \) in staggered \( \text{Cr(B}_{12}\text{)}_2 \) behaves analogous to the well-known \( \text{C}_5\text{H}_5^- \) ligand in \( \text{Fe(C}_5\text{H}_5\text{)}_2 \) and \( \text{C}_6\text{H}_6 \) ligand in \( \text{Cr(C}_6\text{H}_6\text{)}_2 \).\(^{36}\) All of them can contribute six \( \tau \) electrons as effective \( \pi \)-bonding ligands in the sandwich compounds.

![FIG. 2. Vibrational frequencies of \( \text{B}_{12} \cdot \text{Cr} \cdot \text{B}_{12} \) (\( D_{3d} \) and \( D_{3h} \)) compound, the arrow shows the imaginary frequency.](image)

![FIG. 3. Delocalized \( \pi \) orbitals of \( \text{B}_{12} \) (\( \text{C}_{12} \)) cluster (molecular visualization was performed using MOLEKEL 5.4).](image)

![FIG. 4. The results of the AdNDP localization for cyclopentadienyl anion (a, \( \text{C}_5\text{H}_5^- \)), benzene (b, \( \text{C}_6\text{H}_6 \)), and the quasi-planar \( \text{B}_{12} \) cluster (c) (molecular visualization was performed using MOLEKEL 5.4).](image)
Next, we study the chemical bonding of the three sandwich compounds by MO analysis (all the canonical MOs can be found in the supplementary material). It is well known that sandwich Fe(C5H5)2 is an electronic closed-shell structure, following the 18-electron principle. Curiously, why are the 18-electron complex series very stable? We think that the 18 valence electrons should occupy nine MOs and the electronic configuration should be $s^{10}p^6d^{10}$ for shell closure similar to the one of the inert gas Ar. As expected, the nine MOs (Figure 5(a)) are identified from the canonical MO diagrams. HOMO-14 can be viewed as a super $s$-$\pi$ orbital, formed from the $4s$ orbital of metal and $\pi$ orbital of ligand. Similarly, HOMO-7 is a $4p_z$-$\pi$ orbital, HOMO-6 ($3d_{x^2-y^2}$) and HOMO-5 ($3d_{xy}$-$\pi$) are double-degenerate orbitals, HOMO-2 is a $3d_{z^2}$-$\pi$ orbital. HOMO-1 ($3d_{xy}, 3d_{xz}, 3d_{yz}$) and HOMO ($3d_{x^2-y^2}$) are also double-degenerate orbitals. According to MO analysis, the sandwich Fe(C5H5)2 has not only $d$-$\pi$ interaction, nine $spd$ orbitals of Fe atom corporately interact with the $\pi$ orbital of ligand, which is called “$spd$-$\pi$ interaction” in this work. From the shapes of orbitals we can see that the contributions of $\pi$ electrons are very small in HOMO-2, HOMO-1, and HOMO orbitals, so we presume that the three orbitals may be mainly occupied by six lone pair (LP) electrons on Fe ($3d^{10}4s^2$) atom. To confirm the above supposition, we set a very low thresholds (ON $= 0.1$ lel) in NBO analysis, and the MOs will be considered to be occupied by lone pair (LP) electrons from metal. In this way, we can evaluate the contributions of electrons from metal and ligand for each MO. Here, NBO analysis was used to calculate LP electron occupancies of MOs. For $s$, $p_x$, $p_y$, and $p_z$ orbitals of Fe (Figure 5(b)), the ONs of LPs are only 0.17 lel. For $d_{z^2}$ and $d_{xy}$ orbitals, the ONs of LPs are 0.99 lel. For $d_{x^2-y^2}$ orbital, the ON of LP is high to 1.98 lel. For $d_{xy}$ and $d_{yz}$ orbitals, the ONs of LPs are 1.85 lel. From these data we can see that $spd$-$\pi$ interaction plays an important role in Fe(C5H5)2 and HOMO-2 ($d_{z^2}$), HOMO-1 ($d_{xy}$), and HOMO ($d_{x^2-y^2}$) orbitals are mainly occupied by LP electrons from Fe ($3d^{10}4s^2$) atom instead. Thereby, the remaining two valence electrons on Fe atom are shared by Fe and two C5H5. Thus, Fe in the sandwich Fe(C5H5)2 displays bispotive (+2) valence, which is in agreement with the previous study.

Similarly, the nine $spd$-$\pi$ valence MOs of sandwich compound Cr(C6H6)2 can also be found, as shown in Figure 6. The valence MOs of Cr(C6H6)2 are analogous to the ones of Fe(C5H5)2. According to the results of NBO analysis, HOMO-2 ($d_{xy}$, ON (LP) = 1.42 lel), HOMO-1 ($d_{xy}$, ON (LP) = 1.42 lel), and HOMO ($d_{x^2-y^2}$, ON (LP) = 1.96 lel) are mainly occupied by six LP electrons from Cr ($3d^{4}4s^2$) atom, so Cr displays zero valence in the sandwich Cr(C6H6)2, which is in agreement with the previous study. In addition, the $spd$-$\pi$ interaction is also confirmed to exist in Cr(C6H6)2.

As well as Fe(C5H5)2 and Cr(C6H6)2, the nine $spd$-$\pi$ valence MOs (Figure 7(a)) of sandwich Cr(B12)2 ($D_{2d}$) are identified from the canonical MO diagrams. HOMO-25 is a $4s$-$\pi$ orbital. HOMO-19 is a $4p_z$-$\pi$ orbital, HOMO-11 ($4p_y$-$\pi$) and HOMO-10 ($4p_x$-$\pi$) are double-degenerate orbitals, HOMO-9 ($3d_{x^2}$-$\pi$) and HOMO-8 ($3d_{y^2}$-$\pi$) are double-degenerate orbitals. HOMO-7 is a $3d_{x^2-y^2}$-$\pi$ orbital. HOMO-3 ($3d_{xy}$-$\pi$) and HOMO-2 ($3d_{x^2}2\gamma$-) are also double-degenerate orbitals.
C. Aromaticity

“Aromaticity” is usually associated with the high stability, so we analyze aromaticity of the sandwich compounds Fe(C₅H₅)$_2$, Cr(C₆H₆)$_2$, and Cr(B₁₂)$_2$ ($D_{3d}$). Nucleus-independent chemical shift (NICS) value is the most widely used as a quantitative measure for aromaticity (negative NICS values mean aromaticity and positive NICS values mean anti-aromaticity). Here, we first employ NICSzz-scan method to analyze aromaticity of ligands C₆H₆, C₅H₅$^-$, and B₁₂. The NICSzz-scan analysis is analogous to the aromatic ring current shieldings approach, which can provide a clear picture of the type of the ring current in aromatic and anti-aromatic systems and can be used to characterize whether an inorganic system is aromatic, non-aromatic, and anti-aromatic. Recently, the use of NICS to indicate aromaticity has been criticized by Lazzeretti group, but currently it can be only used to monocyclic planar unsaturated molecules. B₁₂ is a bowl-like quasi-planar structure, so the formula given by Lazzeretti group is not applicable to our systems. And the NICS of our molecules are very large, which are less influenced by correction factor. Thus, we still apply the previous NICS to analyze the aromaticity.

Figure 8 plots the NICSzz-scan curves for C₆H₆, C₅H₅$^-$, and B₁₂, within the range of −5.0 to 5.0 Å above the geometric centers of the systems. From this figure, we can draw the following conclusions: (1) B₁₂ is more aromatic than C₆H₆ and C₅H₅$^-$, and the reason is that B₁₂ has triply aromaticity, namely, double $\sigma$ and $\pi$ aromaticity. (2) B₁₂ displays a narrow peak in the NICSzz-scan curve, because the $\sigma$ aromaticity decays more rapidly than $\pi$ aromaticity above the geometric centers of the systems. Note that the NICS calculated at 1 Å above the geometric center of the system (NICS(1)) describes the $\pi$ aromaticity. (3) At the geometric centers of the systems, the NICSzz-scan curve of C₆H₆ displays a raised peak, but C₅H₅$^-$ has five C–C $\sigma$-bonds (12 electrons), which is different. We think the reason may be that C₆H₆ has six C–C $\sigma$-bonds (12 electrons), which satisfies Hückel’s 4n+2 rule for $\sigma$ aromatic. In a word, B₁₂ is a very stable ligand, as well as C₅H₅$^-$ and C₆H₆.

Then, Figure 9 depicts the NICSzz-scan curves for sandwich compounds Cr(B₁₂)$_2$ ($D_{3d}$), Cr(C₆H₆)$_2$, and Fe(C₅H₅)$_2$, within the range of 0.3 to 4.0 Å above the geometric centers of the systems. From this figure we can see that the aromaticity of staggered Cr(B₁₂)$_2$ is lower than the ones of Cr(C₆H₆)$_2$ and Fe(C₅H₅)$_2$, but the sandwich Cr(B₁₂)$_2$ ($D_{3d}$) is still very aromatic (NICS $\approx$ −80 ppm). In addition, staggered Cr(B₁₂)$_2$...
decays more slowly than Fe(C5H5)2 and Cr(C6H6)2 in aromaticity. The reason may be that Fe(C5H5)2 and Cr(C6H6)2 only have π aromaticity, but staggered Cr(B12)2 has π aromaticity and the original double σ aromaticity of ligand B12. In brief, the sandwich compound Cr(B12)2 (D3d) has high aromaticity and stability.

IV. CONCLUSIONS

In this work, we have studied structural stability and electronic properties of a new sandwich compound Cr(B12)2 (D3d) by using DFT. We found that the sandwich Cr(B12)2 (D3d) is a stable compound with large binding energy, HOMO-LUMO gap, and VIP-VEA gap, as well as Fe(C5H5)2 and Cr(C6H6)2. The detailed MO and NBO analyses show that B12 is a stable ligand and the sandwich compound Cr(B12)2 (D3d) meets the 18-electron principle and it is a close shell in electronic structure. The spd-π interaction plays an important role in staggered Cr(B12)2. The NICSzz-scan analysis indicates that the sandwich compound Cr(B12)2 (D3d) is very aromatic. In conclusion, theoretical confirmations have been provided on B12 as a new ligand of the stable sandwich compound Cr(B12)2 (D3d). The bowl B12 cluster will be one of the promising molecules for coordination chemistry as potential new ligands and for materials science as new building blocks. We hope that our work will lead to more studies on the synthesis of sandwich compound Cr(B12)2 in experiments, which will further extend the rich boron and sandwich chemistry. If such compounds are synthesized, it will be significant in all-boron cluster coordination chemistry.

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55 See supplementary material at http://dx.doi.org/10.1063/1.4773281 for XYZ coordinates of B$_{12}$·Cr·B$_{12}$ (D$_{3d}$ and D$_{3h}$) compound, UV-vis absorption spectra for B$_{12}$·Cr·B$_{12}$ (D$_{3d}$) compound at the TPSSH/6-31G* and lanl2dz level, and the canonical valence molecular orbital figures of three sandwich compounds.
75 M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., GAUSSIAN 09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2009.
76 See supplementary material at http://dx.doi.org/10.1063/1.4773281 for XYZ coordinates of B$_{12}$·Cr·B$_{12}$ (D$_{3d}$ and D$_{3h}$) compound, UV-vis absorption spectra for B$_{12}$·Cr·B$_{12}$ (D$_{3d}$) compound at the TPSSH/6-31G* and lanl2dz level, and the canonical valence molecular orbital figures of three sandwich compounds.