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From inverse sandwich Ta_2B_7^+ and Ta_2B_8 to spherical trihedral $\text{Ta}_3\text{B}_{12}^-$: prediction of the smallest metallo-borospherene†

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Transition-metal-doped boron nanoclusters exhibit interesting structures and bonding. Inspired by the experimentally discovered inverse sandwich D_{6h} Ta_2B_6 and spherical trihedral D_{3h} $\text{La}_3\text{B}_{18}^-$ and based on extensive first-principles theory calculations, we predict herein the structural transition from perfect di-metal-doped inverse sandwich D_{7h} Ta_2B_7^+ (1) and D_{8h} Ta_2B_8 (2) to tri-metal-doped spherical trihedral D_{3h} $\text{Ta}_3\text{B}_{12}^-$ (3). As the smallest metallo-borospherene reported to date, $\text{Ta}_3\text{B}_{12}^-$ (3) contains three octa-coordinate Ta atoms as integral parts of the cage surface coordinated in three equivalent $\eta^8\text{-B}_8$ rings which share two eclipsed equilateral B_3 triangles on the top and bottom interconnected by three B_2 units on the waist. Detailed orbital and bonding analyses indicate that both Ta_2B_7^+ (1) and Ta_2B_8 (2) possess $\sigma + \pi$ dual aromaticity, while $\text{Ta}_3\text{B}_{12}^-$ (3) is $\sigma + \pi + \delta$ triply aromatic in nature. The IR, Raman, and UV-vis or photoelectron spectra of the concerned species are computationally simulated to facilitate their future spectroscopic characterizations.

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1. Introduction

Boron exhibits strong propensity to form multicentre-two-electron bonds (mc-2e bonds) in both polyhedral molecules and bulk allotropes due to its prototypical electron-deficiency.^{1–4} Joint photoelectron (PE) spectroscopy experimental and first-principles theory investigations in the past two decades have unveiled a rich landscape for $\text{B}_n^{-/0}$ boron nanoclusters from planar or quasi-planar structures ($n = 3\text{--}38, 41\text{--}42$) to cage-like borospherenes ($n = 39, 40$).^{3–7} Cage-like D_{2d} $\text{B}_{40}^{-/0}$ are the first borospherenes discovered in 2014,⁵ while C_{3h}/C_{2v} B_{39}^- are the first axially chiral borospherenes confirmed in experiments as the global minima (GM) of the B_n^- monoanions.⁶ These discoveries mark the onset of borospherene chemistry parallel to fullerene chemistry. The borospherene family has been systematically expanded by our group at first-principles theory levels to the cage-like B_n^q series in different charge states ($n = 36\text{--}42, q = n\text{--}40$) which all possess twelve delocalized π bonds on the surface and follow the universal $\sigma + \pi$ double delocalization bonding pattern.^{5–10} Sea-shell-like C_{2v} $\text{B}_{28}^{-/0}$ and C_s B_{29}^- were later observed as minor isomers of the monoanions in PES experiments^{11,12} and sea-shell-like C_s B_{29}^+, C_{2v} B_{31}^+, C_{2v} B_{32}, C_{2v} B_{34}, C_{2v} B_{35}^+ , and cage-like C_s B_{39}^+ have also been predicted recently in theory.^{13–16}

Transition-metal (TM)-doping induces dramatic structural changes and leads to earlier planar $\rightarrow$ tubular $\rightarrow$ spherical structural transitions in boron clusters due to effective TM–B coordination interactions, as evidenced by the experimentally observed pyramidal C_{3v} Ta@B_8^- ,¹⁷ C_s Ta@B_9^- ,¹⁸ and perfect planar D_{10h} Ta@B_{10}^- which has the highest coordination number of CN = 10 in planar species¹⁹ and the theoretically predicted half-sandwich TaB_{12}^- .²⁰ A family of transition-metal-centred double-ring tubular boron complexes in staggered motifs were recently observed in experiments, including D_{8d} Co@B_{16}^- ,²¹ D_{9d} Rh@B_{18}^- ,²² and C_s Ta@B_{20}^- ,²³ with C_s Ta@B_{20}^- ($\text{B}_2\text{--}[\text{Ta@B}_{18}]^-$) behaving like a tubular molecular rotor at 900 K facilitated by prototypical multicentre fluxional bonds (FBs) which form and break constantly.²⁴ A series of perfect di-metal-doped inverse sandwich complexes have also been observed in PE experiments, including D_{6h} $\text{Ta}_2\text{B}_6^{-/0}$,²⁵ D_{8h} La_2B_8 , and D_{8h} Pr_2B_8 .²⁶ Our group recently reported the smallest core-shell-like tubular molecular rotor C_{2h} $\text{La}_2[\text{B}_2\text{@B}_{18}]$ which contains a B_2 core rotating inside a B_{18} tube almost freely.²⁷ The first experimentally observed tri-metal-doped inverse triple-decker C_{2v} $\text{La}_3\text{B}_{14}^-$ exhibits a tilted $\text{La--B}_8\text{--La--B}_8\text{--La}$ triple-decker structure with two conjoined $\eta^8\text{-B}_8$ rings sharing a B–B unit on one edge.²⁸ With increasing cluster size, the first perfect spherical trihedral metallo-borospherenes D_{3h} $\text{Ln}_3\text{B}_{18}^-$ ($\text{Ln} = \text{La, Tb}$) were very recently discovered in a joint PE experimental and first-principles theory investigation.²⁹ These metallo-borospherenes represent a new class of unusual geometry with tunable magnetic or catalytic properties, with three deca-coordinate Ln centres as integral parts of the cage surface coordinated in three equivalent $\eta^{10}\text{-B}_{10}$ decagons which share two eclipsed

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triangular B_6 units interconnected by three B_2 units. Metallo-borospherenes were previously proposed in theory for MB_{40} ($M = Be, Mg$) and Ni_nB_{40} ($n = 1-4$) which contain hepta-coordinate metal centres on the cage surface of B_{40} , with the corresponding metallo-borophenes with hepta-coordinate metal centres as precursors.^{30,31} However, it remains unknown at current stage what is the possible smallest size of metallo-borospherenes and if such coordination-stabilized metallo-borospherenes can be characterized in experiments.

Based on extensive first-principles theory calculations, we predict in this work the possibility of the perfect di-TM-doped inverse sandwich D_{7h} $Ta_2B_7^+$ (1) and D_{8h} Ta_2B_8 (2) and, more importantly, the smallest tri-TM-doped cage-like metallo-borosphere D_{3h} $Ta_3B_{12}^-$ (3) which contains three octa-coordinate Ta centres as integral parts of the cage surface coordinated in three equivalent η^8-B_8 octagons that share two equilateral B_3 triangles interconnected by three B_2 units. Detailed analyses indicate that both $Ta_2B_7^+$ (1) and Ta_2B_8 (2) are $\sigma + \pi$ dually aromatic in nature, while $Ta_3B_{12}^-$ (3) is the first transition-metal-doped boron complex reported to date with $\sigma + \pi + \delta$ triple aromaticity.

2. Theoretical procedure

Extensive global minimum (GM) searches were performed on $Ta_2B_7^+$, Ta_2B_8 , and $Ta_3B_{12}^-$ using the Tsinghua Global Minimum (TGMin) package^{32,33} based on a constraint Basin-Hopping algorithm,³⁴ with more than 2000 singlet or triplet stationary points explored for each cluster at PBE/DZVP level.³⁵ Low-lying isomers were then fully optimized at the PBE0 (36) level with the 6-311+G* basis set³⁷ for B and Stuttgart relativistic small-core pseudopotential^{38,39} for Ta using the Gaussian 16 program suite,⁴⁰ with vibrational frequencies checked to make sure that all isomers reported are true minima. The 15 lowest-lying isomers were subsequently fully re-optimized at both PBE0 and BP86 (ref. 41 and 42) levels with the basis sets of aug-cc-pVTZ for B^{43,44} and Stuttgart+2f1g for Ta. Relative energies for the four lowest-lying isomers were further refined using the more accurate coupled cluster method with triple excitations CCSD(T)⁴⁵⁻⁴⁷ implemented in Gaussian 16 with the same basis sets. Natural bonding orbital (NBO) analyses were performed using the NBO 6.0 program⁴⁸ and detailed bonding analyses carried out utilizing the adaptive natural density partitioning (AdNDP) approach.^{49,50} Molecular dynamics (MD) simulations were performed on $Ta_2B_7^+$ (1), Ta_2B_8 (2), and $Ta_3B_{12}^-$ (3) for 30 ps using the CP2K software suite at different temperatures.⁵¹ The anisotropy of the current-induced density (ACID) analysis⁵² was realized using the ACID code, with the ring-current maps generated using POV-Ray 3.7.⁵³ The iso-chemical shielding surfaces (ICSSs)^{54,55} were generated with the Multiwfn 3.7 code.⁵⁶ The UV-vis and PES spectra were simulated using the time-dependent TD-DFT-PBE0 approach.⁵⁷

3. Results and discussions

3.1 Structures and stabilities

We start from $Ta_2B_7^+$, the smallest di-metal-doped Ta-B complex concerned in this work. Extensive GM searches

indicate that inverse sandwich D_{7h} $Ta_2B_7^+$ (1, 1A_1) is the deep-lying GM of the monocation which lies 1.58 eV lower than the second lowest-lying isomer C_{2v} $Ta_2B_7^+$ (1A_1) at CCSD(T) level (Fig. S1†), with the large HOMO–LUMO gap of $\Delta E_{\text{gap}} = 3.77$ eV at PBE0. The monocation contains a perfect B_7 ring sandwiched between two Ta atoms along the C_7 molecular axis at the two ends (similar to the experimentally observed inverse sandwich D_{6h} Ta_2B_6 which has a perfect B_6 ring sandwiched between two Ta atoms²⁴), with the B–B bond length of $r_{B-B} = 1.54$ Å, Ta–B distance of $r_{Ta-B} = 2.28$ Å, and Ta–Ta distance of $r_{Ta-Ta} = 2.86$ Å (which is obviously larger than the proposed Ta–Ta single bond length of 2.46 Å⁵⁸). With one more B atom added in, the perfect inverse sandwich D_{8h} Ta_2B_8 (2, $^1A_{1g}$) is achieved which is the deep-lying GM of the neutral lying 0.62 eV lower in energy than the second lowest-lying isomer C_s Ta_2B_8 ($^1A'$) at CCSD(T) (Fig. S2†). It encompasses a perfect B_8 ring sandwiched between two Ta atoms along the C_8 molecular axis at the two ends, with the HOMO–LUMO gap of $\Delta E_{\text{gap}} = 2.15$ eV at PBE0. With a B_8 octagon as the ligand, the Ta–Ta distance in Ta_2B_8 (2) is effectively shortened to $r_{Ta-Ta} = 2.52$ Å which is close to the proposed average Ta–Ta single bond length.⁵⁸ The highly stable inverse sandwich $Ta_2B_7^+$ (1) and Ta_2B_8 (2) may serve as building blocks to form tri-metal-doped Ta–B complexes, similar to the situation in the experimentally observed triple-decker C_{2v} $La_3B_{14}^-$ (28) and spherical trihedral D_{3h} $La_3B_{18}^-$.²⁹

Following the direction, we obtained the lowest-lying C_{2v} $Ta_3B_{10}^+$ (1A_1) for $Ta_3B_{10}^+$, C_s $Ta_3B_{11}^-$ ($^1A'$) for $Ta_3B_{11}^-$, and C_s $Ta_3B_{11}^-$ ($^2A'$) for $Ta_3B_{11}^-$ which all possess incomplete spherical-trihedral structures with one edge broken (Fig. S3†). The smallest perfect spherical trihedron was achieved at D_{3h} $Ta_3B_{12}^-$ (3, 1A_1) which, as the GM of the monoanion, lies 0.24 eV lower than the second lowest-lying C_{2v} $Ta_3B_{12}^-$ (1A_1) and 1.06 eV lower than the third lowest-lying C_s $Ta_3B_{12}^-$ ($^1A'$) (which both belong to metallo-borospherenes) at the most reliable CCSD(T) level (Fig. S4†). As shown in Fig. 1, $Ta_3B_{12}^-$ (3) contains three equivalent octa-coordinate Ta centres as integral parts of the cage surface coordinated in three equivalent η^8-B_8 rings which share two eclipsed equilateral B_3 triangles at the top and bottom interconnected by three B_2 units on the waist. It has the calculated B–B bond lengths of $r_{B-B} = 1.58-1.74$ Å, Ta–B coordination distances of $r_{Ta-B} = 2.26-2.27$ Å, and elongated Ta–Ta distances

Fig. 1 Optimized structures of D_{7h} $Ta_2B_7^+$ (1), D_{8h} Ta_2B_8 (2), and D_{3h} $Ta_3B_{12}^-$ (3) at PBE0//B/aug-cc-pVTZ/Ta/Stuttgart+2f1g level, with bond lengths indicated in Å.

of $r_{\text{Ta-Ta}} = 3.04 \text{ \AA}$, respectively, with the large HOMO(e'')-LOMO(e') gap of $\Delta E_{\text{gap}} = 2.50 \text{ eV}$ at PBE0 which is comparable with the corresponding value of 2.70 eV calculated for the experimentally observed $D_{3h} \text{ La}_3\text{B}_{18}^-$ (29) at the same theoretical level. $\text{Ta}_3\text{B}_{12}^-$ (3) can be constructed from Ta_2B_8 (2) by adding one B_4 edge (B-B-B-B) perpendicular to the B_8 ring in the front and one Ta atom coordinated to the newly formed B_8 ring, forming three interconnected Ta_2B_8 inverse sandwiches around the C_3 main molecular axis (Fig. 1). In comparison with $D_{3h} \text{ Ln}_3\text{B}_{18}^-$ ($\text{Ln} = \text{La}, \text{Tb}$) which possess a perfect cage-like $D_{3h} \text{ B}_{18}$ ligand with three equivalent $\eta^{10}\text{-B}_{10}$ decagons sharing two eclipsed B_6 triangles at the top and bottom interconnected by three B_2 units on the waist,²⁹ $\text{Ta}_3\text{B}_{12}^-$ (3) has a perfect cage-like $D_{3h} \text{ B}_{12}$ ligand with three equivalent $\eta^8\text{-B}_8$ octagons sharing two eclipsed B_3 triangles at the top and bottom interconnected by three B_2 units on the waist. $\text{Ta}_3\text{B}_{12}^-$ (3) has the same symmetry (D_{3h}) as $\text{Ln}_3\text{B}_{18}^-$, but smaller in size with six less B atoms in the ligand. Such a structural change can be understood based on the fact that Ta ($[\text{Xe}]5d^36s^2$) has a smaller atomic radius ($1.46 \text{ \AA}$) than that ($1.83 \text{ \AA}$) of La ($[\text{Xe}]5d^16s^2$),⁵⁹ but possesses two more 5d valence electrons than the latter. The Ta centres appear to have the right atomic radii and electronic configurations to match the $D_{3h} \text{ B}_{12}$ ligand both electronically and geometrically. $\text{Ta}_3\text{B}_{12}^-$ (3) is therefore the smallest metallo-borospherene reported to date. Perfect spherical trihedral $D_{3h} \text{ Nb}_3\text{B}_{12}^-$ and $D_{3h} \text{ V}_3\text{B}_{12}^-$ also appear to be true minima of the systems at both PBE0 and BP86 levels (Fig. S5†), with the HOMO-LUMO gaps of $\Delta E_{\text{gap}} = 2.59$ and 2.67 eV at PBE0, respectively.

Extensive MD simulations (Fig. S6†) indicate that Ta_2B_7^+ (1), Ta_2B_8 (2), and $\text{Ta}_3\text{B}_{12}^-$ (3) are dynamically stable at 1200 K, 700 K, and 1200 K, with the small calculated average root-mean-square-deviations of $\text{RMSD} = 0.11, 0.10$, and $0.11 \text{ \AA}$ and maximum bond length deviations of $\text{MAXD} = 0.27, 0.24$, and $0.29 \text{ \AA}$, respectively. No high-lying isomers were observed during the MD simulation. Ta-B complexes with larger HOMO-LUMO energy gaps appear to be dynamically more stable than the ones with narrower energy gaps.

3.2 Natural orbital and bonding analyses

The high stabilities of these high-symmetry complexes originate from their unique electronic structures and bonding patterns. Detailed natural bonding orbital (NBO) analyses show that the Ta centres in Ta_2B_7^+ (1), Ta_2B_8 (2), and $\text{Ta}_3\text{B}_{12}^-$ (3) possess the electronic configurations of Ta $[\text{Xe}]6s^{0.21}5d^{3.46}$, Ta $[\text{Xe}]6s^{0.22}5d^{3.64}$, and Ta $[\text{Xe}]6s^{0.24}5d^{3.72}$, natural atomic charges of $q_{\text{Ta}} = +1.34|e|$, $+1.12|e|$ and $+1.01|e|$, and total Wiberg bond indexes of $\text{WBI}_{\text{Ta-B}} = 4.85, 4.80$, and 5.07 , respectively, indicating that each Ta centre in these complexes donates its $6s^2$ electrons almost completely to the B_n ligand ($n = 7, 8, 12$), while, in return, accepts roughly one electron in its partially filled 5d orbitals from the B_n ligands *via* $p \rightarrow d$ back-donations. The formations of effective Ta-B coordination interactions in 1–3 are strongly supported by the calculated Ta-B bond orders of $\text{WBI}_{\text{Ta-B}} = 0.59, 0.40$, and $0.50\text{--}0.53$ (Ta-B interactions within TaB_7 or TaB_8 pyramids) which appear to be systematically higher than the typical Cr-C coordination bond orders of

$\text{WBI}_{\text{Cr-C}} = 0.34$ in $D_{6h} \text{ Cr}(\text{C}_6\text{H}_6)_2$. As mentioned above, a Ta centre in $\text{Ta}_3\text{B}_{12}^-$ (3) has the total bond order of $\text{WBI}_{\text{Ta}} = 5.07$ which is also obviously higher than the corresponding value of $\text{WBI}_{\text{Cr}} = 4.12$ calculated for Cr in $D_{6h} \text{ Cr}(\text{C}_6\text{H}_6)_2$.

Detailed AdNDP bonding analyses unveil both the localized and delocalized bonds of the concerned systems. As shown in Fig. 2a, Ta_2B_8 (2) possesses 8 $2c\text{--}2e$ B-B σ bonds on the periphery of the $\eta^8\text{-B}_8$ ligand with the occupation numbers of $\text{ON} = 1.82|e|$ and 1 $2c\text{--}2e$ Ta-Ta σ bond between the two Ta centres with $\text{ON} = 2.00|e|$ in the first row. The remaining 16 valence electrons form 8 totally delocalized $10c\text{--}2e$ coordination bonds between the $\eta^8\text{-B}_8$ ligand and two Ta coordination centres with $\text{ON} = 2.00|e|$, including 3 $10c\text{--}2e$ σ bonds in the second row, 3 $10c\text{--}2e$ π bonds in the third row, and 2 $10c\text{--}2e$ (p-d) δ bonding interactions in the fourth row. Both the

Fig. 2 AdNDP bonding patterns of (a) $D_{8h} \text{ Ta}_2\text{B}_8$ (2) and (b) $D_{3h} \text{ Ta}_3\text{B}_{12}^-$ (3), with the occupation numbers (ON) indicated.

delocalized 6e σ -system and delocalized 6e π -system match the $4n + 2$ aromatic rule ($n = 1$) and together they render $\sigma + \pi$ dual aromaticity to Ta_2B_8 (2). Similarly, both the experimentally observed D_{6h} Ta_2B_6 (ref. 25) and D_{7h} Ta_2B_7^+ (1) are $\sigma + \pi$ doubly aromatic in nature, as clearly indicated in their canonical molecular orbitals (CMOs) depicted in Fig. S7.†

The AdNDP bonding pattern of spherical trihedral $\text{Ta}_3\text{B}_{12}^-$ (3) (Fig. 2b) exhibits certain similarity with that of the inverse sandwich Ta_2B_8 (2), but it is more complex and intriguing. $\text{Ta}_3\text{B}_{12}^-$ (3) possesses 9 localized 2c–2e σ B–B bonds in the three B_2 units and between the B_2 units and the six apexes of the two B_3 triangles and 2 equivalent 3c–2e σ bonds on the two B_3 triangles at the top and bottom in the first row and 6 equivalent 3c–2e B_2 –Ta σ bonds between the three Ta atoms and the two B_3 triangles at the top and bottom in the second row. The remaining 18 valence electrons form 9 delocalized 9c–2e bonds evenly distributed on three equivalent C_{2v} TaB_8 octagonal pyramids (which are similar to the experimentally observed C_{8v} TaB_8^- octagonal pyramid¹⁷) around the C_3 main molecular axis, including 3 equivalent 9c–2e $\text{B}_8(\sigma)$ –Ta(d_π) bonds in the third row, 3 equivalent 9c–2e $\text{B}_8(\pi)$ –Ta(d_σ) bonds in the fourth row, and 3 equivalent $\text{B}_8(\pi)$ –Ta(d_δ) bonds in the fifth row. Each TaB_8 octagonal pyramid thus possesses 1 9c–2e $\text{B}_8(\sigma)$ –Ta(d_π) bond, 1 9c–2e $\text{B}_8(\pi)$ –Ta(d_σ) bond, and 1 $\text{B}_8(\pi)$ –Ta(d_δ) bond. Overall, the $\text{Ta}_3\text{B}_{12}^-$ (3) spherical trihedron has 3 equivalent (d–p) σ bonds, 3 equivalent (d–p) π bonds, and 3 equivalent (d–p) δ bonds evenly distributed on three equivalent TaB_8 octagonal pyramids around the C_3 molecular axis, forming one delocalized 6e σ -system, one delocalized 6e π -system, and one delocalized 6e δ -system on the cage surface each matching the $4n + 2$ rule ($n = 1$) independently. Such a delocalized bonding pattern renders $\sigma + \pi + \delta$ triple aromaticity to the smallest metallo-borospherene of $\text{Ta}_3\text{B}_{12}^-$ (3) which is a highly stable D_{3h} spherical trihedron with 18 delocalized electrons evenly distributed on the cage surface.⁶⁰

The aromatic nature of Ta_2B_7^+ (1), Ta_2B_8 (2), and $\text{Ta}_3\text{B}_{12}^-$ (3) is further evidenced by their calculated nucleus-independent chemical shift (NICS) values of NICS = –110.5, –101.9, and –86.6 ppm at the geometrical centres, respectively. Based on the calculated NICS-ZZ components, Fig. 3 plots their iso-chemical-shielding surfaces^{54,55} with Z-axis parallel to the designated C_7 , C_8 , or C_2 molecular axes to illuminate the chemical shielding around the TaB_7 or TaB_8 pyramids in these complexes. Obviously, the space inside the spherical trihedron surrounded by the delocalized Ta–B_n coordination bonds in horizontal direction or within about 1.0 Å above the Ta centres in vertical direction belong to chemical shielding regions (highlighted in yellow) with negative NICS-ZZ values, indicating that the aromatic contribution mainly comes from Ta(5d)–B(2p) coordination interactions between the Ta centres and B_n ligands around them ($n = 7$ or 8), while the chemical de-shielding areas (highlighted in green) with positive NICS values are located outside the B_n ring in horizontal direction. The ICSSs of these complexes appear to be analogous to that of the prototypical aromatic benzene.^{54–56}

Fig. S8† depicts the corresponding ring current maps of Ta_2B_7^+ (1), Ta_2B_8 (2), and $\text{Ta}_3\text{B}_{12}^-$ (3). Consistent magnetic

Fig. 3 Calculated iso-chemical shielding surfaces (ICSSs) of (a) Ta_2B_7^+ (1), (b) Ta_2B_8 (2), and (c) $\text{Ta}_3\text{B}_{12}^-$ (3), with the corresponding NICS-ZZ components indicated. The C_7 axis of Ta_2B_7^+ (1), C_8 axis of Ta_2B_8 (2), and C_2 axis of $\text{Ta}_3\text{B}_{12}^-$ (3) are designated as z axis in vertical direction to compare the shielding effects around the TaB_n pyramids ($n = 7, 8$). Yellow regions stand for chemical shielding areas, while green areas represent chemical de-shielding areas.

responses occur in 1, 2, and 3 in an external magnetic field in the vertical direction parallel to the assigned molecular axes, irrespective of the electron type, similar to the situations in both benzene^{52,53} and double-ring tubular B_{20} (61) which are known to possess typical planar or tubular aromaticity. Such diatropic ring currents well support the aromatic nature of these Ta-doped boron complexes.

3.3 Simulated IR, Raman, and PE spectra of $\text{Ta}_3\text{B}_{12}^-$ (3)

We computationally simulate the IR, Raman, and UV-vis or PES spectra of Ta_2B_7^+ (1), Ta_2B_8 (2), and $\text{Ta}_3\text{B}_{12}^-$ (3) at PBE0 level to facilitate their future spectral characterizations. PE measurements and infrared photodissociation (IR-PD) spectra in combination with first-principles theory calculations have proven to be powerful approaches in characterizing novel clusters in gas phases.^{3–7,17–28,62} As shown in Fig. 4, the high-symmetry $\text{Ta}_3\text{B}_{12}^-$ (3) exhibits relatively simple IR and Raman spectral patterns, with the major IR active peaks at 507 (e'), 559 (e'), 668 (a_2''), and 881 (e') cm^{-1} (Fig. 4a) and main Raman spectral features at 209 (a_1'), 881 (e'), 998 (e''), and 1201 (a_1') cm^{-1} (Fig. 4b), respectively. The first Raman active symmetrical vibrational mode (a_1') at 209 cm^{-1} corresponds to typical “radial breathing mode” (RBM) of the metallo-borospherene which may be used to characterize the hollow structures of single-walled boron nanoclusters in experiments.⁶³

The calculated PE spectrum of $\text{Ta}_3\text{B}_{12}^-$ (3) in Fig. 4c exhibits major spectral features at 2.95 ($^2E''$), 3.17 ($^2A_1'$), 3.66 ($^2A_2''$), 3.98 ($^2E'$), 4.17 ($^2A_1'$), 5.32 ($^2E'$), 5.68 ($^2E'$), and 5.98 ($^2A_2''$), respectively, corresponding to vertical electronic transitions from the ground state of the anion ($^1A_1'$) to the excited states of the neutral at the ground-state geometry of the anion. The open-shell neutral Ta_3B_{12} has a slightly distorted C_{2v} Ta_3B_{12} (2A_2) ground-state structure due to Jahn–Teller effect, with the calculated electron affinity of EA = 2.87 eV. The simulated IR, Raman, and UV-vis spectra of Ta_2B_7^+ (1) and Ta_2B_8 (2) are depicted in Fig. S9.†

Fig. 4 Simulated (a) IR, (b) Raman, and (c) PES spectra of D_{3h} $Ta_3B_{12}^-$ (3) at PBE0//B/aug-cc-pVTZ/Ta/Stuttgart+2f1g level.

4. Conclusions

Extensive first-principles theory calculations performed in this work indicate a structural transition from perfect inverse sandwich D_{7h} $Ta_2B_7^+$ (1) and D_{8h} Ta_2B_8 (2) to the smallest metallo-borospherene D_{3h} $Ta_3B_{12}^-$ (3). As the first transition-metal-doped boron complex reported to date with $\sigma + \pi + \delta$ triple aromaticity, $Ta_3B_{12}^-$ (3) possesses three octa-coordinate Ta centres as integral parts of the cage surface coordinated in three equivalent η^8-B_8 octagons. The results obtained in this work suggest that a large family of coordination-stabilized multi-TM-doped TM_mB_n metallo-borospherenes with tunable magnetic and electronic properties may exist in experiments in which the transition metal dopants and B_n ligands match both geometrically and electronically.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- W. N. Lipscomb, *Science*, 1977, **196**, 1047.
- F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann, *Advanced Inorganic Chemistry*, Wiley, New York, 6th edn, 1999.
- L. S. Wang, *Int. Rev. Phys. Chem.*, 2016, **35**, 69.

- T. Jian, X. N. Chen, S. D. Li, A. I. Boldyrev, J. Li and L. S. Wang, *Chem. Soc. Rev.*, 2019, **48**, 3550.
- H. J. Zhai, Y. F. Zhao, W. L. Li, Q. Chen, H. Bai, H. S. Hu, Z. A. Piazza, W. J. Tian, H. G. Lu, Y. B. Wu, Y. W. Mu, G. F. Wei, Z. P. Liu, J. Li, S. D. Li and L. S. Wang, *Nat. Chem.*, 2014, **6**, 727.
- Q. Chen, W. L. Li, Y. F. Zhao, S. Y. Zhang, H. S. Hu, H. Bai, H. R. Li, W. J. Tian, H. G. Lu, H. J. Zhai, S. D. Li, J. Li and L. S. Wang, *ACS Nano*, 2015, **9**, 754.
- Q. Chen, S. Y. Zhang, H. Bai, W. J. Tian, T. Gao, H. R. Li, C. Q. Miao, Y. W. Mu, H. G. Lu, H. J. Zhai and S. D. Li, *Angew. Chem., Int. Ed.*, 2015, **54**, 8160.
- Q. Chen, H. R. Li, C. Q. Miao, Y. J. Wang, H. G. Lu, Y. W. Mu, G. M. Ren, H. J. Zhai and S. D. Li, *Phys. Chem. Chem. Phys.*, 2016, **18**, 11610.
- W. J. Tian, Q. Chen, H. R. Li, M. Yan, Y. W. Mu, H. G. Lu, H. J. Zhai and S. D. Li, *Phys. Chem. Chem. Phys.*, 2016, **18**, 9922.
- Q. Chen, H. R. Li, W. J. Tian, H. G. Lu, H. J. Zhai and S. D. Li, *Phys. Chem. Chem. Phys.*, 2016, **18**, 14186.
- Y. J. Wang, Y. F. Zhao, W. L. Li, T. Jian, Q. Chen, X. R. You, T. Ou, X. Y. Zhao, H. J. Zhai, S. D. Li, J. Li and L. S. Wang, *J. Chem. Phys.*, 2016, **144**, 064307.
- H. R. Li, T. Jian, W. L. Li, C. Q. Miao, Y. J. Wang, Q. Chen, X. M. Luo, K. Wang, H. J. Zhai, S. D. Li and L. S. Wang, *Phys. Chem. Chem. Phys.*, 2016, **18**, 29147.
- L. Pei, H. R. Li, M. Yan, Q. Chen, Y. W. Mu, H. G. Lu, Y. B. Wu and S. D. Li, *Phys. Chem. Chem. Phys.*, 2018, **20**, 15330.
- L. Pei, M. Yan, X. Y. Zhao, Y. W. Mu, H. G. Lu, Y. B. Wu and S. D. Li, *RSC Adv.*, 2020, **10**, 10129.
- H. Liu, Q. Chen, H. R. Li, X. Y. Zhao, X. X. Tian, Y. W. Mu, H. G. Lu and S. D. Li, *Phys. Chem. Chem. Phys.*, 2018, **20**, 15344.
- X. Y. Zhao, Q. Chen, H. R. Li, Y. W. Mu, H. G. Lu and S. D. Li, *Phys. Chem. Chem. Phys.*, 2017, **19**, 10998.
- W. L. Li, A. S. Ivanov, J. Federiĉ, C. Romanescu, I. Ćernuřak, A. I. Boldyrev and L. S. Wang, *J. Chem. Phys.*, 2013, **139**, 104312.
- C. Romanescu, T. R. Galeev, W. L. Li, A. I. Boldyrev and L. S. Wang, *J. Chem. Phys.*, 2013, **138**, 134315.
- T. R. Galeev, C. Romanescu, W. L. Li, L. S. Wang and A. I. Boldyrev, *Angew. Chem., Int. Ed.*, 2012, **51**, 2101.
- B. L. Chen, W. G. Sun, X. Y. Kuang, C. Lu, X. X. Xia, H. X. Shi and G. Maroulis, *Inorg. Chem.*, 2018, **57**, 343.
- I. A. Popov, T. Jian, G. V. Lopez, A. I. Boldyrev and L. S. Wang, *Nat. Commun.*, 2015, **6**, 8654.
- T. Jian, W. L. Li, X. Chen, T. T. Chen, G. V. Lopez, J. Li and L. S. Wang, *Chem. Sci.*, 2016, **7**, 7020.
- W. L. Li, T. Jian, X. Chen, H. R. Li, T. T. Chen, X. M. Luo, S. D. Li, J. Li and L. S. Wang, *Chem. Commun.*, 2017, **53**, 1587.
- M. Yan, H. R. Li, X. Y. Zhao, X. Q. Lu, Y. W. Mu, H. G. Lu and S. D. Li, *J. Comput. Chem.*, 2019, **40**, 966.
- W. L. Li, L. Xie, T. Jian, C. Romanescu, X. Huang and L. S. Wang, *Angew. Chem.*, 2014, **126**, 1312.
- W. L. Li, T. T. Chen, D. H. Xing, X. Chen, J. Li and L. S. Wang, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, **115**, E6972.

- 27 X. Q. Lu, Q. Chen, X. X. Tian, Y. W. Mu, H. G. Lu and S. D. Li, *Nanoscale*, 2019, **11**, 21311.
- 28 T. T. Chen, W. L. Li, W. J. Chen, J. Li and L. S. Wang, *Chem. Commun.*, 2019, **55**, 7864.
- 29 T. T. Chen, W. L. Li, W. J. Chen, X. H. Yu, X. R. Dong, J. Li and L. S. Wang, *Nat. Commun.*, 2020, **11**, 2766.
- 30 H. Bai, Q. Chen, H. J. Zhai and S. D. Li, *Angew. Chem., Int. Ed.*, 2015, **54**, 941.
- 31 H. R. Li, X. X. Tian, X. M. Luo, M. Yan, Y. W. Mu, H. G. Lu and S. D. Li, *Sci. Rep.*, 2017, **7**, 5701.
- 32 Y. F. Zhao, X. Chen and J. Li, *Nano Res.*, 2017, **10**, 3407.
- 33 X. Chen, Y. F. Zhao, L. S. Wang and J. Li, *Comput. Theor. Chem.*, 2017, **1107**, 57.
- 34 D. J. Wales and J. P. Doye, *J. Phys. Chem. A*, 1997, **101**, 5111.
- 35 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 36 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158.
- 37 D. Feller, *J. Comput. Chem.*, 1996, **17**, 1571.
- 38 D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123.
- 39 J. M. L. Martin and A. Sundermann, *J. Chem. Phys.*, 2001, **114**, 3408.
- 40 M. J. Frisch, *et al.*, *Gaussian 16, Revision A.03*, Gaussian Inc., Wallingford, CT, 2016.
- 41 A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, **38**, 3098.
- 42 J. P. Perdew, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1986, **33**, 8822.
- 43 T. H. Dunning Jr, *J. Chem. Phys.*, 1989, **90**, 1007.
- 44 R. A. Kendall, T. H. Dunning Jr and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6796.
- 45 J. Čížek, *Adv. Chem. Phys.*, 1969, **14**, 35.
- 46 G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.*, 1982, **76**, 1910.
- 47 K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.*, 1989, **157**, 479.
- 48 P. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, *NBO 6.0*, Theoretical Chemistry Institute, University of Wisconsin, Madison, 2013.
- 49 D. Y. Zubarev and A. I. Boldyrev, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5207.
- 50 N. V. Tkachenko and A. I. Boldyrev, *Phys. Chem. Chem. Phys.*, 2019, **21**, 9590.
- 51 J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing and J. Hutter, *Comput. Phys. Commun.*, 2005, **167**, 103.
- 52 D. Geuenich, K. Hess, F. Köhler and R. Herges, *Chem. Rev.*, 2005, **105**, 3758.
- 53 Povray, *Persistence of vision raytracer, POV-Ray 3.7*, <http://www.povray.org/>.
- 54 S. Klod and E. Kleinpeter, *J. Chem. Soc., Perkin Trans. 2*, 2001, **2**, 1893.
- 55 E. Kleinpeter, S. Klod and A. Koch, *J. Mol. Struct.*, 2007, **811**, 45.
- 56 T. Lu and F. W. Chen, *J. Comput. Chem.*, 2012, **33**, 580.
- 57 R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.*, 1996, **256**, 454.
- 58 P. Pykkö and M. Atsumi, *Chem.-Eur. J.*, 2009, **15**, 186.
- 59 J. A. Dean, *Lange's Hand book of Chemistry*, McGraw-Hill Book Co., 1999, Table 4.6.
- 60 A. Tlahuice-Flores and A. Muñoz-Castro, *Int. J. Quantum Chem.*, 2019, **119**, e25756.
- 61 M. P. Johansson, *J. Phys. Chem. C*, 2009, **113**, 524.
- 62 G. J. Wang, M. F. Zhou, J. T. Goettel, G. J. Schrobilgen, J. Su, J. Li, T. Schlöder and S. Riedel, *Nature*, 2014, **514**, 475.
- 63 D. Ciuparu, R. F. Klie, Y. Zhu and A. L. Pfeifferle, *J. Phys. Chem. B*, 2004, **108**, 3967.