

New theoretical insight into high coordination number complexes in actinides-centered borane

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Table S1. The multiplicities, the relative energies (ΔE , kcal/mol) compared with the most stable multiplicity isomer and the reaction energies (RE, kcal/mol) of $An + B_{24} \rightarrow AnB_{24}$ for AnB_{24}

structure	State	RE	ΔE_{pbe}	ΔE_{b3lyp}
Th	¹ A	-157.08	0.00	0.00
	³ A	-145.3	13.35	20.38
	⁵ A	-128.94	31.27	41.80
Pa	² A	-193.55	0.00	0.00
	⁴ A	-181.6	13.71	21.29
	⁶ A	-161.99	35.11	41.73
U	¹ A	-173.06	1.28	19.75
	³ A	-172.66	0.00	0.00
	⁵ A	-162.71	12.69	61.61
Np	² A	-143.61	7.00	8.19
	⁴ A	-150.89	0.00	0.00
	⁶ A	-136.39	16.45	28.19
	⁸ A	-118.76	35.3	49.14
Pu	¹ A	-128.88	15.13	42.69
	³ A	-137.65	6.36	16.09
	⁵ A	-144.01	0.00	0.00
	⁷ A	-133.72	10.29	8.86
Am	² A	-26.97	37.76	33.40
	⁴ A	-48.84	17.30	15.05
	⁶ A	-65.66	0.00	0.00
	⁸ A	-51.57	15.39	9.53
Cm	¹ A	-52.48	48.5	98.13
	³ A	-73.97	27.75	22.66
	⁵ A	-100.53	1.01	6.30
	⁷ A	-101.33	0.00	0.00

Table S2. The bond length (\AA) of An-B in AnB_{24} at the PBE/TZ2P level of theory.

An-B	Th	Pa	U	Np	Pu	Am	Cm
1	2.676	2.635	2.628	2.596	2.633	2.642	2.645
2	3.085	3.035	2.997	2.979	2.972	2.969	3.030
3	2.748	2.713	2.708	2.732	2.724	2.730	2.713
4	2.693	2.622	2.562	2.608	2.596	2.593	2.604
5	2.676	2.635	2.628	2.596	2.633	2.642	2.645
6	3.085	3.035	2.997	2.979	2.972	2.969	3.030
7	2.861	2.765	2.671	2.646	2.694	2.705	2.772
8	2.693	2.622	2.562	2.608	2.596	2.593	2.604
9	2.789	2.781	2.785	2.734	2.742	2.755	2.760
10	2.693	2.622	2.562	2.608	2.596	2.593	2.604
11	2.861	2.765	2.671	2.646	2.694	2.705	2.772
12	2.779	2.730	2.696	2.723	2.680	2.676	2.682
13	2.861	2.765	2.671	2.646	2.694	2.705	2.772
14	3.085	3.035	2.997	2.979	2.972	2.969	3.030
15	2.779	2.730	2.696	2.723	2.680	2.676	2.682
16	2.789	2.781	2.785	2.734	2.742	2.755	2.760
17	2.748	2.713	2.708	2.732	2.724	2.730	2.713
18	2.748	2.713	2.708	2.732	2.724	2.730	2.713
19	2.676	2.635	2.628	2.596	2.633	2.642	2.645
20	2.676	2.635	2.628	2.596	2.633	2.642	2.645
21	2.748	2.713	2.708	2.732	2.724	2.730	2.713
22	2.861	2.765	2.671	2.646	2.694	2.705	2.772
23	3.085	3.035	2.997	2.979	2.972	2.969	3.030
24	2.693	2.622	2.562	2.608	2.596	2.593	2.604
Ave.	2.808	2.754	2.718	2.715	2.722	2.726	2.747

Table S3. The multiplicities and the relative energies (ΔE , kcal/mol) compared with the most stable multiplicity isomer for $\text{AnB}_{24}\text{H}_{24}$.

An	State	ΔE_{pbe}	$\Delta E_{\text{DLPNO-CCSD(T)}}$
Th	^1A	0.00	0.00
	^3A	24.00	29.01
Pa	^2A	0.00	0.00
	^4A	46.81	55.37
U	^1A	0.00	0.00
	^3A	20.49	32.98
	^5A	49.59	60.92

Np	² A	14.37	48.57
	⁴ A	0.00	0.00
	⁶ A	33.23	75.25
Pu	¹ A	21.10	67.60
	³ A	12.47	27.17
	⁵ A	0.00	0.00
	⁷ A	12.47	19.53
Am	² A	38.76	48.70
	⁴ A	20.62	41.65
	⁶ A	0.00	0.00
	⁸ A	10.94	17.95
Cm	¹ A	53.06	98.55
	³ A	54.39	77.04
	⁵ A	23.34	66.02
	⁷ A	0.00	0.00

Table S4. The bond length (Å) of An-B in AnB₂₄H₂₄ at the PBE/TZ2P level of theory.

An-B	Th	Pa	U	Np	Pu	Am	Cm
1	2.551	2.718	2.889	2.564	2.633	2.742	2.597
2	2.539	2.503	2.453	2.596	2.609	2.486	2.621
3	2.627	2.709	2.779	2.563	2.665	2.775	2.833
4	2.632	2.804	2.611	2.716	2.705	2.721	2.675
5	2.632	2.701	2.684	2.652	2.663	2.776	2.804
6	2.706	2.721	2.629	2.729	2.664	2.718	2.636
7	2.605	2.573	2.667	2.397	2.420	2.535	2.591
8	2.639	2.622	2.639	2.469	2.481	2.528	2.682
9	2.623	2.680	2.842	2.485	2.513	2.646	2.762
10	2.753	2.772	2.747	2.700	2.711	2.774	2.823
11	2.523	2.500	2.561	2.567	2.705	2.523	2.505
12	2.572	2.444	2.505	2.490	2.438	2.366	2.444
13	2.548	2.443	2.368	2.687	2.575	2.456	2.532
14	2.579	2.586	2.410	2.660	2.702	2.520	2.485
15	2.642	2.546	2.512	2.698	2.508	2.641	2.468
16	2.616	2.444	2.518	2.463	2.437	2.366	2.409
17	2.641	2.707	2.591	2.658	2.674	2.717	2.742
18	2.760	2.601	2.759	2.447	2.480	2.527	2.513
19	2.677	2.648	2.896	2.725	2.708	2.770	2.811
20	2.688	2.832	2.529	2.634	2.637	2.735	2.588
21	2.600	2.554	2.450	2.567	2.588	2.508	2.627

22	2.547	2.596	2.468	2.628	2.605	2.485	2.556
23	2.644	2.556	2.468	2.731	2.680	2.491	2.612
24	2.673	2.528	2.518	2.588	2.583	2.510	2.523
Average	2.626	2.616	2.604	2.601	2.599	2.597	2.618

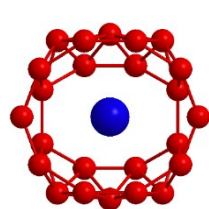
Table S5. The multiplicities and the relative energies (ΔE , kcal/mol) compared with the most stable multiplicity isomer for $AnB_{24}H_{12}$.

structure	State	ΔE_{pbe}
Th	1A	0.00
	3A	9.10
Pa	2A	0.00
	4A	11.30
U	1A	0.00
	3A	40.55
	5A	53.89
Np	2A	45.74
	4A	0.00
	6A	28.46
Pu	1A	40.16
	3A	43.24
	5A	38.23
	7A	0.00
Am	2A	67.71
	4A	90.36
	6A	16.70
	8A	0.00
Cm	1A	123.05
	3A	114.90
	5A	28.02
	7A	0.00
	9A	5.71

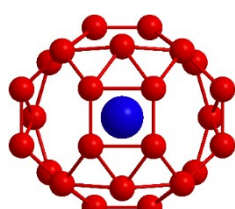
Table S6. The bond length (\AA) of An-B for $AnB_{24}H_{12}$ at the PBE/TZ2P level of theory

An-B	Th	Pa	U	Np	Pu	Am	Cm
1	3.945	2.691	3.809	2.864	3.297	2.726	2.623
2	2.563	2.440	2.446	2.668	2.687	2.871	2.797
3	2.645	2.558	2.431	2.596	2.506	2.787	2.638
4	2.908	2.722	2.828	2.507	2.530	2.819	2.755
5	2.666	2.601	2.351	2.661	2.382	2.811	3.235
6	2.790	2.717	2.619	3.560	2.880	2.556	3.635

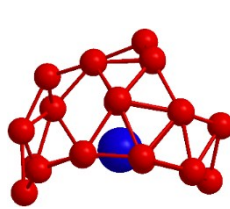
7	2.921	2.492	2.773	3.641	2.860	2.746	3.650
8	2.556	2.202	2.405	3.145	2.819	2.639	3.350
9	2.980	2.544	2.928	3.742	3.543	2.936	3.304
10	2.625	2.309	2.521	2.637	2.644	2.815	3.622
11	2.761	2.460	2.586	3.504	2.514	4.656	2.694
12	3.983	2.468	3.805	3.943	2.644	4.118	2.528
13	2.888	2.380	2.753	2.531	3.049	4.100	2.718
14	2.873	3.355	2.665	2.776	2.641	4.391	2.595
15	3.514	3.832	3.545	2.786	3.104	3.872	2.897
16	3.266	2.556	3.211	2.627	2.715	4.163	2.745
17	3.146	2.978	2.871	2.792	2.315	3.361	3.705
18	3.418	3.074	3.515	2.291	2.841	3.875	4.443
19	2.983	2.991	2.765	2.616	2.668	3.862	3.630
20	3.776	3.080	3.703	2.355	2.619	3.560	4.023
21	3.812	2.671	2.862	2.920	2.385	4.037	4.204
22	4.175	3.649	3.342	2.610	2.836	3.458	3.861
23	3.650	3.626	3.016	2.406	2.769	3.722	3.997
24	3.540	3.796	2.824	3.763	2.629	3.807	4.037
Average	3.183	2.841	2.941	2.914	2.745	3.445	3.320



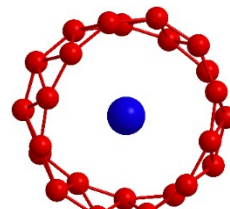
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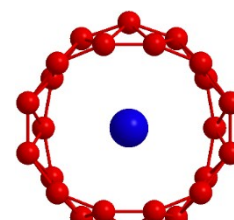
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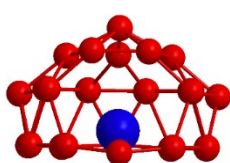
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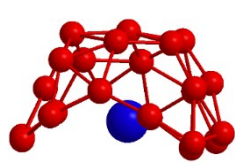
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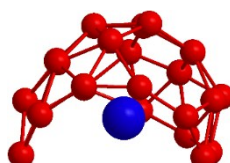
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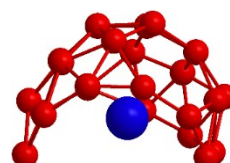
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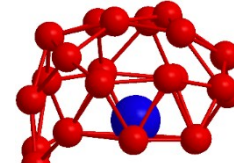
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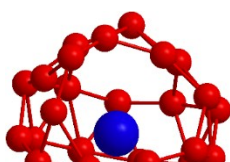
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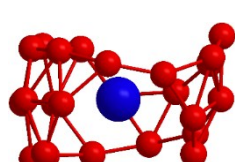
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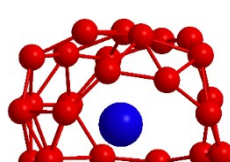
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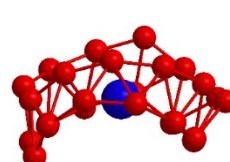
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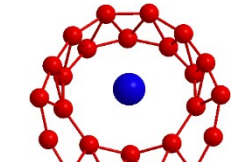
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ISO15 3C_1 42.29

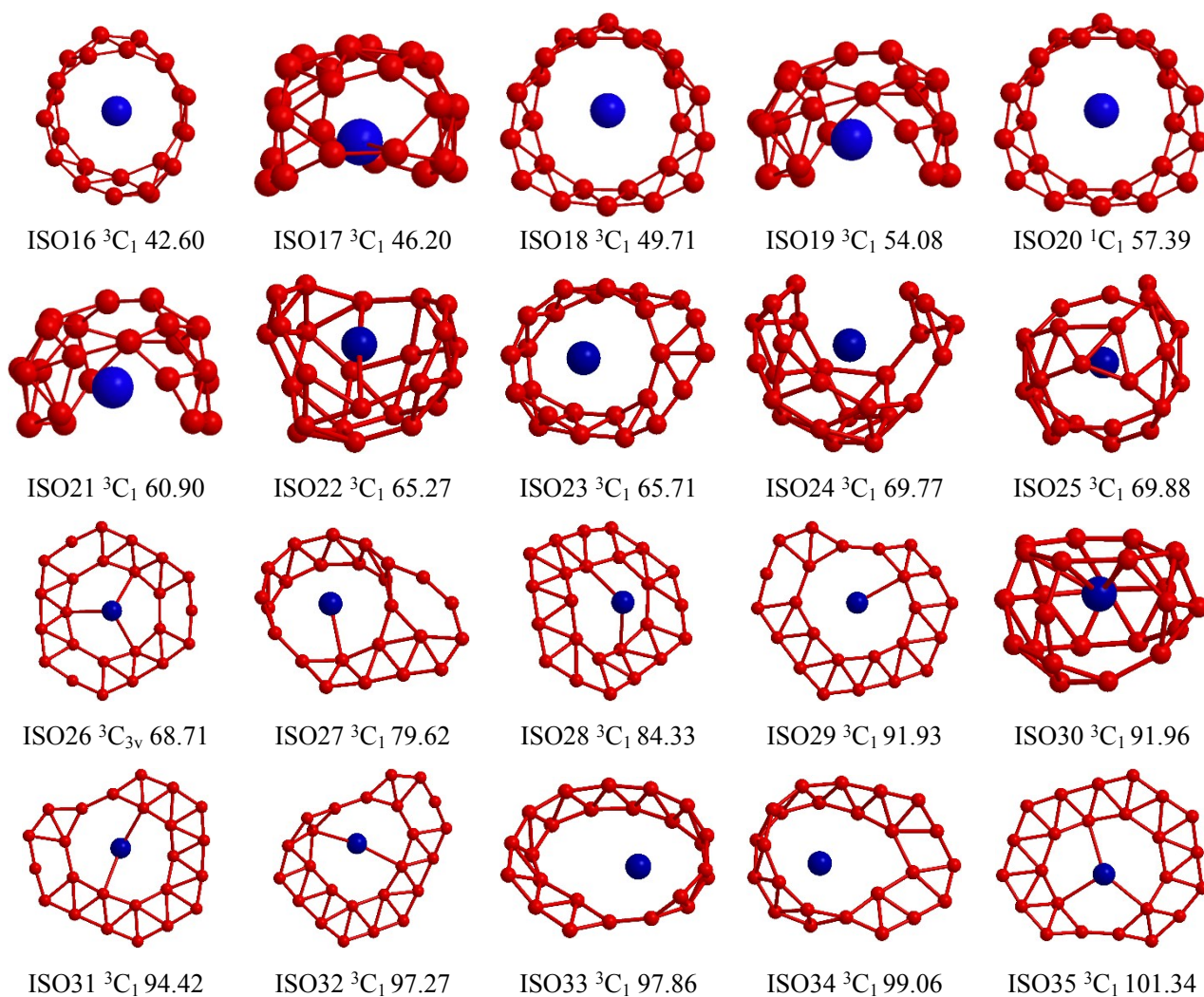
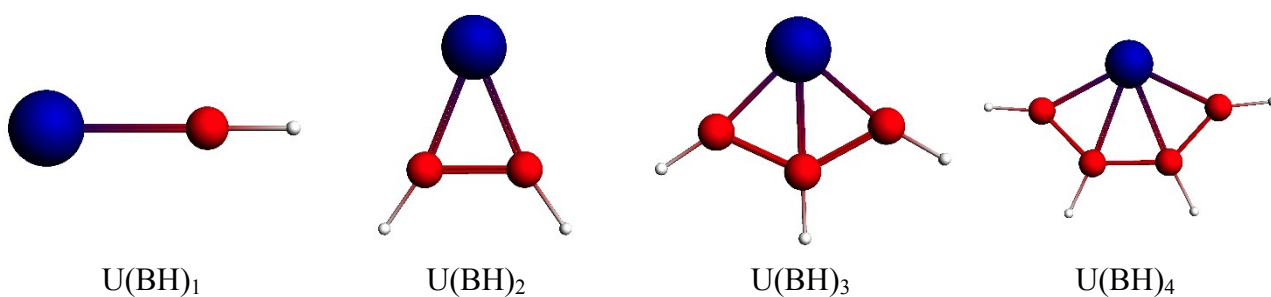
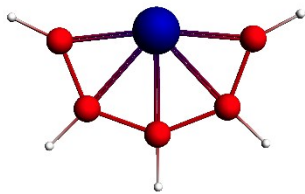
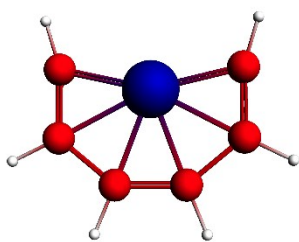


Figure S1. The global minimum and low-lying isomers of UB_{24} . Relative energies for the isomers of UB_{24} are given in kcal/mol at the PBE/TZ2P levels of theory.

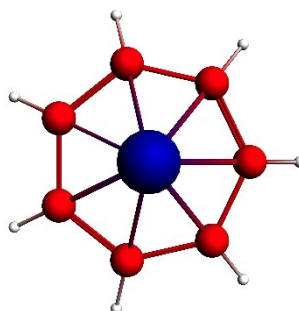




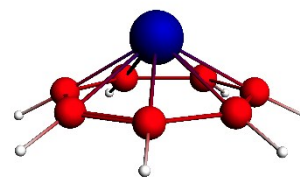
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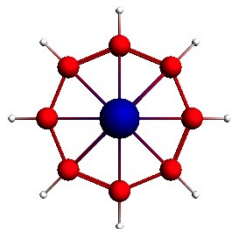
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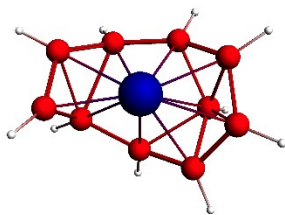
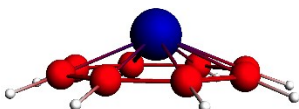
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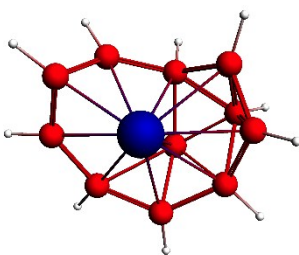
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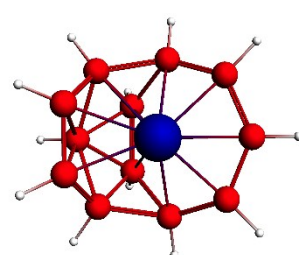
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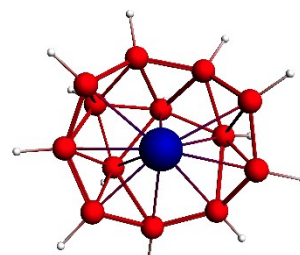
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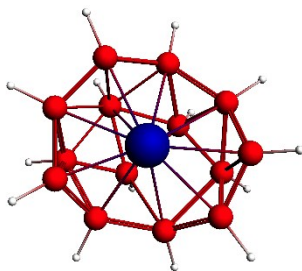
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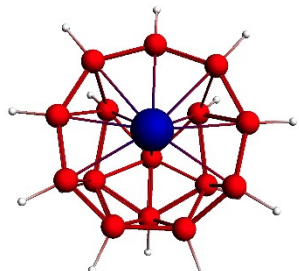
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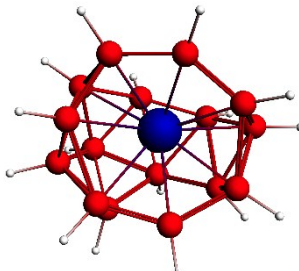
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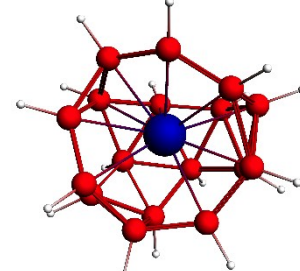
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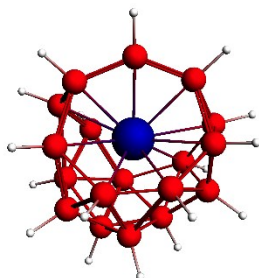
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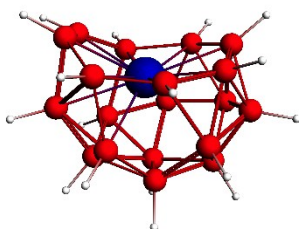
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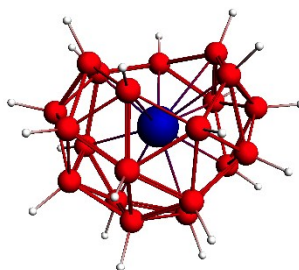
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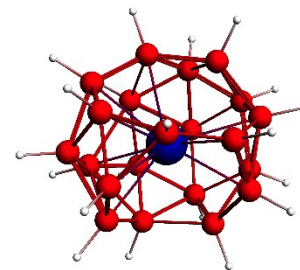
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U(BH)₁₉



U(BH)₂₀



U(BH)₂₁

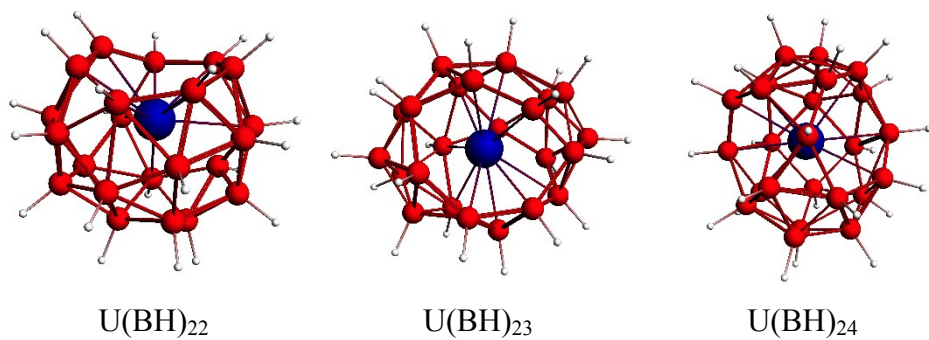


Figure S2. The optimized geometries for U(BH)_n ($n = 1$ to 24) at PBE/TZ2P level.

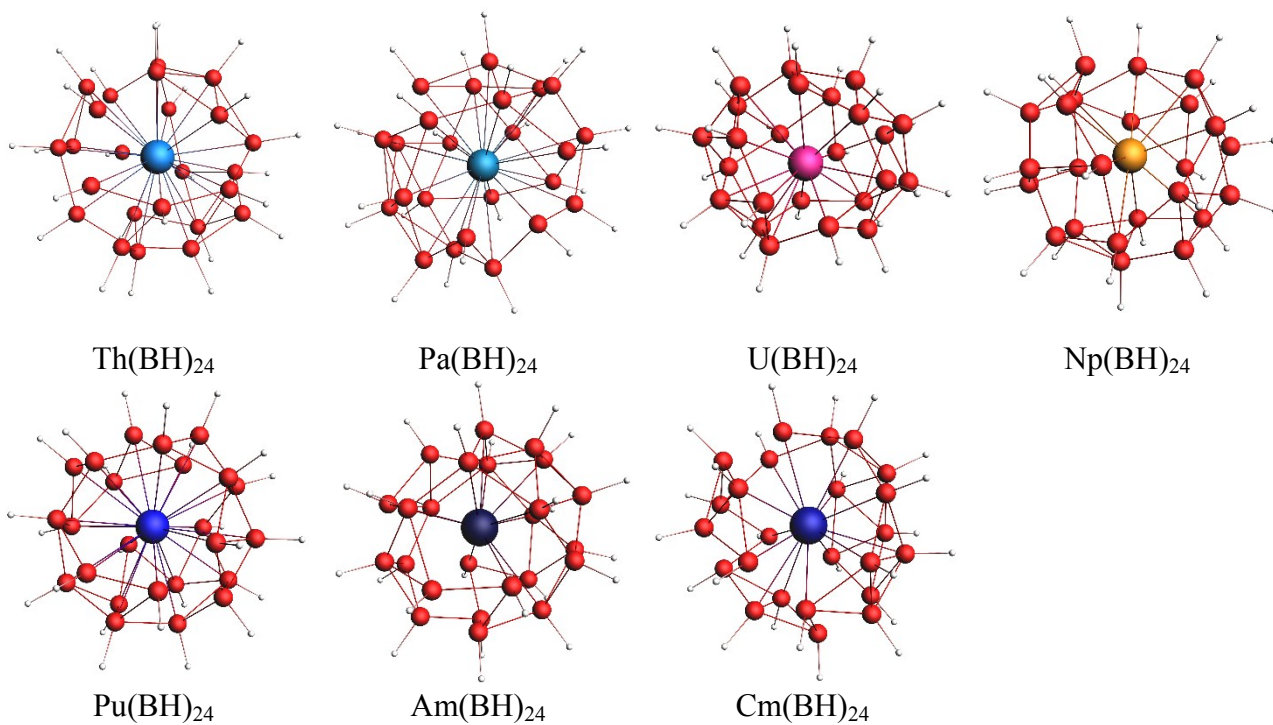


Figure S3. The optimized geometries for An(BH)₂₄ (An = Th to Cm) at PBE/TZ2P level.

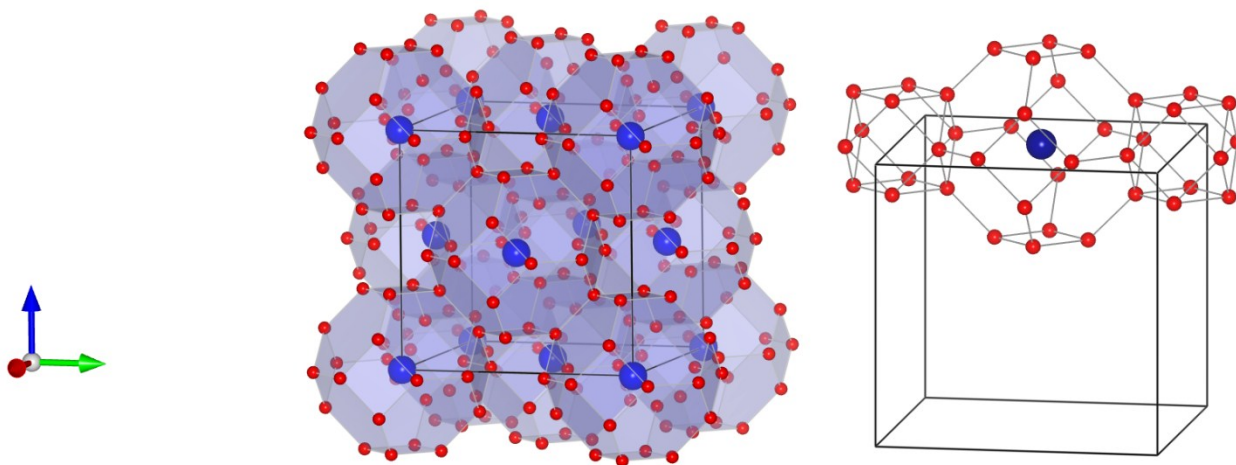


Figure S4. The fcc structure of PuB₁₂ (left); Boron polyhedral structure of PuB₁₂ (right) showing the large B₂₄ truncated octahedron, centered by the Pu atoms as well as the empty B₁₂ cuboctahedral polyhedra. Pu in dark blue and B in red.