## **Boron Clusters**

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## $PrB_7^-$ : A Praseodymium-Doped Boron Cluster with a $Pr^{II}$ Center Coordinated by a Doubly Aromatic Planar $\eta^7$ - $B_7^{3-}$ Ligand

Teng-Teng Chen<sup>+</sup>, Wan-Lu Li<sup>+</sup>, Tian Jian, Xin Chen, Jun Li,\* and Lai-Sheng Wang\*

Abstract: The structure and bonding of a Pr-doped boron cluster  $(PrB_7^{-})$  are investigated using photoelectron spectroscopy and quantum chemistry. The adiabatic electron detachment energy of  $PrB_7^-$  is found to be low [1.47(8) eV]. A large energy gap is observed between the first and second detachment features, indicating a highly stable neutral PrB7. Global minimum searches and comparison between experiment and theory show that  $PrB_7^{-}$  has a half-sandwich structure with  $C_{6\nu}$ symmetry. Chemical bonding analyses show that  $PrB_7^-$  can be viewed as a  $Pr^{II}[\eta^7-B_7^{3-}]$  complex with three unpaired electrons, corresponding to a  $Pr(4f^26s^1)$  open-shell configuration. Upon detachment of the 6s electron, the neutral  $PrB_7$  cluster is a highly stable  $Pr^{III}[\eta^7 - B_7^{3-}]$  complex with Pr in its favorite +3 oxidation state. The  $B_7^{3-}$  ligand is found to be highly stable and doubly aromatic with six delocalized  $\pi$  and six delocalized  $\sigma$  electrons and should exist for a series of lanthanide  $M^{III}/\eta^7$ - $B_7^{3-}$  complexes.

he electron deficiency of boron leads to electron sharing/ delocalization in many boron compounds and the concepts of  $\pi$  and  $\sigma$  double aromaticity. Hoffmann and Berndt reviewed doubly aromatic boron compounds that contain a pair of both delocalized  $\pi$  and  $\sigma$  electrons over three boron centers.<sup>[1]</sup> In these compounds, both the delocalized electron systems ( $\pi$ and  $\sigma$ ) satisfy the Hückel rule (4N+2) with N=0. The simplest such system is in fact the bare  $B_3^-$  cluster,<sup>[2]</sup> which contains three localized B-B bonds and a pair of delocalized  $\pi$  and  $\sigma$  bonds, making it the smallest doubly aromatic species. The  $B_3^+$  cation is only  $\pi$  aromatic with three B–B bonds and a pair of delocalized  $\pi$  electrons.<sup>[3]</sup> Its complexes with CO and N<sub>2</sub> have been recently characterized using infrared spectroscopy.<sup>[4]</sup> The  $D_{3h}$  B<sub>3</sub>H<sub>3</sub><sup>2-</sup> species is also  $\pi$  aromatic analogous to cyclopropenyl cation  $(C_3H_3^+)^{[5]}$  and its more complicated  $B_3R_3^{2-}$  analogue by substituting the H atoms with three bulky R ligands has been synthesized recently.<sup>[6]</sup> Here we report a lanthanide boron complex, PrB7<sup>-</sup>, which contains a doubly

[*]	T. T. Chen, <sup>[+]</sup> T. Jian, Prof. Dr. L. S. Wang
	Department of Chemistry, Brown University
	Providence, RI 02912 (USA)
	E-mail: Lai-Sheng_Wang@brown.edu
	W. L. Li,[+] X. Chen, Prof. Dr. J. Li
	Department of Chemistry and Key Laboratory of Organic Optoelec-
	tronics & Molecular Engineering of Ministry of Education, Tsinghua
	University
	Beijing 100084 (China)
	E-mail: junli@tsinghua.edu.cn
[+]	These authors contributed equally to this work.

 Supporting information and the ORCID identification number(s) for
 the author(s) of this article can be found under: https://doi.org/10.1002/anie.201703111. aromatic boron cluster with N = 1 in both the  $\pi$  and  $\sigma$  systems, i.e., six delocalized  $\pi$  and six delocalized  $\sigma$  electrons.

Joint photoelectron spectroscopy (PES) and quantum chemistry studies over the past decade have shown that sizeselected anionic boron clusters  $(B_n^{-})$  are planar over a wide size range and their chemical bonding are dominated by multiple  $\pi$  and  $\sigma$  aromaticity.<sup>[7-10]</sup> The first cluster which was found to be doubly aromatic with N = 1 was the  $B_0^-$  cluster,<sup>[11]</sup> which has a  $D_{8h}$  structure with six delocalized  $\pi$  and  $\sigma$  electrons, that has led to the design and observation of a series of borometallic doubly aromatic  $MOB_n^{-}$  clusters.<sup>[12]</sup> The bonding in  $B_8^{2-}$  observed in  $LiB_8^{--}$  (i.e.  $Li^+[B_8^{2--}]$ ) is similar to that in  $B_9^-$  with double aromaticity for N = 1.<sup>[13]</sup> The ground state of the B<sub>7</sub><sup>-</sup> cluster was first found to be a triplet state with  $C_{6\nu}$  symmetry and doubly aromatic; its degenerate HOMO  $(3e_1)$  is half-filled and fulfills the Hückel rule (4N) for triplet-state aromaticity.<sup>[14]</sup> Thus, the B<sub>7</sub><sup>3-</sup> species would be the smallest closed-shell boron cluster with double  $\pi$  and  $\sigma$  aromaticity with N=1. It was first observed in AlB<sub>7</sub><sup>-</sup>  $\{AI^{II}[B_{7}^{3-}]\}$ , although the  $\pi$  aromaticity was disrupted in neutral AlB<sub>7</sub> because the first electron detachment occurred from the  $3e_1(\pi)$  orbital on the  $B_7^{3-}$  moiety.<sup>15</sup>

The lanthanide elements have very low electronegativities and should be ideal to form M<sup>III</sup>[B<sub>7</sub><sup>3-</sup>]-type complexes with the smallest doubly aromatic boron cluster containing six delocalized  $\pi$  and  $\sigma$  electrons. Lanthanide borides represent a class of important magnetic, superconducting, and thermoelectric materials.<sup>[16]</sup> However, very few lanthanide dopedboron clusters have been investigated experimentally.<sup>[17]</sup> In the current article, we present a joint PES and ab initio study on the electronic structure and chemical bonding of the PrB<sub>7</sub><sup>-</sup> cluster. The experiment was done with a magnetic-bottle type PES apparatus equipped with a laser vaporization supersonic cluster source and a time-of-flight mass spectrometer, details of which have been published elsewhere.<sup>[9,18]</sup> Briefly, the  $PrB_7^{-}$  cluster was generated by laser ablation of a  $Pr/^{11}B$ mixed target followed by supersonic expansion with a He carrier gas containing 5% argon. Various  $PrB_n^{-}$  clusters were produced (Figure S1 in the Supporting Information) and the PrB7<sup>-</sup> cluster of current interest was mass-selected and decelerated before photodetachment by the 193 nm (6.424 eV) radiation from an ArF excimer laser. The photoelectron spectrum was calibrated using the spectrum of Bi-. The energy resolution of the apparatus was about 2.5%, that is, ca. 25 meV for 1 eV electrons.

The global minimum for  $PrB_7^-$  was investigated using the Tsinghua Global Minimum (TGMin) search program with a constraint Basin Hopping algorithm.<sup>[19]</sup> More than 400 trial structures for both doublet and quartet states were examined using the ADF 2016.101 software<sup>[20]</sup> with the PBE exchange-

correlation functional<sup>[21]</sup> and the TZP basis sets.<sup>[22]</sup> The frozen core approximation was employed for the inner shells, that is, [1s<sup>2</sup>] for B and [1s<sup>2</sup>-4d<sup>10</sup>] for Pr. The scalar relativistic (SR) effects were taken into account by the zero-order-regular approximation (ZORA).<sup>[23]</sup> Calculations using the hybrid PBE0 functional<sup>[24]</sup> and TZP basis sets were further performed to determine the possible electronic states of the global minimum structure. Since two different electron configurations of Pr ( $f^2s^1$  or  $f^3$ ) were possible, single-point calculations at the CCSD(T) level were carried out for the two lowest energy isomers with these electron configurations using the corresponding PBE0/TZP optimized geometries. In the CCSD(T) calculations, the valence triple- $\zeta$  basis set (ccpVTZ) was applied for B<sup>[25]</sup> and the Stuttgart energyconsistent relativistic pseudopotential ECP28MWB (Pr) with the corresponding ECP28MWB\_ANO basis set was used for Pr.<sup>[26-28]</sup> The CCSD T1 diagnostic factors were calculated to be 0.026 and 0.037, indicating that the multiconfigurational character was not significant for the PrB<sub>7</sub>cluster.

Vertical detachment energies (VDEs) were calculated using the  $\Delta$ SCF-TDDFT approach, as described before.<sup>[29]</sup> The first VDE (VDE<sub>1</sub>) was calculated as the difference in energy between the anionic ground state and the corresponding neutral ground state at the anion geometry. Vertical excitation energies of the neutral species calculated using the time-dependent DFT method at the SAOP functional (TD-SAOP) level<sup>[30]</sup> were added to  $VDE_1$  to yield the higher VDEs. The first adiabatic detachment energy (ADE), calculated only for the global minimum  $C_{6\nu}$  isomer, was obtained as the energy difference between the anionic and neutral species at their respective optimized geometries. The chemical bonding and orbital interactions were analyzed using the Kohn-Sham canonical molecular orbitals at the PBE0/TZP level and the adaptive natural density partitioning (AdNDP) method.<sup>[31]</sup>

The PE spectrum of  $PrB_7^-$  (Figure 1) shows a relatively simple pattern in the low binding energy region. There is a large energy gap between the ground state band X and the strong band A, beyond which the spectrum becomes more congested. The labels B to E are given only for the sake of discussion, because they may represent multiple detachment



**Figure 1.** The photoelectron spectrum of  $PrB_7^-$  at 193 nm (6.424 eV). The vertical bars represent the calculated vertical detachment energies (see Table 1).

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transitions. The lowest binding energy band X corresponds to detachment transition from the ground electronic state of  $PrB_7^{-}$  to that of  $PrB_7$ , while the higher binding energy bands from A to E denote detachment transitions to excited electronic states of neutral PrB<sub>7</sub>. The band X gives rise to a VDE of 1.61 eV from the band maximum, and an ADE of 1.47(8) eV, which also represents the electron affinity (EA) of neutral PrB<sub>7</sub>. The EA measured for PrB<sub>7</sub> is lower than that of B<sub>7</sub> or any known boron clusters,<sup>[9]</sup> indicating that the first electron detachment from PrB7- occurs from a Pr-based orbital. The spectral width of the X band indicates some geometry changes between the ground states of the anion and the neutral. Band A with a VDE of 3.15 eV is the most intense band and is also quite broad. The low ADE and the large gap between the X and A bands suggest that neutral PrB7 is a highly stable electronic system. The experimental VDEs of all the observed PES bands are given in Table 1, as well as in Figure 1 as vertical bars (see below).

**Table 1:** Experimental vertical detachment energies (VDEs) for  $PrB_7^-$  compared with the calculated data at the  $\Delta$ SCF-TDDFT level with the SAOP functional.

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	VDE [eV] (expt.)	Final state and electron configuration	VDE [eV] (theor.)
Х	1.61(6)	${}^{3}B_{1}, \{4a_{1}{}^{4}5a_{1}{}^{2}1b_{2}{}^{2}3e_{1}{}^{4}4e_{1}{}^{4}1b_{1}{}^{1}6a_{1}{}^{1}7a_{1}{}^{0}\}$	1.61
А	3.15(6)	<sup>5</sup> E <sub>2</sub> , {4a <sub>1</sub> <sup>4</sup> 5a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 3e <sub>1</sub> <sup>4</sup> 4e <sub>1</sub> <sup>3</sup> 1b <sub>1</sub> <sup>1</sup> 6a <sub>1</sub> <sup>1</sup> 7a <sub>1</sub> <sup>1</sup> }	2.96
		${}^{3}E_{2}, \{4a_{1}{}^{4}5a_{1}{}^{2}1b_{2}{}^{2}3e_{1}{}^{4}4e_{1}{}^{3}1b_{1}{}^{1}6a_{1}{}^{1}7a_{1}{}^{1}\}$	3.11
В	$\approx$ 3.8	${}^{3}B_{1}, \{4a_{1}{}^{4}5a_{1}{}^{2}1b_{2}{}^{2}3e_{1}{}^{4}4e_{1}{}^{4}1b_{1}{}^{1}6a_{1}{}^{0}7a_{1}{}^{1}\}$	3.93
		${}^{3}A_{1}, \{4a_{1}{}^{4}5a_{1}{}^{2}1b_{2}{}^{2}3e_{1}{}^{4}4e_{1}{}^{4}1b_{1}{}^{0}6a_{1}{}^{1}7a_{1}{}^{1}\}$	4.26
С	$\approx$ 4.7	${}^{5}E_{2}$ , {4 $a_{1}{}^{4}5a_{1}{}^{2}1b_{2}{}^{2}3e_{1}{}^{3}4e_{1}{}^{4}1b_{1}{}^{1}6a_{1}{}^{1}7a_{1}{}^{1}$ }	4.45
		${}^{3}E_{2}, \{4a_{1}{}^{4}5a_{1}{}^{2}1b_{2}{}^{2}3e_{1}{}^{3}4e_{1}{}^{4}1b_{1}{}^{1}6a_{1}{}^{1}7a_{1}{}^{1}\}$	4.54
		<sup>5</sup> A <sub>2</sub> , {4a <sub>1</sub> <sup>4</sup> 5a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>1</sup> 3e <sub>1</sub> <sup>4</sup> 4e <sub>1</sub> <sup>4</sup> 1b <sub>1</sub> <sup>1</sup> 6a <sub>1</sub> <sup>1</sup> 7a <sub>1</sub> <sup>1</sup> }	4.79
		${}^{3}A_{2}, \{4a_{1}{}^{4}5a_{1}{}^{2}1b_{2}{}^{1}3e_{1}{}^{4}4e_{1}{}^{4}1b_{1}{}^{1}6a_{1}{}^{1}7a_{1}{}^{1}\}$	4.79
D	$\approx$ 5.4	${}^{5}B_{1}, \{4a_{1}{}^{4}5a_{1}{}^{1}1b_{2}{}^{2}3e_{1}{}^{4}4e_{1}{}^{4}1b_{1}{}^{1}6a_{1}{}^{1}7a_{1}{}^{1}\}$	5.68
Е	$\approx$ 6.0	${}^{3}B_{1}, \{4a_{1}{}^{4}5a_{1}{}^{1}1b_{2}{}^{2}3e_{1}{}^{4}4e_{1}{}^{4}1b_{1}{}^{1}6a_{1}{}^{1}7a_{1}{}^{1}\}$	5.76

The optimized structures within  $80 \text{ kcal mol}^{-1}$  of the global minimum at the PBE/TZP level are given in Figure S2. The global minimum of  $PrB_7^-$  was found to have  $C_{6\nu}$ symmetry with a high-spin electronic state  $({}^{4}B_{1})$ , both at the PBE/TZP and PBE0/TZP levels. The low-spin doublet state  $(^{2}A_{1})$  with the same electron configuration of the  $C_{6v}$  structure lies  $\approx 5 \text{ kcal mol}^{-1}$  higher in energy at the PBE/TZP level. All other structures are much higher in energy, indicating the overwhelming stability of the  $C_{6\nu}$  half-sandwich-type structure for  $PrB_7^{-}$ . Due to the strong electron correlation effects among the  $4f^36s^0$ ,  $4f^26s^1$ ,  $4f^1(6s5d)^2$  configurations on Pr, total energies of a number of different electron configurations were determined initially at the PBE/TZP level (Table S1). Isomers with the 4f<sup>2</sup>6s<sup>1</sup> configuration were found to be much more stable than those with  $4f^3$ . Thus, the global minimum  $C_{6\nu}$ structure has three unpaired electrons on Pr ( $4f\phi^1 4f\sigma^1 6s^1$ , <sup>4</sup>B<sub>1</sub>), revealing an uncommon Pr<sup>II</sup> oxidation state. On the other hand, the different configurations of bare Pr<sup>2+</sup> have the following order:  $4f^{3}6s^{0}$  (0.0 eV)  $< 4f^{2}5d^{1}$  (1.66 eV)  $< 4f^{2}6s^{1}$ (3.52 eV).<sup>[32]</sup> The Pr 4f<sup>2</sup>6s<sup>1</sup> configuration in PrB<sub>7</sub><sup>-</sup> is reminiscent of the U  $5f^27s^1$  configuration in UO<sub>2</sub><sup>-</sup>.<sup>[33]</sup> The preference of occupying the *n*s orbitals rather than the (n-2)f orbitals in

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low-oxidation state f-element complexes is due to the more penetrating and diffuse feature of the radial probability distribution of the *ns* orbitals.<sup>[34]</sup> The energy gap between the two lowest  $4f^26s^1$  and  $4f^3$  states (*a* and *e* in Table S1) is calculated to be 9.44 kcalmol<sup>-1</sup> at the PBE/TZP level or 13.59 kcalmol<sup>-1</sup> at the CCSD(T) level.

The VDE<sub>1</sub> and ADE computed at two levels of theory are compared with the measured value in Table S2. The higher VDEs are obtained by adding the TDDFT excitation energies to VDE<sub>1</sub>. The calculated VDE<sub>1</sub> from PBE and PBE0 are both ca. 0.1 eV lower than the measured value. To facilitate comparison with the experimental data, the computed VDEs in Table 1 are all shifted by aligning the VDE<sub>1</sub> to match the X band. The Kohn-Sham molecular orbital (MO) levels of  $PrB_7^-$  are shown in Figure 2, where the isosurfaces of the five frontier MOs are also displayed. The pictures of all valence MOs are plotted in Figure S3. The MOs associated with the B<sub>7</sub> moiety are all lower in energy than the Pr-derived MOs, ranging from  $4e_1$  to  $3a_1$ . The Pr 4f-based orbitals ( $1b_1$  and  $6a_1$ ) are only slightly above the boron-based MOs, while the Pr 6sbased orbital  $(7a_1)$  lies much higher in energy, because of the antibonding interactions with the boron orbitals. The first electron detachment corresponds to removal of the 6s<sup>1</sup> electron from the highest singly occupied molecular orbital (SOMO,  $7a_1$ ), giving rise to the final triplet state  ${}^{3}B_1$  with



*Figure 2.* The Kohn–Sham molecular orbital energy levels of  $PrB_7^-$  at the PBE0/TZP level.

a  $Pr^{III}$  oxidation state. The calculated  $VDE_1$  values at PBE (1.52 eV) and PBE0 (1.54 eV) are in good agreement with the experimental value of 1.61 eV for band X. The first ADE calculated at PBE (1.43 eV) and PBE0 (1.45 eV) also agree well with the experimental value of 1.47 eV (Table S2).

The next band A is derived from electron detachment from a deeper boron-based bonding 4e<sub>1</sub> orbital (HOMO), rather than the next two SOMO-1 (6a<sub>1</sub>) and SOMO-2 (1b<sub>1</sub>) of Pr 4f character. This breakdown of the Koopmans' theorem is common in strongly correlated f-element systems.<sup>[33,35]</sup> The more contracted Pr 4f orbitals are significantly stabilized upon electron detachment, so that the  $(4e_1)^3(4f)^2$ - $(6s)^1$  configuration becomes energetically more favorable than  $(4e_1)^4(4f)^1(6s)^1$  in neutral PrB<sub>7</sub>. This trend of f-orbitals being increasingly more stabilized upon electron ionization is also observed in other 4f and 5f systems.<sup>[36]</sup> The electron detachment from the 4e1 HOMO orbital leads to two final states,  ${}^{5}E_{2}$  (VDE: 2.96 eV) and  ${}^{3}E_{2}$  (VDE: 3.11 eV). The theoretical VDEs from these two final states agree well with the observed VDE of 3.15 eV for band A. Beyond band A, the PE spectrum becomes congested and less well resolved, in agreement with multiple detachment channels from both the Pr 4f SOMOs and the deeper bonding orbitals from the  $B_7$ moiety (Figure 1 and Table 1). Overall, the theoretical results are in good agreement with the experimental data, providing considerable credence to the  $C_{6\nu}$  global minimum for PrB<sub>7</sub><sup>-</sup> and its high-spin state.

The optimized  $C_{6\nu}$  structures for PrB<sub>7</sub><sup>-</sup> and neutral PrB<sub>7</sub> at the PBE0/TZP level are shown in Figure 3 and the corresponding coordinates are listed in Table S4. The PrB<sub>7</sub><sup>-</sup> anion



Figure 3. The optimized global minimum structures of  $\text{PrB}_7^-$  and neutral  $\text{PrB}_7.$  The bond lengths are given in Å.

can be viewed as  $Pr^{II}(\eta^7-B_7^{3-})$ , whereas neutral  $PrB_7$  can be viewed as  $Pr^{III}(\eta^7-B_7^{3-})$ . The low binding energy of the 6s<sup>1</sup> (7a<sub>1</sub>) electron and the large X–A gap revealed in the PE spectrum of  $PrB_7^-$  (Figure 1) suggest that neutral  $PrB_7$  is a much more stable molecule, in which Pr is in its favorite + 3 oxidation state. The major structural changes between the  $PrB_7^-$  anion and its neutral are the Pr–B distances, which become significantly shorter, in agreement with stronger Pr– $B_7$  bonding and a more stable PrB<sub>7</sub> neutral complex.<sup>[37]</sup> This geometry change upon oxidation from  $Pr^{II}$  to  $Pr^{III}$  is also in agreement with the relatively broad feature of the PES band X (Figure 1). However, there is little geometry change in the  $B_7^{3-}$  moiety between the anionic and neutral PrB<sub>7</sub>. The calculated Mulliken charges and spin densities of the Pr and B atoms in  $PrB_7$  and  $PrB_7^-$  are given in Table S3. The Pr and the

central B atom are both positively charged, which lose electron density to the B<sub>6</sub> ring. The spin density distributions agree with the Pr<sup>III</sup> and Pr<sup>II</sup> oxidation states in PrB<sub>7</sub> and PrB<sub>7</sub><sup>-</sup>, respectively. Previous calculations on FeB<sub>7</sub> and ScB<sub>7</sub> found similar  $C_{6\nu}$  structures as PrB<sub>7</sub>.<sup>[38,39]</sup> However, joint PES and theoretical study on TaB<sub>7</sub><sup>-</sup> revealed that it has a  $C_s$ structure, in which the B<sub>7</sub> moiety is distorted to optimize bonding with the Ta center.<sup>[40]</sup>

To further understand the chemical bonding in  $Pr(\eta^7 - B_7)^$ and  $Pr(\eta^7-B_7)$ , we can examine the MOs in the anion (Figure S3). There are three unpaired electrons in SOMO (7a<sub>1</sub>), SOMO-1 (6a<sub>1</sub>) and SOMO-2 (1b<sub>1</sub>) in  $PrB_7^-$ . The SOMO  $(7a_1)$  is mainly from the Pr 6s orbital with some contribution from the Pr  $6p_z$  orbital. The SOMO-1 ( $6a_1$ ) and SOMO-2 (1b<sub>1</sub>) are basically from the Pr 4f $\sigma$  and 4f $\phi$  orbitals, respectively. The remaining twelve occupied MOs from 4e<sub>1</sub> down to  $3a_1$  essentially describe the bonding in the  $B_7^{3-}$  ligand with relatively small bonding contributions from the Pr center. In fact, these MOs look very similar to those in the bare  $C_{6\nu}$  B<sub>7</sub><sup>-</sup> cluster, in which the HOMO e<sub>1</sub> orbital is halffilled.<sup>[14]</sup> With the exception of the weak  $5d\pi$  contributions, these orbitals are identical to those in the  $C_{6\nu}$  AlB<sub>7</sub><sup>-</sup>, <sup>[15]</sup> which can be viewed as  $Al^{II}(B_7^{3-})$ , albeit neutral  $AlB_7[Al^{II}(B_7^{2-})]$  is quite different from PrB<sub>7</sub>.

The bonding in the  $B_7^{3-}$  moiety can be better appreciated from the AdNDP analyses (Figure 4).<sup>[31]</sup> We see clearly six two-center two-electron (2c-2e) bonds around the peripheral B atoms of the  $B_7^{3-}$  ligand. Of particular importance are the two sets of multi-center bonds: three in-plane seven-center two-electron (7c-2e) bonds and three out-of-plane eightcenter two-electron (8c-2e) bonds, which represent the  $\pi$ bonding within  $B_7^{3-}$  and bonding interactions between the Pr 5d $\pi$  orbitals and the  $B_7^{3-}$  ligand. The delocalized  $\sigma$  and  $\pi$ 



**Figure 4.** AdNDP analyses of the chemical bonding of the  $B_7^{3-}$  moiety in PrB<sub>7</sub> {Pr<sup>III</sup>[ $\eta^7$ - $B_7^{3-}$ ]} at the PBE0/TZP level. The two unpaired and localized 4f electrons on Pr<sup>III</sup> are not shown.

bonds in  $B_7^{3-}$  are reminiscent of the  $\sigma$  and  $\pi$  bonds in both  $B_8^{2-}$  and  $B_9^{-}$ ,<sup>[11]</sup> giving rise to double aromaticity. Both the  $\sigma$  and  $\pi$  bonds fulfill the Hückel 4N + 2 rule with N = 1. The  $C_{6v}$  symmetry of  $B_7^{3-}$  and also in  $B_7^{-}$  is due to the fact that the  $B_6$  ring is too small to fit the central B atom perfectly.<sup>[41]</sup> In fact, the slight bowl-shape of  $B_7^{3-}$  makes it a more suitable ligand to form half-sandwich complexes than the perfect planar  $B_8^{2-}$  and  $B_9^{-}$  species.

In conclusion, we report an investigation of a Pr-doped  $B_7^-$  cluster using photoelectron spectroscopy and quantum chemical calculations. We found that the global minimum of the  $PrB_7^-$  cluster is a  $C_{6\nu}$  half-sandwich structure with a  $Pr^{II}$ center coordinated by a  $\eta^7\mbox{-}B_7^{\ 3-}$  ligand. We observed that the extra electron in PrB7<sup>-</sup> is in a Pr 6s orbital and can be easily detached to produce a highly stable  $Pr(\eta^7-B_7)$  neutral complex, in which the Pr is in its favorite +3 oxidation state with two unpaired 4f electrons. The  $B_7^{3-}$  ligand, which possesses double aromaticity with six delocalized  $\pi$  and  $\sigma$  electrons, is found to be nearly identical in both the PrB<sub>7</sub><sup>-</sup> anion and its neutral. The  $Pr-(\eta^7-B_7)$  ligand bonding is significantly enhanced, making it a viable candidate for possible chemical synthesis. Since all 4f elements prefer the +3 oxidation state, we expect that a whole series of lanthanide  $M^{III}[\eta^7-B_7^{3-}]$ complexes exist, with tunable magnetic and optical properties.

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## **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** ab initio calculation · aromaticity · boron clusters · metal–boron cluster complex · photoelectron spectroscopy

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