Actinides-centered borane molecular clusters with 24-coordination number in the $\text{An}(\text{BH})_{24}$ ($\text{An} = \text{Th to Cm}$)

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Abstract

Herein we report a new record coordination number of 24 for actinide established in the cage-like $\text{An}(\text{BH})_{24}$ ($\text{An} = \text{Th to Cm}$) via using relativistic quantum chemistry methods. Analysis of $\text{U}(\text{BH})_n$ ($n = 1$ to 24) confirms these series of systems being as geometric minima, with the BH as a ligand located in the first shell around the uranium. However, our additional global searches reveal the lowest-energy half-cage structure for UB_{24} , which is extended to the series of AnB_{24} and prevails over the competing structural isomers such as cage. The intrinsic geometric difference for AnB_{24} and $\text{An}(\text{BH})_{24}$ mainly arise from the B sp^3 hybridization in borane inducing strong interactions between An 5f6d7s hybrid orbitals and B $2p_z$ orbitals in $\text{An}(\text{BH})_{24}$ comparing to that of AnB_{24} . The fundamental trend presents a valuable insight for future experimental endeavor searching for isolable complexes with high-coordination actinide and provides a new structural motif of boron clusters and nanostructures.

1. Introduction

The current highest coordination number in molecular chemistry is 17, which has been seen theoretically found in $\text{An}(\text{He})_{17}^{q+}$,¹ although before that theoretical studies have suggested the 15 coordination numbers in PbHe_{15}^{+} and 16 in the Friauf–Laves phases MgZn_2 or MgNi_2 , and 16 in $\text{M}@\text{Li}_{16}$ ($\text{M}=\text{Ca, Sr, Ba, Ti, Zr, and Hf}$).² And the record of high coordination complexes involving the metal elements has been updated from 14 in $\text{U}(\text{BH}_4)_4$,³ then to 15 in $[\text{Th}(\text{H}_3\text{BNMe}_2\text{BH}_3)_4]$ by Daly et al.,⁴ and recently to 16 in CoB_{16} by Popov et al..⁵ These observations show that boron and borane possessing strong bonding capacity have led to a vast variety of molecular structures in chemistry and materials science and to provide suitable coordination environment and possibilities to achieve a larger doped-boron clusters with high coordination number. Although endohedral fullerenes ($\text{M}@\text{C}_{60}$) have been observed, the metal atom does not stay in the center of C_{60} thus does not interact with 60 carbon atom in those cases,⁶ with similarity to $\text{U}@\text{C}_{36}$.⁷ Theoretically authenticated molecular metal-fullerenes have widespread across the group 14 clusters;⁸ however, relatively speaking, the instinct bond involving metallic center is still in its infancy and mainly focusing on the stability of the fullerene structures, but a number of these fullerenes provide electrostatic field that the metal atom in those cases interacts with the fullerenes shell primarily ionically.⁹ Bare boron clusters (B_n) exhibit remarkable structural diversities, ranging from planar structures (borospherene) to fullerene-like cage structures, however, due to its electron deficiency and sp^2 hybrid orbitals as well as the short covalent radius, small B_n clusters favor two-dimensional (2D) structures to three-dimensional (3D) structure until $n = 38$, where a structural transition from 2D quasi-planar structure to highly symmetric 3D fullerene-like structure occurs.¹⁰ As reported, B_{24} possesses a quasi-planar structure.¹¹ Recently, there have been some breakthroughs in searching 3D boron clusters in the metal-doped boron clusters, as a new means of tuning the properties of borophenes.¹² Transition metal dopant boron clusters bring

the structural transit forward, such as $M@B_{12}$ were found to have double rings structures with the metal atoms coordinated above the quasi-planar bowl-shaped B_{12} ,^{12a} and $Fe@B_{14}$ were found to have double rings structures with the Fe atom coordinated by two connected B_7 rings.¹³ Even though the metal-centered boron clusters with spatial structure tubular structures have been also found in molecular CoB_{16}^- , RhB_{18}^- and TaB_{20}^- ,¹⁴ Until recently, the discovery of metal-centered boron cages, $M@B_{24}$ suggested the possibility of endohedral borospherenes by Ma, et.al.,¹⁵ like the family of endohedral fullerenes. Although the reported $M@B_{24}$ resemble the cage structure, whether its lowest energy structure forms a fullerene-like is still under-debatable.¹⁶ Interestingly, solid-state PuB_{12} compound, a cage-like endohedral fullerene B_{24} unit seizes Pu element, arising motivating questions, such as what is the main reason for maintaining the cage structure, and what is electronic structure of Pu, or of other actinide elements. On the other hand, hydrogen-terminated boron clusters prefer stable and well-known borane cages to form 2D structures in bare boron clusters,^{10c, 17} suggesting the possible existence of the *closo* $(BH)_{24}$ borane and derived endohedral complexes.¹⁸ Moreover, despite continuing and burgeoning interest in metal–boron binary clusters in recent years,^{3, 19} investigations of f-block elements doping metallo-borane complexes, and their bonding chemistry remain relatively less explored, especially metal-centered borometallic would greatly extend the chemistry of boron clusters and results in unprecedented structures and novel chemical bonding, giving rise to the large coordination number in a molecular complex. Thus, that actinide–boron binary clusters providing unlimited opportunities to discover new structures and bonding, as well as the field of f-element-doped borane clusters and acting as rich area of scientific research still full of surprises and unexpected results, opens up another new avenue of investigation.

Herein, based on our above demonstration that actinide dopant medium-sized borane clusters candidate the large coordination number compounds, and its derives reflect the intrinsically complicated nature of the potential energy surface (PES), we report an *in silico* study expanding the range of 5f-block metals from the Th to Cm; and the range of ligand filed from $(BH)_{24}$, to B_{24} and $B_{24}H_{12}$. By employing this series of complexes, we deliver a systematic theoretical investigation into a cohesive series of actinide-boron clusters, and the calculations suggest a new record An coordination number in $An(BH)_{24}$ where An-B bonding has significant level of covalence and high bond orders comparing with that of An-B in AnB_{24} . Global searches on UB_{24} reveals a half-cage B_{24} -based motif for constructing uranium-boron clusters. Systematic variations in n as a function of $U(BH)_n$ are computed, reflecting the differences of these assembled uranium and borane ligands, which can act as a blueprint for pursuing experimentally feasible complexes with high coordination metal compounds.

2. Methods

An exhaustive search potential energy surface (PES) of UB_{24} was performed using the CALYPSO²⁰ and Gaussian09 code. Both programs are properly described elsewhere. In CALYPSO, the initial structures was generated, while in Gaussian09 the PBE0/def2-SVP level was employed to optimize those initial structures, including a variety of spin states.²¹ The low-lying isomers (<100 kcal mol⁻¹ above the global minimum) were re-minimized and characterized at the PBE0/def2-TZVP level.

On the other hand, the initial half-cage-like geometries of AnB_{24} ($An = Th$ to Cm) clusters were taken from the lowest-energy Cartesian coordinate of aforementioned global minimum search. Then DFT calculations were performed on all studied clusters using the generalized gradient approximation (GGA) with the PBE²² exchange-correlation functional combined with dispersion correction by Grimme (D3-BJ)²³ as implemented in the Amsterdam Density Functional (ADF 2017.01) program.²⁴ The Slater basis sets with the quality of triple- ζ plus two polarization functions (TZ2P) were used, with the frozen core approximation applied to the inner shells [$1s^2-5d^{10}$] for actinide elements and [$1s^2$] for boron.²⁵ The scalar relativistic (SR) and spin–orbit (SO) coupling effects were taken into

account by the zero-order regular approximation (ZORA).²⁶ Geometries were fully optimized at the SR-ZORA level, and single-point energies were calculated with inclusion of the SO effects via the SO-ZORA approach. To correct the energies, we further carried out ab initio WFT calculations using advanced electron correlation methods implemented in the ORCA program.²⁷ The domain based local pair-natural orbital based singles and doubles coupled cluster method (DLPNO-CCSD(T))²⁸ was used along with the segmented all-electron relativistically contracted basis sets with the DKH2 Hamiltonians (SARC-DKH-TZVP) for actinides and DKH-def2-SVP for boron.²⁹

Further, the bond order analyses based on the Gopinathan-Jug method³⁰ were performed. And the charge analyses based on Mulliken method,³¹ and Hirshfeld analysis³² were calculated as well. In addition to test the dependence of the results on the density functional employed, B3LYP with TZ2P basis set was also used to optimize the geometries, vibrational frequency analyses and spin-orbital coupling correction in ADF, which gives the comparable results to the PBE method. Therefore, the B3LYP results are presented in the Supporting Information (SI) as Table S1.

3. Results

The crystal structure of PuB_{12} suggests the possible existence of the 24-boron-coordination PuB_{24} truncated octahedra and can be described as a fcc-array of independent the fullerene-like boron (B) cages, B_{24} . This B_{24} structural motifs corresponding to B-polyhedral has been existing in other similar MB_{12} compounds,³³ which corresponds to a sort of ‘endohedral system’ such as ScB_{12} whereas the B_{12} cavities are identical to the PuB_{12} structure. In fact, the Pu atom locates inside of the B_{24} cubooctahedral unit, which connects each other by means of additional B–B bonds, giving rise to additional holes which is, actually, B_{72} unit, which describes the charge phenomenon of Pu ion. If we separate the central PuB_{24} truncated octahedron, which is unstable and spontaneous deformation, we end up with half-cage-like PuB_{24} structure represented in Fig. 1.b. Then we add a hydrogen atom on each vertex of the B_{24} octahedron, leading to obtain the 24-coordination cage-like $\text{Pu}(\text{BH})_{24}$, as shown in Fig. 1.c.

Figure 1. Optimized lowest-energy structure of (a) bare B_{24} , (b) PuB_{24} and (c) $\text{Pu}(\text{BH})_{24}$.

3.1 AnB_{24}

Let us start the results with the exploration of the PES of UB_{24} (Fig. S1). There was no surprise that the global minimum for UB_{24} is a half-cage structure and its second lowest-energy isomer is also a C_{2v} half-cage structure and 2.28 kcal/mol less stable (at the PBE0/def2-TZVP level, see Fig. 2). These results agree with those reported by Wang et. al, suggesting that boron itself prefers to form borophene-type structures.^{10c} In contrast, the O -symmetry endohedral complex computationally reported for the ground state of $[\text{Sc}@\text{B}_{24}\text{H}_{24}]^+$ cannot be formed in UB_{24} systems,^{18b} due to boron favors to form triangular structural unit via B-B covalent bond which produce a half-cage structure for B_{24} , comparing to the fullerene-like cage B_{24} , where the large cavity of B_{24} versus medium uranium

radii results in uranium just engaging in strong interactions with half of the cage. Furthermore, our global minimum performed an unbiased search on the fullerene-like cage suggested by Ma. et al.¹⁵ shows 145.36 kcal/mol less stable (at the PBE0/TZP level) than the lowest half-cage one. Our global search also led to a number of other 3D structures, such as cage-like structures and two-layer structures, which are all much higher in energy. To gain insight into the chemical bonding of the UB₂₄ cages, we performed chemical bonding analyses on the global minima structure of UB₂₄ using the Adaptive Natural Density Partitioning (AdNDP) method, which is an extension of the popular natural bond orbital method. The AdNDP approach indicates that the σ -bonding pattern of cluster is composed of 8 peripheral two-center two-electron (2c–2e) B–B σ -bonds with an occupation number (ON) of 1.81|e| and 18-two 3c–2e σ -bonds (ON = 1.82|e|) connecting the edge rings. Comparing to the AdNDP results for bare B₂₄, three sets of delocalized bonds bridging over the U center connecting with boron framework are present. While the first set consists of three 7c-2e σ bonds, the second one involves eight 5c-2e $\sigma + \pi$ bonds and the last one composes of two 17c-2e $\sigma + \pi$ bonds (see Fig. 3).

Figure 2. The global minimum and low-lying isomers of UB₂₄. Relative energies for the isomers of UB₂₄ are given in kcal/mol at the PBE0/def2-TZVP levels of theory.

Figure 3. Chemical bonding picture, obtained for the ISO1 of the UB₂₄ (left) and B₂₄ (right) cluster via the UAdNDP analysis. ON denotes occupation number.

On the other hand, the initial half-cage geometries of AnB₂₄ (An = Th to Cm) clusters were taken from the lowest-energy Cartesian coordinate of aforementioned global minimum search of UB₂₄. Then, the geometry optimizations were performed with PBE in ADF program with various possible multiplicities and followed by a TDDFT calculation on the lowest energy state to determine the ground electronic states of each species. The calculations with full symmetry and partial occupied orbitals give the ideal *O_h* structure. Once localizing electrons onto a specific orbital, the structure is not stable any more, but with large imaginary frequencies leading to break the

symmetric structure. Table S1 summarizes the results for different spin states for the AnB₂₄ complexes. The most stable spin states for ThB₂₄, PaB₂₄, UB₂₄, NpB₂₄, PuB₂₄, AmB₂₄ and CmB₂₄ complexes as determined from both UPBE-D3 and DLPNO-CCSD(T) calculations are the singlet, doublet, singlet, doublet, quintet, octet and quintet state, respectively. The oxidation state of An is derived from the rest of the An valence electrons based on Mulliken population analyses. As denoted by the Mulliken spin in Table 2, the electronic configuration on Np is f², which indicates an oxidation state of +V for Np. Remarkably, for the early actinides, Th^{IV}, Pa^V, U^{VI}, the 5f populations are almost 0, which significantly increases for the neptunium and afterward transuranium elements and becomes 1.52 |e| for Np^{IV}, 4.39|e| for Pu^{IV} (f⁴), 6.13|e| for Am^{III} (f⁶) and 6.26|e| for Cm^{IV} (f⁶). This is one evidence that the oxidation state of An increases from +IV (Th^{IV}) to +VI (U^{VI}) with increasing nuclear charge, as expected. However, the oxidation state gradually decreases to +V for Pu toward Cm, and +III for Am, ascribed to the stable half-occupied 5f-shell electronic state. Obviously, the trend of oxidation state across the actinide series in agreement with the half-cage coordination AnB₁₂ clusters as detailed in our previous work.^{19b} In contrast the formation of spherical aromatic endohedral metallic fullerenes as previously published, the optimized structure has a very low symmetry where the actinide ions trapped in the half-cage B₂₄ unit via metal-boron polarized covalent interactions. As depicted in Table S2, the bond lengths of U-B in UB₂₄ are in the range of 2.562 Å to 2.997 Å, arising an average U-B bond length of ca. 2.713 Å; this value undulates from Th down to U, up to Pu, down to Am, and finally a bit up to Cm along with the increase of atomic number from Th to Cm, as shown in Table 1. In addition, the Gopinathan-Jug method analyzes the bond-order of An-B in terms of density matrix and represents the bond strength increase from Th up to U, down to Am, and then eventually slight up to Cm, indicating a relatively strong U-B bonding interactions among those of An-B (0.184 to 0.333), which is largely resulted from the extended valent RDF rather than the electrostatic interaction implied by the unchanged average Hirshfeld charges on An and on B in the AnB₂₄. The An-B distances as well as its corresponding bond order provide further insights into bonding pattern in AnB₂₄ that the juxtaposition of contracted An radii across the series and the relatively large size of B₂₄ fullerene cage yields insubstantial An-B bonding capacity that can hardly maintain AnB₂₄ in high symmetry. Instead, B₂₄ moiety favor half-cage structure rather than the fullerene cage structure. In addition, the poorly electronegativity of boron create an unfavorable ligand-field effect, especially for B₂₄ unit, which has weak oxidizing capacity that can hardly maintain actinides in high oxidation states. From the bond lengths not all metal-cage interaction induced 24-coordination first coordinate shell. A juxtaposition of factors that include the radial extension contraction of An 5f6d7s valence orbitals reducing the orbital overlap of An-B, the energy level decrease of the An 5f orbitals across the series, and the poorly electronegativity of boron create an unfavorable ligand-field effect, which yields insubstantial oxidizing capacity that can hardly maintain actinides in high oxidation states.

Table 1. The electronic configurations of An, the calculated bond-length (Å) and Gopinathan-Jug bond orders (BO_{G-J}) of An-B, and the Mulliken spins and Hirshfeld charges on B and An for the ground state AnB₂₄ complexes at the PBE/TZP level of theory.

Species	State	Elec. Conf.	Bond Length	BO	charge		Mulliken Spin	
					An	B	An	B
Th	¹ A	f ⁰	2.862	0.184	0.55	-0.02	0.00	0.00
Pa	² A	f ⁰	2.773	0.295	0.65	-0.03	0.23	0.03
U	³ A	f ²	2.713	0.333	0.56	-0.02	1.43	0.00
Np	⁴ A	f ³	2.771	0.312	0.55	-0.02	2.83	-0.02
Pu	⁵ A	f ⁴	2.776	0.179	0.71	-0.03	4.39	-0.02

Am	⁶ A	f ⁵	2.700	0.134	0.55	-0.02	6.13	0.04
Cm	⁷ A	f ⁶	2.927	0.224	0.56	-0.02	6.26	-0.09

3.2 An(BH)₂₄

Geometry optimizations and frequency calculations were firstly performed on the half sandwich structures with different spin states and followed by a TDDFT calculation on the lowest energy state to confirm the ground electronic states of the An(BH)₂₄ (An = Th to Cm) clusters. The relative energies for the considered spin state of each An(BH)₂₄ cluster show that the most stable spin states for Th(BH)₂₄, Pa(BH)₂₄, U(BH)₂₄, Np(BH)₂₄, Pu(BH)₂₄, Am(BH)₂₄ and Cm(BH)₂₄ clusters as determined from DLPNO-CCSD(T) calculations are the singlet, doublet, singlet, quartet, quintet, sextet and septet state, respectively, as detailed in Table S3 in the Supporting Information (SI); selected geometrical parameters are reported in Table 2, and more detailed structural information are provided in Table S4. Surprisingly, the cage size of the (BH)₂₄ unit is strongly reduced upon interacting with the actinide ions, and is however independent of the actinide element. The calculated average An–B bond length gradually shortens from 2.626 Å for thorium down to 2.597 Å for americium, then up to 2.618 Å for curium. The present data suggests that it can be a somewhat larger stability for early actinide An(BH)₂₄ clusters with 24 coordination number structure, depicted in Fig. 4. Extending to the Pa(BH)₂₄, Pa does also retain all of the BH unit in the first coordination shell, albeit with a wider range of metal–boron distances (2.443–2.823 Å) than for the Th analog (2.523–2.760 Å). The average Pa–BH E_B in this system is -240.61 kcal/mol, slightly larger than that for Th–BH (-237.92kcal/mol), as expected given the shorter bond distance as well as the larger charge of the metal ion in the latter. U(BH)₂₄ has an even much wider range of U–BH distances (2.368–2.896 Å) than that of in either Th(BH)₂₄ or Pa(BH)₂₄, making its description as a genuine 24 coordination number structure debatable, but the geometry of Np(BH)₂₄ is more compact than that of U(BH)₂₄, with Np–BH distances in the range of 2.397–2.731 Å, and an average Np–BH E_B of -240.72 kcal/mol. A smaller range of Pu–BH distances (2.420–2.708 Å) of the stable first-shell structures locates at Pu(BH)₂₄, while this range enlarges to 2.366–2.775 Å in Am(BH)₂₄, afterward expands to 2.409–2.811 Å in Cm(BH)₂₄, which has very similar geometry that of Pa(BH)₂₄, denoting that the declined stability in transplutonic clusters is opposite to the contracted radii. An(BH)₂₄ (An = Th to Cm) is therefore the most likely of the new record of 24 coordination number systems to be experimentally accessible, especially for early actinide clusters. As noticed, these average An–B bond distances are all slightly longer than the sum of Pyykkö’s single-bond covalent radii for the An–B bonds,³⁴ indicative of the small values of average An–B bond order by Gopinathan-Jug method. However, the considerably substantial bonding interaction between metal and BH via sum of 24 An–B bond orders, leads to abundantly exoergic in the formation of An(BH)₂₄. Thus, the An(BH)₂₄ complex features very strong bonding interactions between the actinide metal and the BH moiety with an effective computed bond order of 3.23–8.29 is predicted. As noticed, the substantial decrease in the average bond length but the substantial increase in the bond strength from Th to U results from both the actinide contraction and the increasing Hirshfeld charge in the series, consistent with the decrease of the metallic atomic radii. The marked decline in bond strength from U to Am, opposite to the actinide contraction, implies a weaker An–B bonding interaction, which is in accord with the decrease in the formation energies that reflects the reduced ability of transuraniums to maintain the 24-coordination number structure. As a common bonding feature for actinide complexes, the bond strength turns stronger at An = Cm than its previous element. As derived from rest of the An valence electrons based on Mulliken population, the oxidation state of An exists the highest oxidation state for the early three actinides and tetravalent transuranic afterward, according to the corresponding 5f populations as 0.13 |e| for Pa^V (f⁰), 2.75|e| for Np^{IV} (f³), 3.86|e| for Pu^{IV} (f⁴), 5.11|e| for Am^{IV} (f⁶),

and 6.05|e| for Cm^{IV} (f⁶). Obviously, the turning-point of oxidation state in An(BH)₂₄ is late than that of AnB₂₄, because the formation of BH unit destabilizes the B 2p orbitals into virtual band thus provides more available electronic acceptor holes, and reduces the self-polymerized ability of boron thus yields highly reasonable and new record first shell coordination number. These data are consistent with the bonding analysis detailed below.

Table 2. The electronic configurations of An, the calculated bond-length (Å) and Gopinathan-Jug bond orders (BO_{G-J}) of An-B, and the Mulliken spins and Hirshfeld charges on B and An for the ground state An(BH)₂₄ complexes at the PBE/TZP level of theory.

Species	State	Elec. Conf.	OS	Bond Length	BO	Hirshfeld charge		Mulliken Spin	
						An	B	An	B
Th	¹ A	f ⁰	IV	2.626	0.199	0.21	0.00	0.00	0.00
Pa	² A	f ⁰	V	2.616	0.307	0.50	-0.02	0.13	0.04
U	¹ A	f ⁰	VI	2.604	0.345	0.48	-0.02	0.00	0.00
Np	⁴ A	f ³	IV	2.601	0.270	0.37	-0.01	2.75	0.01
Pu	⁵ A	f ⁴	IV	2.599	0.143	0.61	-0.02	3.86	0.00
Am	⁶ A	f ⁵	IV	2.462	0.134	0.54	-0.02	5.11	0.03
Cm	⁷ A	f ⁶	IV	2.618	0.213	0.31	-0.01	6.05	-0.01

3.3 U(BH)₂₄ (n = 1 to 24)

To evaluate the An can be coordinated by 24 (BH) ligand, seen in Table 3 and Fig. S2, the average U-BH distances increase by just ~ 0.33 Å from n=1 to n=24, as expected as more BH ligands coordinate to the metal center. Because uranium has an 5f³6d¹7s² ground electron configuration and the electron spin multiplicities of the U(BH)_n clusters are determined by the orientation of the metal-based electrons, we considered the singlet, triplet and quintet states for the neutral species. The lowest energy state found for U(BH)₁ is a ⁵A' linear structure with the five valent electrons in U 5f7s based molecular orbitals, consisting of an electronic configuration of f_σ²f_σ¹s², suggesting that an unprecedented U^I oxidation state exists in U(BH)₁. Low-valent uranium is usually considered to be quite reductivity, but here the uranium is bonded by such weak electronic acceptor that it is now essentially reducing in nature. The lowest energy state found for U(BH)_n (n = 2 toward 6) is a triplet planar C_{nv} structure with two unpaired electrons located on the 5f orbitals of U, giving rise to an electronic configuration of [f_π¹f_φ¹] for U center. Results of calculations on U(BH)₃ suggest that planar C_{3v} structure with the shortest U-B bond length of 2.152 Å is a favored structural motif, in qualitative terms of that electronic structure is an ³E state and can be described as (f²) electronic configuration, which gives rise to the strong orbital hybrid between U 5f and B 2p in the HOMO-LUMO range, implied by the percent compositions of the highest occupied and lowest unoccupied valence molecular orbitals listed in Table 4. Surprisingly, the U(BH)₇ is the smallest cluster that predicted to have a ¹A₁ ground state with the U (f⁰) occupancy, favoring a quasi-planar structure in which the HOMO and LUMO gap is enlarged to 0.998 eV, being 0.568 eV larger in energy comparing to that of the planar U(BH)₆, indicating the stability of U^{VI} oxidation state in U(BH)₇. Afterward, the U(BH)_n favors a singlet ground state with a 5f⁰ subshell occupancy on metal center, as summarized in Table 3 with the average formation energies vs n (RE) based on the reaction of U + n BH → U(BH)_n, average U-B bond lengths and the corresponding Gopinathan-Jug bond order (BO_{G-J}). As can be seen in Table 3, the average U-BH distances expectedly locate with the range of 2.198 Å to 2.604 Å for the series of U(BH)_n,

reflecting that although the slightly lengthening of the U-BH distances, all 24 BH units are clearly indeed in the first coordination shell. The incremental BH binding energy $E_B(n)$, calculated $U(BH)_{n-1} + BH \rightarrow U(BH)_n$ shown in Figure 4, illustrates that the energy gain upon attaching a BH ligand to $U(BH)_{n-1}$. Notable, the trend for $E_B(n)$ is unchanged, unlike that $AcHe_n^{3+}$ ($n=1-17$) has a gradual decrease as reported by Nicolas et al,¹ thus reflecting a totally different bonding nature in the $U(BH)_{24}$ clusters.

Table 3. Electronic configurations of An, the binding energies for n BH + U $\rightarrow$ $U(BH)_n$, the average calculated U-B bond-length (Å), and Gopinathan-Jug bond orders of U-B for series of $U(BH)_n$ ($n = 1$ to 24) complexes at the PBE/TZP level of theory.

structure	2S+1	Elec. Conf. of U	RE	Bond Length	BO _{G-J}
1	5	f^2s^2	-97.78	2.275	2.018
2	3	f^2	-119.98	2.198	1.793
3	3	f^2	-118.64	2.152	1.786
4	3	f^2	-122.00	2.285	1.219
5	3	f^2	-119.49	2.288	1.218
6	3	f^2	-117.74	2.310	1.115
7	1	f^0	-123.60	2.326	1.071
8	1	f^0	-122.67	2.383	0.928
9	1	f^0	-123.00	2.374	0.835
10	1	f^0	-121.60	2.418	0.740
11	1	f^0	-122.00	2.485	0.661
12	1	f^0	-121.48	2.439	0.664
13	1	f^0	-122.58	2.482	0.584
14	1	f^0	-123.29	2.514	0.527
15	1	f^0	-122.91	2.536	0.513
16	1	f^0	-123.14	2.424	0.549
17	1	f^0	-121.88	2.462	0.506
18	1	f^0	-122.39	2.502	0.474
19	1	f^0	-123.21	2.532	0.436
20	1	f^0	-123.01	2.505	0.423
21	1	f^0	-123.01	2.554	0.402
22	1	f^0	-123.36	2.574	0.383
23	1	f^0	-122.87	2.585	0.369
24	1	f^0	-122.71	2.604	0.345

Figure 4. $E_B(n)$ for $U(BH)_n$ ($n = 1-24$).

4. Discussion

Metallaboron cage compounds of the main group metals have been of interest for many years, because they might be considered as the embryos for boron fullerenes. However, such cage-like structures have never been observed experimentally for bare boron clusters, even though they have been shown to be stable computationally. Due to trigonal sp^2 hybrids bare boron clusters are found to be 2D up to B_{36} , while some transition metal-doped boron clusters are found to preserve the planar boron or tubular boron framework on metal doping. For the UB_{24} cluster, the half-cage structure was suggested to be the global minimum, whereas the cage-like structures of B_{24} were found to be high-energy isomers, being 134.17 kcal/mol higher in energy than the lowest one. Clearly, the dominant sp^2 hybridization boron AOs in the half-cage-like B_{24} gives rise to its main interaction with the actinide atoms via delocalized $\sigma + \pi$ bonds thus stabilize the half-cage-like global minima (structures 1 to 3) for UB_{24} . Consistently, the typical AdNDP molecular orbitals (MOs) shown in Fig. 3 as well as average An–B distance presented in Table 1 for AnB_{24} complexes, indicating An–B bond predominantly possessing an ionic bonding feature.

To understand the inherent difference in chemical interaction of the half-cage UB_{24} and cage-like $U(BH)_{24}$ clusters, we analyzed the Kohn–Sham molecular orbitals (MOs) of the B_{24} and $(BH)_{24}$ fragments and their MO energy levels with correlation to the atomic orbitals (AOs), shown in Fig. 5 and Fig. 6, respectively. Because of the B ($2s^22p^1$) configuration, the MOs from the 2s manifold are fully occupied, and the bonding and antibonding MOs from the 2p orbitals are both occupied in B_{24} . In addition, B 2s and 2p AOs mix strongly due to their sufficiently close in energy, and the chemical bonding pattern indicates significant sp^2 hybridization, that therefore contributes to the narrow energy separation between the fully occupied $8b_1$ bonding orbital and unoccupied $9b_1$ antibonding orbitals. The orbital interactions within the B_{24} framework can be approximately classified as σ - and π -type bonding and antibonding pairs. Of particular interest are the virtual π -type delocalized antibonding orbitals, which are mainly formed by B 2p orbitals on each B atom. Those MOs of the B_{24} fragment are the major contributor in overlapping with actinide 7s6d5f AOs on the four sites because they directly point to the metal center from the cyclic directions, which provide a suitable space to fit the actinide atoms to allow optimal interactions with the surrounding boron atoms, mainly electrostatic interaction with considerable covalent contributions, as shown in Fig. 7.

Figure 5. Energy levels of the scalar-relativistic Kohn–Sham molecular orbital isosurfaces of C_{2v} B_{24} in correlation with the orbitals from boron fragments (isovalue = 0.03 a.u.) by using a PBE/TZ2P calculation. Virtual MOs coloured by brown and light blue and occupied MOs coloured by yellow and blue.

The energy levels of the frontier 5d- and 6s-based MOs of the $(BH)_{24}$ fragment with D_{4d} symmetry together with the corresponding MO isosurfaces are shown in Fig. 6. Firstly, hydrogenation of pure boron clusters was expected to break the peripheral B–B σ bonds, and reduce the delocalized B–B π bonds and cause its orbital hybrid changing from sp^2 to sp^3 .³⁵ Second, the bonding model of donor–acceptor interactions straightforwardly explains the strongly linear equilibrium geometry of BH, in accord with the results of the bonding analysis discussed below which shows that the [BH] molecule has one doubly occupied orbital involving B $2p_z$ to H $1s$ σ –back donation interaction, whereas the virtual σ –antibonding orbital composes of B $2p_z$ AOs, thus actinide valence electrons can enter the empty $2p_z$ atomic orbitals to stabilize clusters. Based on group theory, the $2p_z$ orbitals of B atoms in D_{4d} $(BH)_{24}$ transform into a group of $a_2 + b_2 + e_1 + e_3$, such as the region ranging from -6 eV to -2 eV where is dominantly composed of unoccupied states from the virtual B $2p_z$ based MOs. The selections of these $(BH)_{24}$ fragments are simplified for understanding the orbital interactions between the two fragments of the clusters, although they turn out to be adequate for illustrative purposes. Within a simple MO approximation, the B $2p_z$ based molecular orbitals in $(BH)_{24}$ strong orbital interactions with the actinide $5f6d7s$ hybrid valence AOs significantly stabilize the B $2p_z$ MOs to result in the stability for the cage-like $An(BH)_{24}$ structure.

Figure 6. Energy levels of the scalar-relativistic Kohn–Sham molecular orbital isosurfaces of D_{4d} $(BH)_{24}$ in correlation with the orbitals from boron and hydrogen fragments (isovalue = 0.03 a.u.) by a PBE/TZ2P calculation. Virtual MOs coloured by brown and light blue and occupied MOs coloured by yellow and blue.

Unravelling the origins for the trends in structures of actinide boron and actinide borane clusters, taking uranium as an examples, inspection of the MO diagrams difference between UB_{24} and $U(BH)_{24}$ shows that upon actinide metal doped, $U(BH)_{24}$ directly strong covalent interaction of the 6d and 5d AOs of U with the lone-pair MOs of borane bring out the HOMO-LUMO gap of around 1.773 eV, whereas UB_{24} cluster has a SOMO-LUMO gap of around 0.268 eV, denoting a comparatively weaker orbital interactions between the U atom and the B_{24} host. The discrepancy of bonding interaction between uranium and the ligand moieties arises two types of bonding feature in UB_{24} and $U(BH)_{24}$, that is the ionic U–B bond with covalent contributions in UB_{24} *vs* the leading covalent U–B bonding with substantial ionicity $U(BH)_{24}$, and further forms two patterns of structures. In addition, the Hirshfeld charges (Tables 1 and 2) on the An atoms in $An(BH)_{24}$ is generally smaller than in AnB_{24} , within the range of 0.21–0.61|e|, indicating a less charge transfer from An atoms to the borane motif. Thus, the stability of $An(BH)_{24}$ may be due to the significant covalent bonding of An–B, being different from the half-cage AnB_{24} which is a charge transfer compound, where the interaction between An and the boron fragment is mostly ionic. The B sp^3 hybridization along with the predominate orbital interactions creates a perfect field to seize the An atoms with 24-coordination number in $An(BH)_{24}$.

Figure 7. The molecular orbital energy level schemes obtained at B3LYP/TZ2P level, illustrating the correlations of the MOs of the UB_{24} complexes in terms of U with B_{24} and of the $U(BH)_{24}$ complexes in terms of U with $(BH)_{24}$.

For $An(BH)_{24}$ ($An = Th$ to Cm) clusters, according to energy levels for all species (Fig.8), the HOMO-SOMO energy gaps of the $U(BH)_{24}$ and $Pa(BH)_{24}$ are the largest (1.842 eV and 1.843 eV, respectively), suggesting their stability. When $An = Th$, the energy gap becomes smaller (0.743 eV), largely due to the longer bond distance as well as higher energy of Th valence orbital inducing weaker interaction of Th–B. As the contracted of An 5f and 6d orbitals are generally reduced in their radial distribution compared to those of U, the 2p-5f/6d bonding in the $Np(BH)_{24}$ and afterward species turns out much weaker, causing the small splitting of bonding and antibonding An–B MOs. Consequently, a relatively high spin state of $An(BH)_{24}$ ($An = Np, Pu, Am$ and Cm) species is stable. Furthermore, the reduced 5f energy levels as well as the increasing orbital interaction between B 2p_z and An 5f orbitals when traversing the actinide series from Th to Cm consequently, reveals the An–B bonds generally transit from strengthening to weakening at $An = U$, which has been a general trend in actinide chemistry emerging in accordance with the atomic number of the actinides.³⁶ Besides, the net consequence of these orbital interactions upon formation of the $An(BH)_{24}$ complex can be basically viewed as the An valence orbitals being destabilized energetically in Fig. 8, leading to An cations in the complexes. Referred to Table 2, the natural populations of each species show that the oxidation states of An increase from +IV in Th to +VI in U, and being +IV in Np and afterward actinides, regardless of the increasing nuclear charge from Np to Cm of the series, because the fragment orbitals of B 2p_z and An 5f lie in the same energy range and thus the possibility of electron transferring from metal to ligand is drastically difficult.

Figure 8. Frontier Kohn-sham molecule orbitals of the $\text{An}(\text{BH})_{24}$ complexes.

5. Conclusions

We have characterized a series of actinides-doped boron and borane clusters, AnB_{24} and $\text{An}(\text{BH})_{24}$, via the means of quantum chemical calculations. Exhausted computational searches established the C_{2v} half-cage-like structures with An hosted by the B_{24} bowl and the non-symmetry cage-like structures with An centred by the $(\text{BH})_{24}$ motif. Extensive chemical bonding analyses reveal that the B sp^3 hybridization originally rises the difference of An–B bonding in $\text{An}(\text{BH})_{24}$ and $\text{An}(\text{B})_{24}$ to have totally different structures. The $\text{An}(\text{BH})_{24}$ molecular cages represent the 24-coordination number for an actinide metal atom known as the highest in actinide chemistry and opens new possibilities for designing novel borane-based nanomaterials. Moreover, the $(\text{BH})_n$ clusters can be considered as the ligand to make filled boron fullerenes practical due to the significant B–B bonding and the high stability. Furthermore, there are possibilities to observe larger actinide-doped-borane clusters with even higher coordination and to further update the coordination number in actinide chemistry.

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Conflicts of interest

There are no conflicts to declare.

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