Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Structure and Bonding of Molecular Stirrers with formula $B_7M_2^-$ and B_8M_2 (M=Zn, Cd, Hg)

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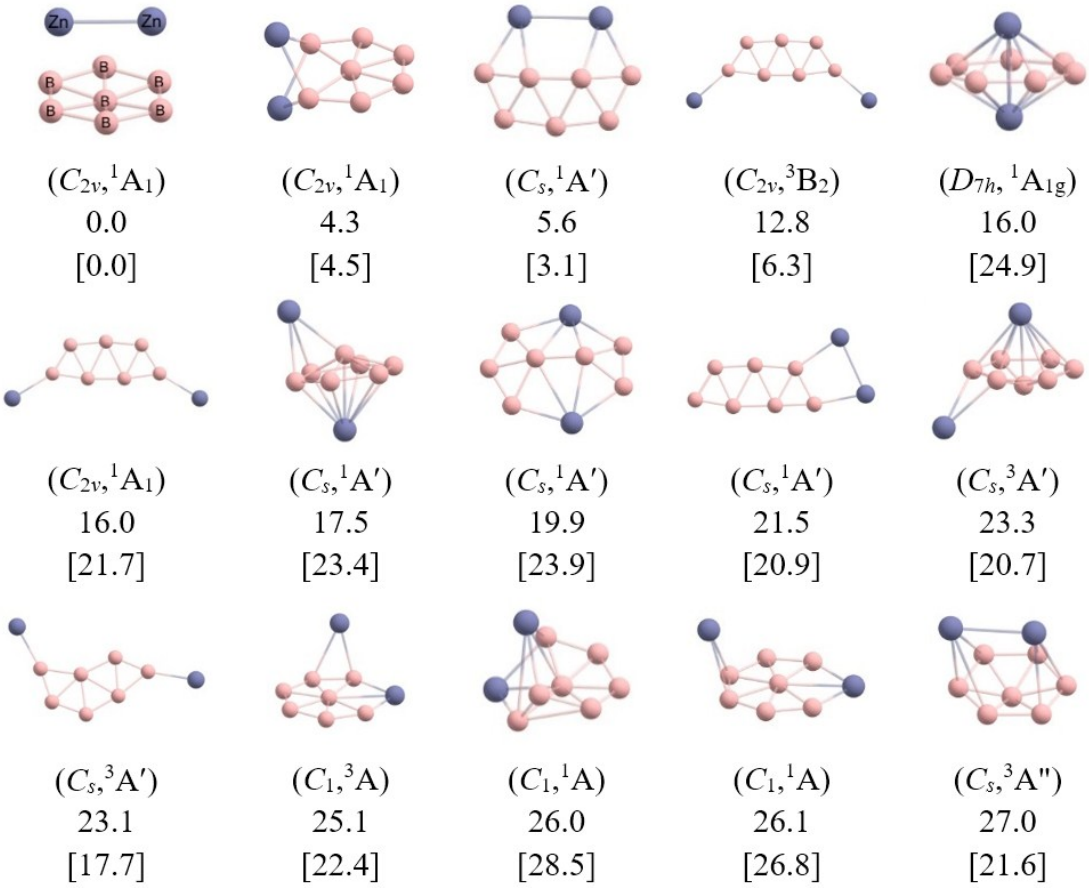


Figure S1. PBE0/def2-TZVP structures of $B_7Zn_2^-$. Relative energy in kcal·mol^{-1} were computed at the CCSD(T)/def2-TZVP//PBE0/def2-TZVP level, including the ZPE correction at the PBE0/def2-TZVP level. The relative energy computed at the PBE0/def2-TZVP is given in square brackets. The point group and spectroscopic states are given in parentheses.

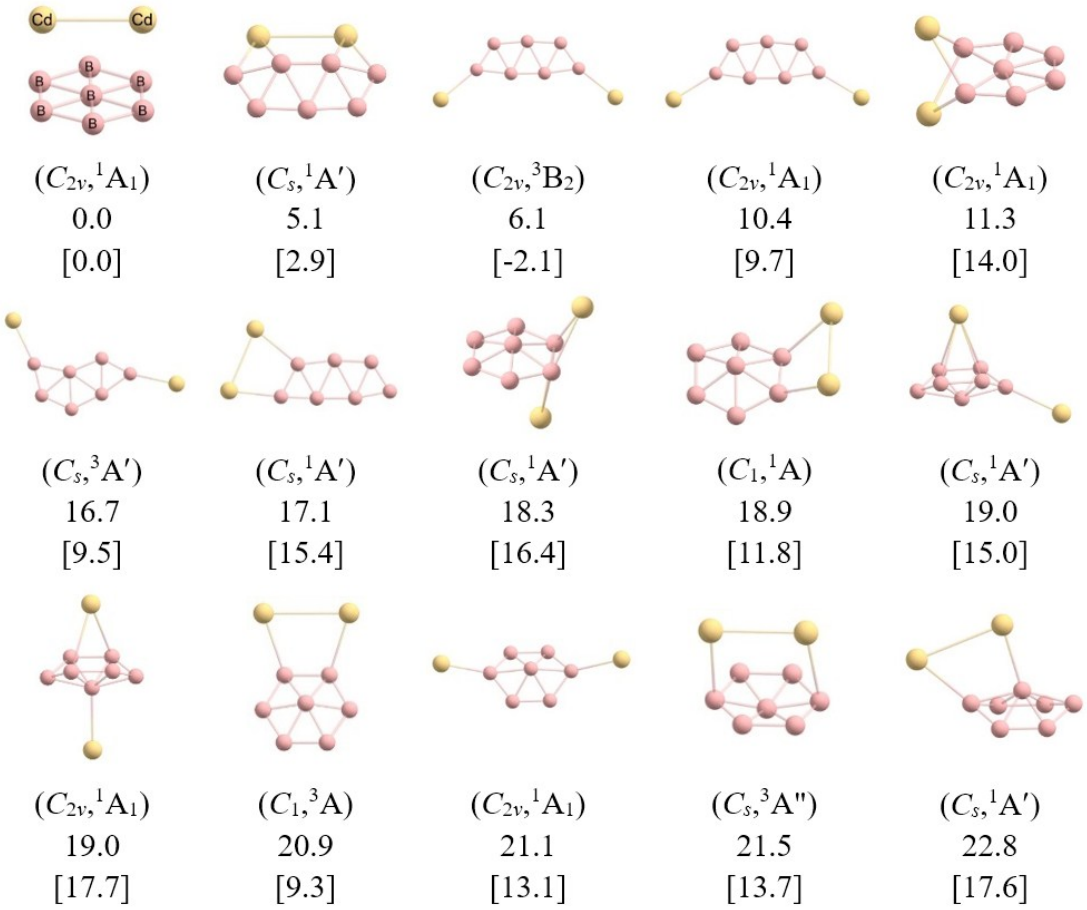
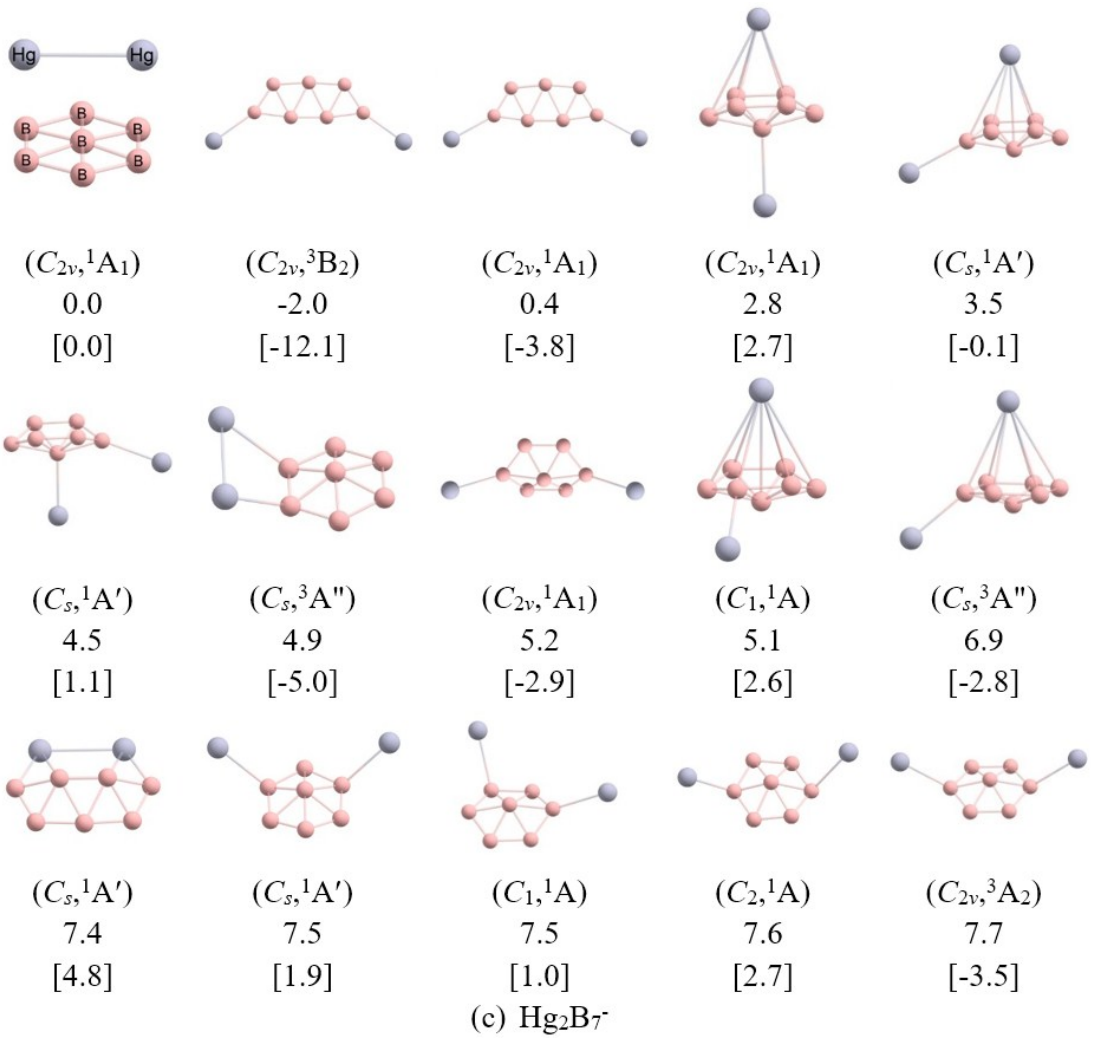


Figure S2. PBE0/def2-TZVP structures of $B_7Cd_2^-$. Relative energy in kcal·mol^{-1} were computed at the CCSD(T)/def2-TZVP//PBE0/def2-TZVP level, including the ZPE correction at the PBE0/def2-TZVP level. The relative energy computed at the PBE0/def2-TZVP is given in square brackets. The point group and spectroscopic states are given in parentheses.



(c) $Hg_2B_7^-$

Figure S3. PBE0/def2-TZVP structures of $B_7Hg_2^-$. Relative energy in kcal·mol^{-1} were computed at the CCSD(T)/def2-TZVP//PBE0/def2-TZVP level, including the ZPE correction at the PBE0/def2-TZVP level. The relative energy computed at the PBE0/def2-TZVP is given in square brackets. The point group and spectroscopic states are given in parentheses.

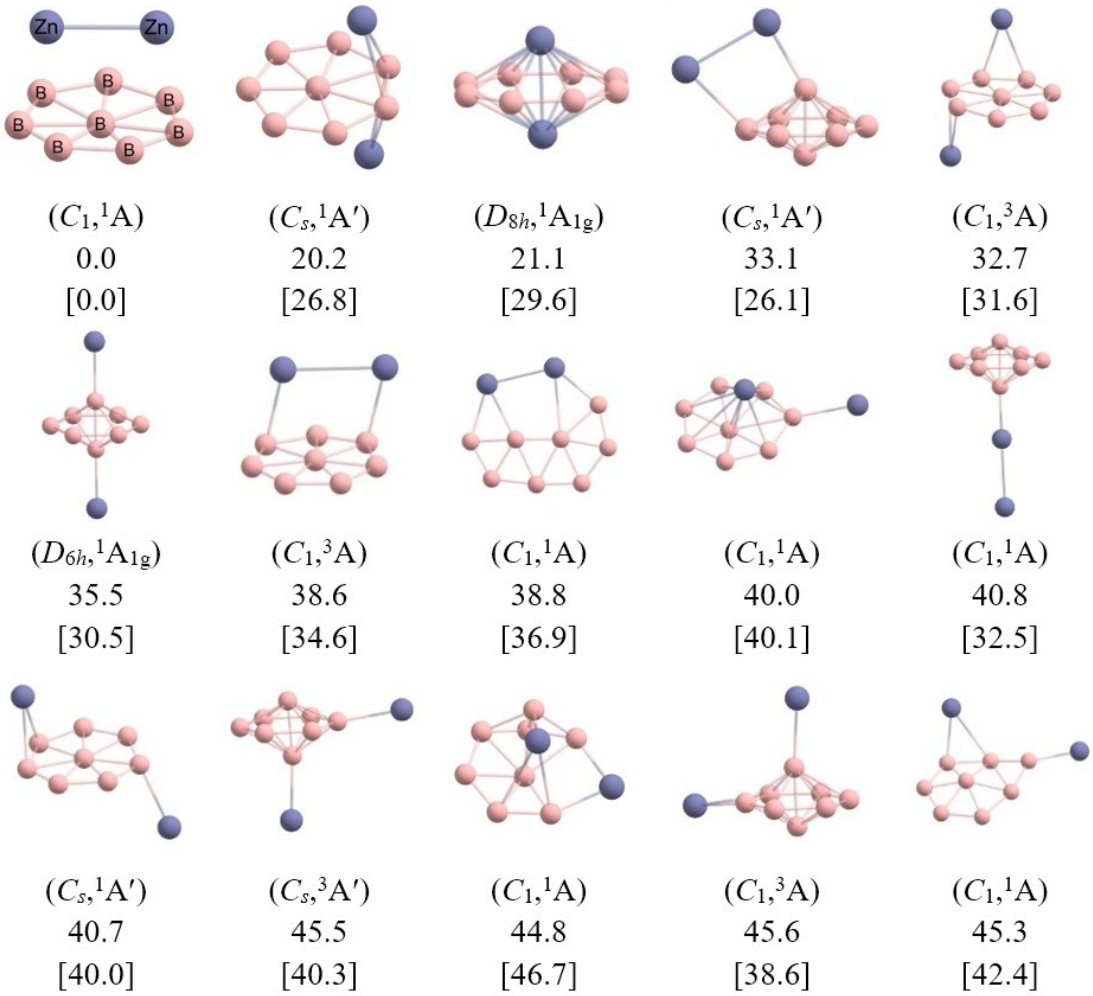


Figure S4. PBE0/def2-TZVP structures of B_8Zn_2. Relative energy in kcal·mol^{-1} were computed at the CCSD(T)/def2-TZVP//PBE0/def2-TZVP level, including the ZPE correction at the PBE0/def2-TZVP level. The relative energy computed at the PBE0/def2-TZVP is given in square brackets. The point group and spectroscopic states are given in parentheses.

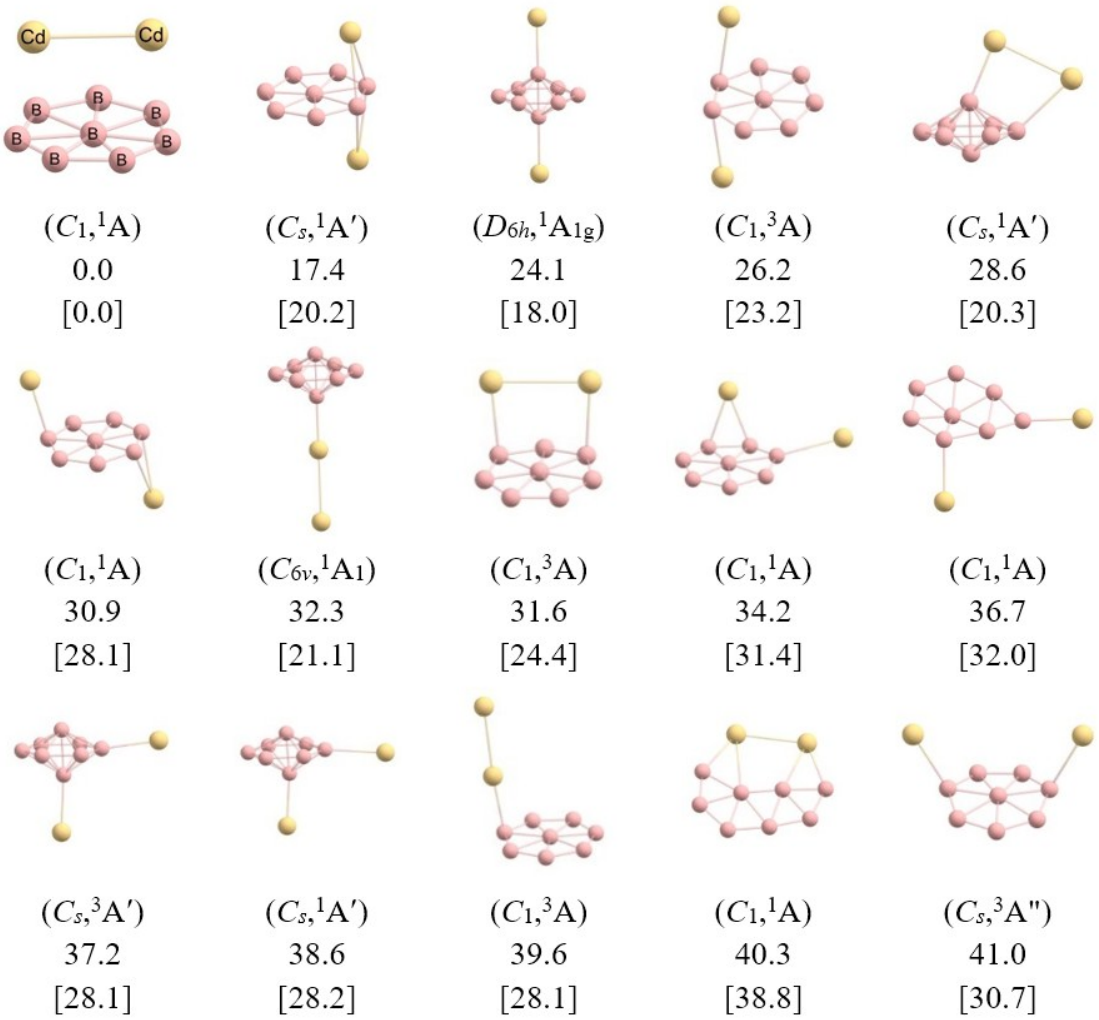


Figure S5. PBE0/def2-TZVP structures of B_8Cd_2. Relative energy in kcal·mol^{-1} were computed at the CCSD(T)/def2-TZVP//PBE0/def2-TZVP level, including the ZPE correction at the PBE0/def2-TZVP level. The relative energy computed at the PBE0/def2-TZVP is given in square brackets. The point group and spectroscopic states are given in parentheses.

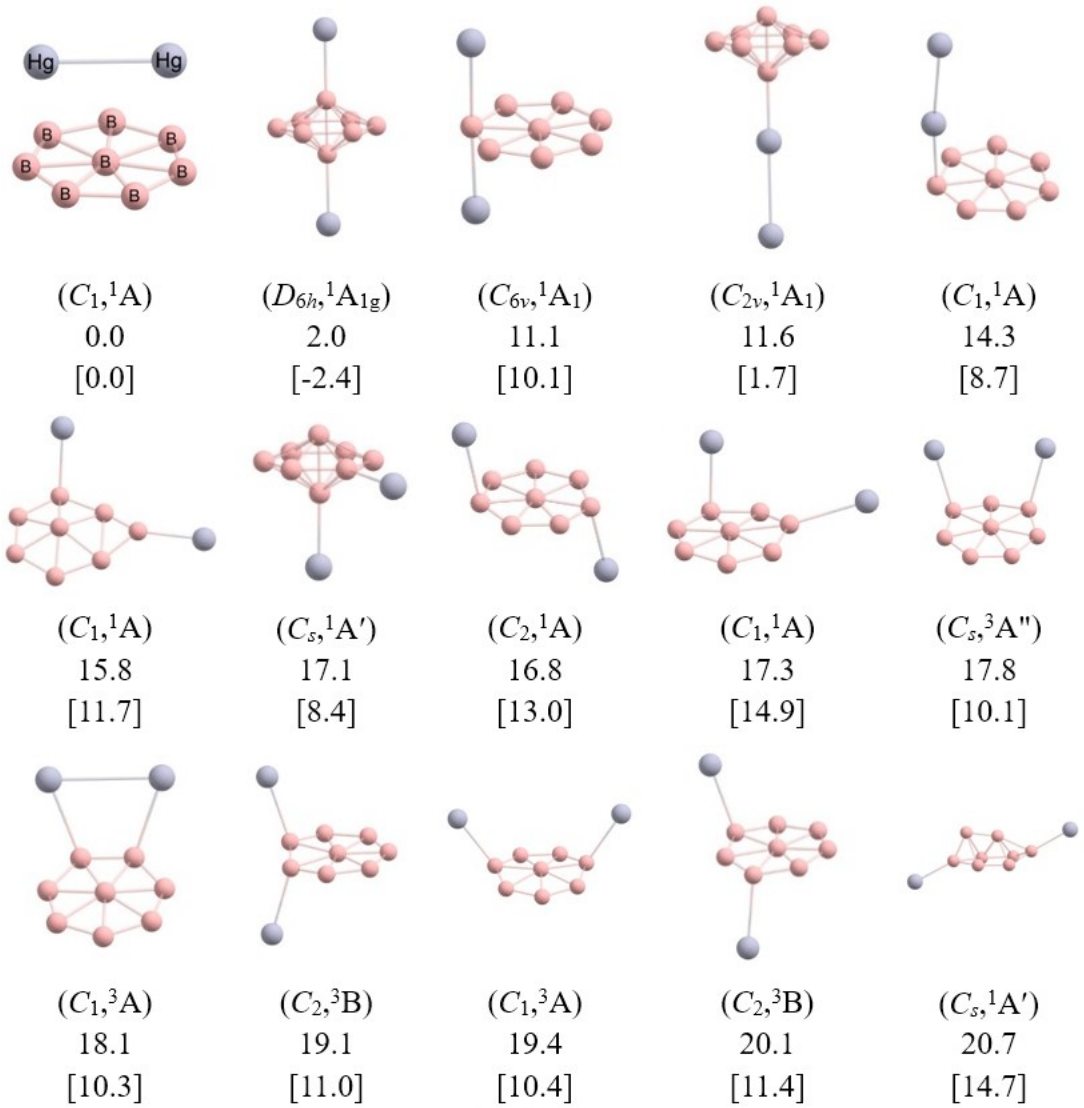


Figure S6. PBE0/def2-TZVP structures of B_8Hg_2. Relative energy in kcal·mol^{-1} were computed at the CCSD(T)/def2-TZVP//PBE0/def2-TZVP level, including the ZPE correction at the PBE0/def2-TZVP level. The relative energy computed at the PBE0/def2-TZVP is given in square brackets. The point group and spectroscopic states are given in parentheses.

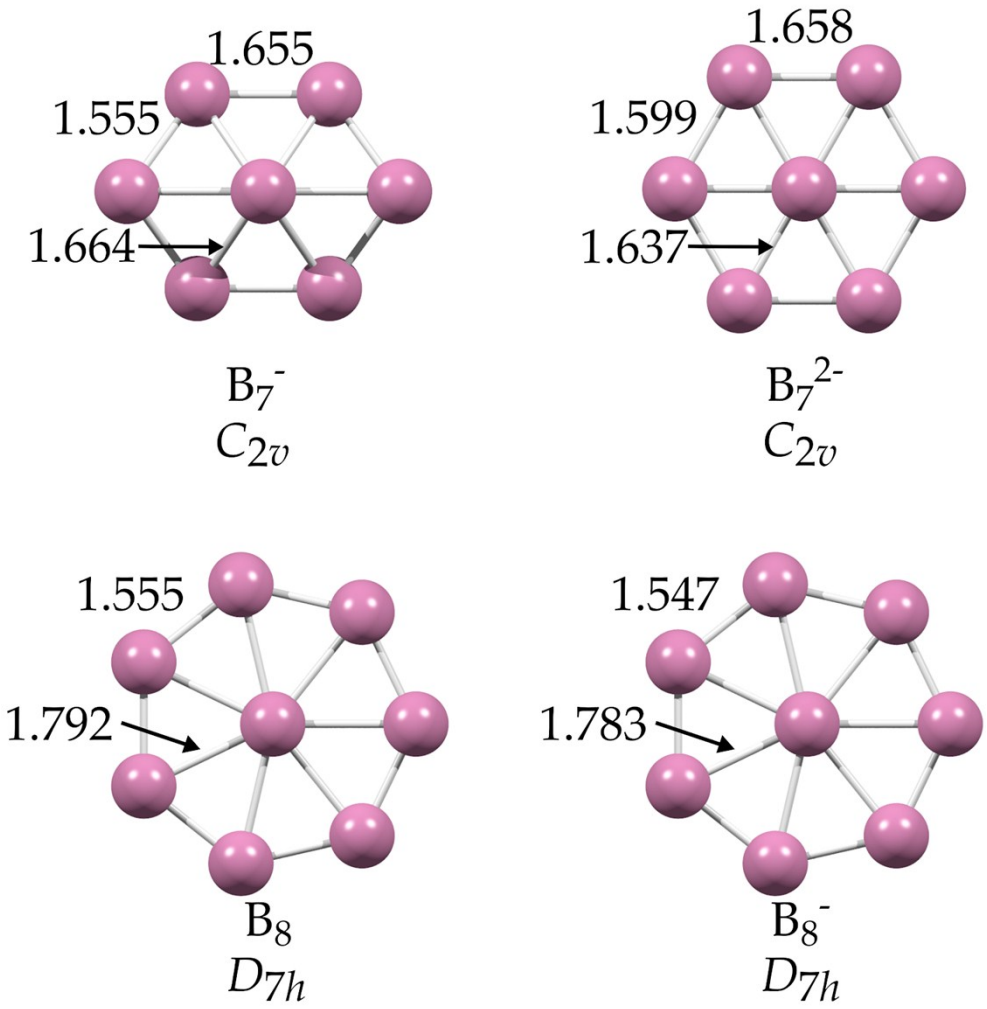


Figure S7. PBE0/def2-TZVP structures for the putative global minimum of $B_7^{-/2-}$ and $B_8^{0/-}$.

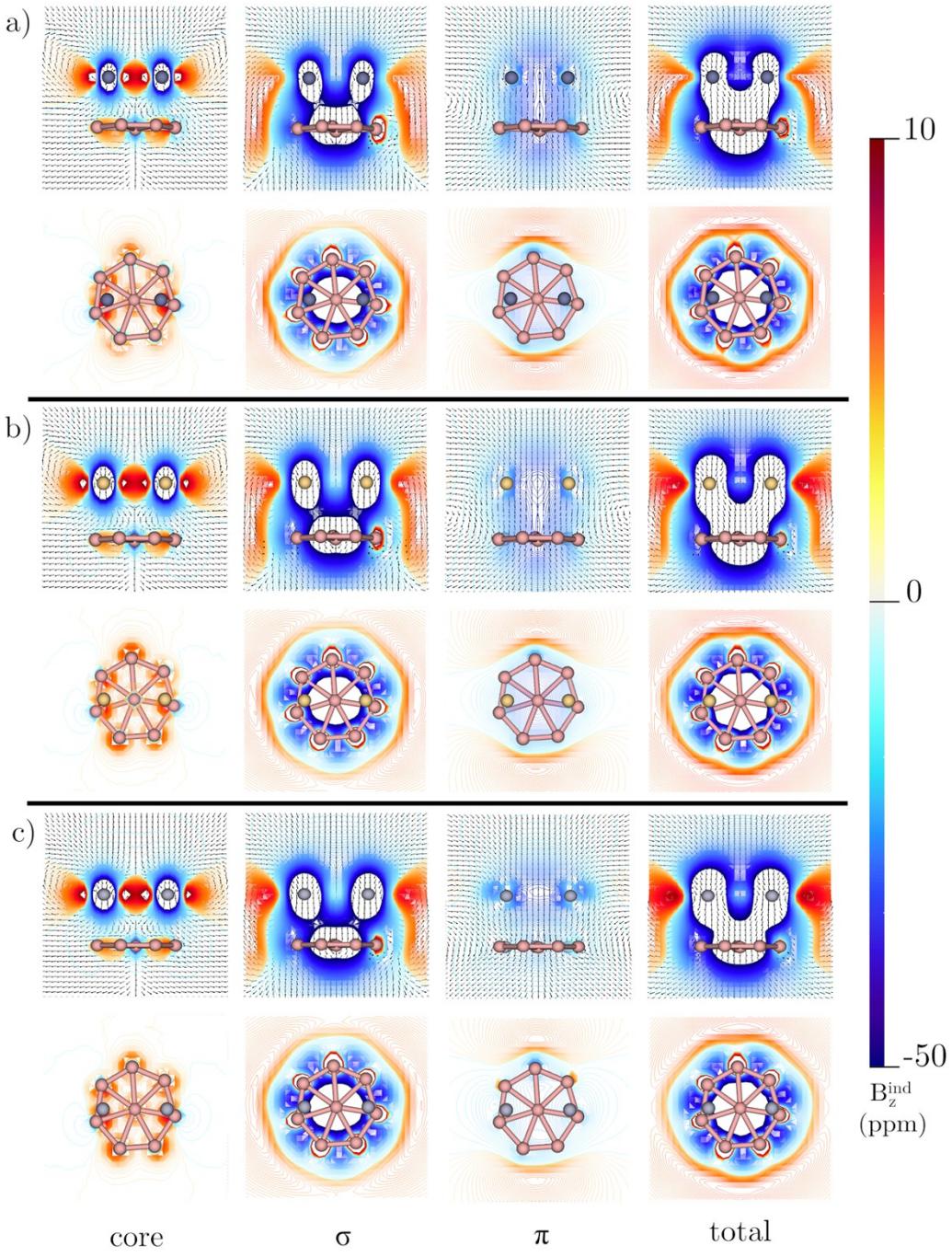


Figure S8. $\mathbf{B}^{ind}$ vector plots dissected into its orbital contributions for $M_2B_7^-$ (M = Zn, Cd, Hg) at the PBE0/def2-TZVP level. The arrows point in the direction of $\mathbf{B}^{ind}$, while the color contours its *z*-component.

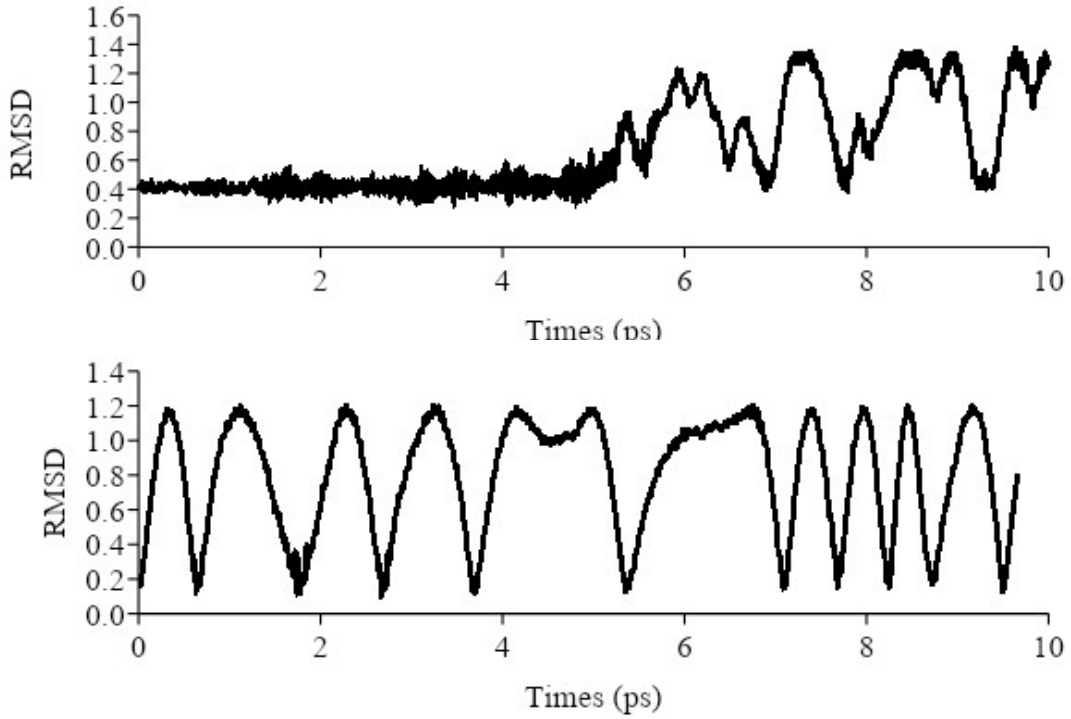


Figure S9. The RMSD versus time of the BOMDs simulations of $Cd_2B_7^-$ (top) and Cd_2B_8 (bottom) computed at 373 K and at the PBE0/def2-SVP level.

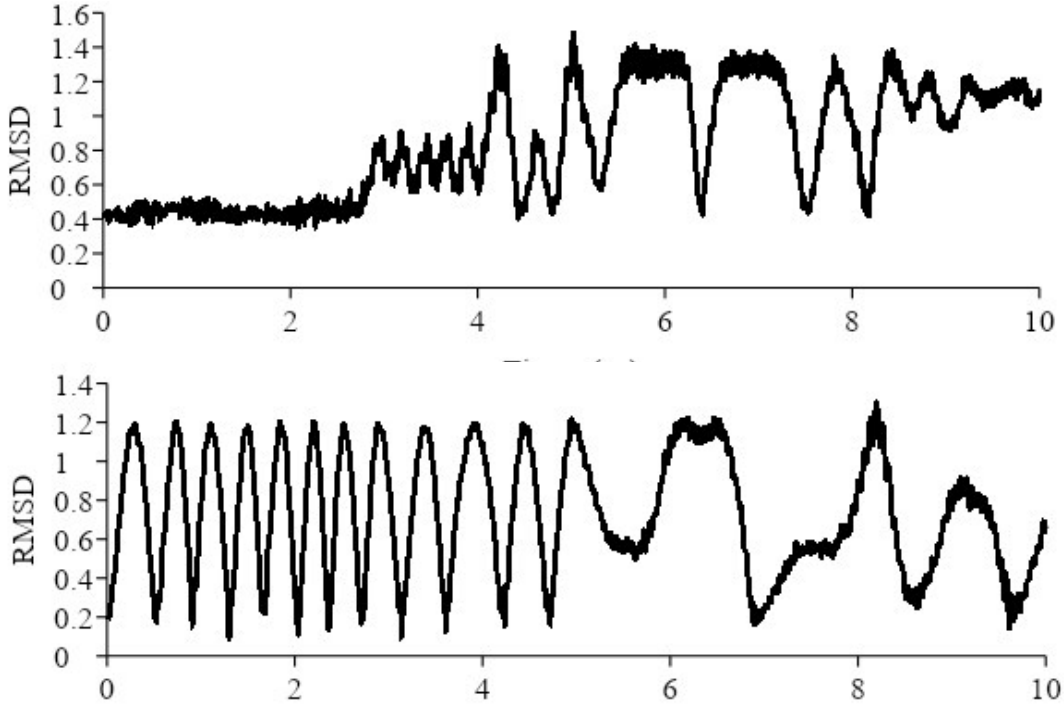


Figure S10. The RMSD versus time of the BOMDs simulations of $Cd_2B_7^-$ (top) and Cd_2B_8 (bottom) computed at 573 K and at the PBE0/def2-SVP level.

Table S1. The NPA charge, q, of the M_2 fragment in |e|, the distances corresponding to

M-M, and the one from the metallic dimer to the boron framework in (M-B) Å, Wiberg bond index (WBI), and HOMO-LUMO energy gap (Δ_{H-L}, eV) of the putative global minima of the $B_7M_2^-$ and B_8M_2 (M=Zn, Cd, Hg) combinations computed at the PBE0/def2-TZVP level.

	q_{M-M}	M-M	M-B	WBI_{M-M}	Δ_{H-L}
$Zn_2B_7^-$	0.84	2.376	2.272	0.76	0.11
$Cd_2B_7^-$	0.72	2.753	2.382	0.62	0.12
$Hg_2B_7^-$	0.42	2.913	2.416	0.39	0.11
Zn_2B_8	1.12	2.371	2.295	0.77	0.14
Cd_2B_8	1.12	2.711	2.473	0.67	0.15
Hg_2B_8	0.84	2.817	2.523	0.45	0.13

Table S2. Radial and peripheral B-B, and M_2 lengths of the $B_7M_2^-$ and B_8M_2 (M=Zn, Cd, Hg) clusters at the PBE0/def2-TZVP level.

		Zn	Cd	Hg
$B_7M_2^-$	radial	1.635	1.630	1.634
	peripheral	1.611	1.607	1.596
	M_2	2.376	2.754	2.912
B_8M_2	radial	1.784	1.799	1.808
	peripheral	1.544	1.550	1.533
	M_2	2.372	2.711	2.817

Cartesian coordinates

$B_7Zn_2^-$ 0.0 kcal·mol^{-1}

B	0.000000000	0.000000000	1.483824000
B	0.000000000	1.623898000	1.297300000
B	1.399375000	0.827423000	1.345821000
B	1.399375000	-0.827423000	1.345821000
B	0.000000000	-1.623898000	1.297300000
B	-1.399375000	-0.827423000	1.345821000
B	-1.399375000	0.827423000	1.345821000
Zn	-1.187954000	0.000000000	-0.788476000
Zn	1.187954000	0.000000000	-0.788476000

$B_7Zn_2^-$ 4.3 kcal·mol^{-1}

B	-0.773189000	0.000000000	2.798324000
B	-1.483746000	0.000000000	0.058502000
B	-1.737602000	0.000000000	1.579561000
B	0.000000000	0.000000000	1.266397000
B	0.773189000	0.000000000	2.798324000
B	1.483746000	0.000000000	0.058502000
B	1.737602000	0.000000000	1.579561000
Zn	0.000000000	1.262732000	-0.846150000
Zn	0.000000000	-1.262732000	-0.846150000

$B_7Zn_2^-$ 5.6 kcal·mol^{-1}

B	2.256613000	0.886897000	-0.036881000
B	-1.598066000	2.259957000	-0.328466000
B	0.801481000	1.239818000	0.678878000
B	0.005946000	2.510943000	-0.210801000
B	-0.795156000	1.243168000	0.678816000
B	1.608843000	2.252797000	-0.328561000
B	-2.252101000	0.897101000	-0.036592000
Zn	1.247020000	-0.943551000	-0.034668000
Zn	-1.251613000	-0.938229000	-0.034730000

$B_7Zn_2^-$ 12.8 kcal·mol^{-1}

B	0.000000000	-2.440903000	0.683123000
B	0.000000000	1.591521000	1.946154000
B	0.000000000	-0.800308000	0.474152000
B	0.000000000	0.000000000	2.049429000
B	0.000000000	0.800308000	0.474152000
B	0.000000000	-1.591521000	1.946154000
B	0.000000000	2.440903000	0.683123000
Zn	0.000000000	-3.998841000	-0.688008000
Zn	0.000000000	3.998841000	-0.688008000

$B_7Zn_2^-$ 16.0 kcal·mol^{-1}

B	0.000000000	1.845490000	0.000000000
B	-0.800728000	-1.662729000	0.000000000
B	-1.799220000	-0.410660000	0.000000000
B	1.799220000	-0.410660000	0.000000000
B	0.800728000	-1.662729000	0.000000000

B	-1.442862000	1.150644000	0.000000000
B	1.442862000	1.150644000	0.000000000
Zn	0.000000000	0.000000000	-1.246479000
Zn	0.000000000	0.000000000	1.246479000

$B_7Cd_2^-$ 0.0 kcal·mol^{-1}

B	0.000000000	0.000000000	1.744021000
B	1.629667000	0.011661000	1.728659000
B	0.843948000	-1.390140000	1.761580000
B	-0.824009000	-1.402039000	1.761493000
B	-1.629667000	-0.011661000	1.728659000
B	-0.843948000	1.390140000	1.761580000
B	0.824009000	1.402039000	1.761493000
Cd	-0.010491000	1.377105000	-0.637665000
Cd	0.010491000	-1.377105000	-0.637665000

$B_7Cd_2^-$ 11.3 kcal·mol^{-1}

B	0.147371000	3.148372000	-0.774589000
B	0.015918000	0.432217000	-1.496524000
B	0.089289000	1.945861000	-1.748828000
B	0.072067000	1.611150000	0.000000000
B	0.147371000	3.148372000	0.774589000
B	0.015918000	0.432217000	1.496524000
B	0.089289000	1.945861000	1.748828000
Cd	1.426130000	-0.723929000	0.000000000
Cd	-1.485363000	-0.596307000	0.000000000

$B_7Cd_2^-$ 5.1 kcal·mol^{-1}

B	2.298926000	1.328296000	-0.005058000
B	-1.597897000	2.673527000	-0.335627000
B	0.803019000	1.641340000	0.660594000
B	0.008331000	2.905550000	-0.230435000
B	-0.792499000	1.644983000	0.660537000
B	1.613452000	2.665600000	-0.335577000
B	-2.290194000	1.339943000	-0.004446000
Cd	1.399262000	-0.742673000	-0.021332000
Cd	-1.403755000	-0.736414000	-0.021376000

$B_7Cd_2^-$ 6.1 kcal·mol^{-1}

B	0.000000000	2.436985000	0.918112000
B	0.000000000	-1.591515000	2.182035000
B	0.000000000	0.801671000	0.707179000
B	0.000000000	0.000000000	2.281237000
B	0.000000000	-0.801671000	0.707179000
B	0.000000000	1.591515000	2.182035000
B	0.000000000	-2.436985000	0.918112000
Cd	0.000000000	4.160444000	-0.517485000
Cd	0.000000000	-4.160444000	-0.517485000

$B_7Cd_2^-$ 54.8 kcal·mol^{-1}

B	1.679160000	0.808641000	0.000000000
B	-1.162015000	-1.457120000	0.000000000
B	0.414718000	-1.816999000	0.000000000
B	-1.162015000	1.457120000	0.000000000
B	-1.863727000	0.000000000	0.000000000
B	1.679160000	-0.808641000	0.000000000
B	0.414718000	1.816999000	0.000000000
Cd	0.000000000	0.000000000	1.520747000
Cd	0.000000000	0.000000000	-1.520747000

$B_7Hg_2^-$ 0.0 kcal·mol^{-1}

B	0.000000000	0.000000000	1.968547000
B	-1.632252000	-0.005909000	2.039134000
B	-0.848765000	1.384157000	2.064078000
B	0.837990000	1.390573000	2.064345000
B	1.632252000	0.005909000	2.039134000
B	0.848765000	-1.384157000	2.064078000
B	-0.837990000	-1.390573000	2.064345000
Hg	0.000015000	-1.456311000	-0.447079000
Hg	-0.000015000	1.456311000	-0.447079000

$B_7Hg_2^-$ 16.4 kcal·mol^{-1}

B	0.030760000	3.409286000	0.778585000
B	-0.005503000	0.703578000	1.470371000
B	0.015545000	2.212126000	1.755410000
B	0.009740000	1.878268000	0.000000000
B	0.030760000	3.409286000	-0.778585000
B	-0.005503000	0.703578000	-1.470371000
B	0.015545000	2.212126000	-1.755410000
Hg	-1.484024000	-0.447051000	0.000000000
Hg	1.478331000	-0.460973000	0.000000000

$B_7Hg_2^-$ 7.4 kcal·mol^{-1}

B	-0.007552000	1.540712000	2.252034000
B	0.392714000	2.874866000	-1.599257000
B	-0.727626000	1.974379000	0.795047000
B	0.269053000	3.138933000	0.000000000
B	-0.727626000	1.974379000	-0.795047000
B	0.392714000	2.874866000	1.599257000
B	-0.007552000	1.540712000	-2.252034000
Hg	0.012640000	-0.497903000	1.399162000
Hg	0.012640000	-0.497903000	-1.399162000

$B_7Hg_2^-$ -2.0 kcal·mol^{-1}

B	0.000000000	-2.429724000	0.980849000
B	0.000000000	1.592279000	2.249132000
B	0.000000000	-0.801989000	0.766410000
B	0.000000000	0.000000000	2.336562000
B	0.000000000	0.801989000	0.766410000
B	0.000000000	-1.592279000	2.249132000

B	0.000000000	2.429724000	0.980849000
Hg	0.000000000	-4.230876000	-0.322787000
Hg	0.000000000	4.230876000	-0.322787000

B_8Zn_2 0.0 kcal·mol^{-1}

B	-1.283641000	1.275380000	1.250475000
B	1.476200000	1.320570000	0.980788000
B	-0.931223000	1.256006000	-1.531780000
B	0.601725000	1.255829000	-1.682970000
B	0.161471000	1.239138000	1.786981000
B	-0.011192000	1.422606000	0.001422000
B	-1.772339000	1.342383000	-0.228592000
B	1.672811000	1.353841000	-0.568156000
Zn	-1.178464000	-0.879674000	-0.000708000
Zn	1.192828000	-0.864618000	-0.000654000

B_8Zn_2 20.2 kcal·mol^{-1}

B	-0.007684000	2.685984000	0.000000000
B	-0.000202000	0.975932000	0.000000000
B	1.391619000	2.013100000	0.000000000
B	-0.788581000	-0.739474000	0.000000000
B	0.801703000	-0.732424000	0.000000000
B	-1.401200000	2.001396000	0.000000000
B	1.744140000	0.507976000	0.000000000
B	-1.741228000	0.493432000	0.000000000
Zn	0.000734000	-0.202085000	2.149523000
Zn	0.000734000	-0.202085000	-2.149523000

B_8Zn_2 21.1 kcal·mol^{-1}

B	-2.036396000	0.000000000	0.000000000
B	0.000000000	2.036396000	0.000000000
B	1.439949000	-1.439949000	0.000000000
B	-1.439949000	1.439949000	0.000000000
B	2.036396000	0.000000000	0.000000000
B	-1.439949000	-1.439949000	0.000000000
B	1.439949000	1.439949000	0.000000000
B	0.000000000	-2.036396000	0.000000000
Zn	0.000000000	0.000000000	-1.194877000
Zn	0.000000000	0.000000000	1.194877000
Zn	0.000000000	0.000000000	1.194877000

B_8Zn_2 35.5 kcal·mol^{-1}

B	0.000000000	0.000000000	0.865074000
B	0.000000000	1.575628000	0.000000000
B	0.000000000	0.000000000	-0.865074000
B	0.000000000	-1.575628000	0.000000000
B	-1.364534000	-0.787814000	0.000000000
B	-1.364534000	0.787814000	0.000000000
B	1.364534000	0.787814000	0.000000000
B	1.364534000	-0.787814000	0.000000000

Zn	0.000000000	0.000000000	-3.010212000
Zn	0.000000000	0.000000000	3.010212000

B_8Zn_2 32.7 kcal·mol^{-1}

B	-0.818879000	1.790278000	-1.122975000
B	0.000770000	0.714178000	0.000853000
B	-0.000489000	2.465976000	-0.004685000
B	0.397130000	-0.935646000	0.673544000
B	0.950860000	0.289425000	1.451317000
B	-0.947221000	0.278957000	-1.448084000
B	0.819621000	1.798511000	1.117239000
B	-0.392682000	-0.940310000	-0.661751000
Zn	-2.492467000	-0.454438000	0.170589000
Zn	2.490949000	-0.455790000	-0.171499000

B_8Cd_2 0.0 kcal·mol^{-1}

B	-1.264529000	1.685657000	1.275291000
B	1.486968000	1.721082000	0.964449000
B	-0.952050000	1.681079000	-1.522204000
B	0.574765000	1.677940000	-1.695375000
B	0.185170000	1.654627000	1.790479000
B	-0.011631000	1.761622000	0.002811000
B	-1.774972000	1.737906000	-0.201908000
B	1.661938000	1.746961000	-0.593498000
Cd	-1.349895000	-0.718393000	-0.001057000
Cd	1.359722000	-0.705240000	-0.001031000

B_8Cd_2 17.4 kcal·mol^{-1}

B	-0.007650000	2.722863000	0.000000000
B	-0.000007000	1.006411000	0.000000000
B	1.393866000	2.057852000	0.000000000
B	-0.791654000	-0.678729000	0.000000000
B	0.805573000	-0.671774000	0.000000000
B	-1.403331000	2.046066000	0.000000000
B	1.754218000	0.562338000	0.000000000
B	-1.751038000	0.547581000	0.000000000
Cd	0.000029000	-0.395428000	2.406463000
Cd	0.000029000	-0.395428000	-2.406463000

B_8Cd_2 45.8 kcal·mol^{-1}

B	-1.457286000	1.457286000	0.000000000
B	1.457286000	1.457286000	0.000000000
B	0.000000000	-2.060914000	0.000000000
B	0.000000000	2.060914000	0.000000000
B	1.457286000	-1.457286000	0.000000000
B	-2.060914000	0.000000000	0.000000000
B	2.060914000	0.000000000	0.000000000
B	-1.457286000	-1.457286000	0.000000000
Cd	0.000000000	0.000000000	-1.425556000
Cd	0.000000000	0.000000000	1.425556000

B_8Cd_2 24.1 kcal·mol^{-1}

B	0.000000000	0.000000000	0.864249000
B	0.000000000	1.574569000	0.000000000
B	0.000000000	0.000000000	-0.864249000
B	0.000000000	-1.574569000	0.000000000
B	-1.363617000	-0.787285000	0.000000000
B	-1.363617000	0.787285000	0.000000000
B	1.363617000	0.787285000	0.000000000
B	1.363617000	-0.787285000	0.000000000
Cd	0.000000000	0.000000000	-3.170539000
Cd	0.000000000	0.000000000	3.170539000

B_8Cd_2 26.2 kcal·mol^{-1}

B	0.009925000	2.685893000	0.013274000
B	0.000140000	0.933566000	0.000068000
B	-0.769289000	2.029776000	-1.141859000
B	0.387152000	-0.725003000	0.656921000
B	-0.402205000	-0.710721000	-0.682243000
B	0.780697000	2.003951000	1.159392000
B	-0.912208000	0.521880000	-1.479936000
B	0.907988000	0.489567000	1.474866000
Cd	2.751802000	-0.376586000	-0.094686000
Cd	-2.752031000	-0.376425000	0.094636000

B_8Hg_2 0.0 kcal·mol^{-1}

B	1.231117000	1.997210000	-1.298701000
B	-1.505708000	1.999192000	-0.947542000
B	0.957743000	1.986813000	1.521833000
B	-0.558085000	1.978786000	1.715915000
B	-0.218323000	1.978505000	-1.793044000
B	0.001342000	2.024562000	0.000792000
B	1.765862000	1.987017000	0.182158000
B	-1.661027000	1.993737000	0.626516000
Hg	1.408137000	-0.498783000	-0.000253000
Hg	-1.408945000	-0.497831000	-0.000242000

B_8Hg_2 84.4 kcal·mol^{-1}

B	-1.467443000	1.467443000	0.000000000
B	1.467443000	1.467443000	0.000000000
B	0.000000000	-2.075277000	0.000000000
B	0.000000000	2.075277000	0.000000000
B	1.467443000	-1.467443000	0.000000000
B	-2.075277000	0.000000000	0.000000000
B	2.075277000	0.000000000	0.000000000
B	-1.467443000	-1.467443000	0.000000000
Hg	0.000000000	0.000000000	-1.442420000
Hg	0.000000000	0.000000000	1.442420000

B_8Hg_2 2.0 kcal·mol^{-1}

B	0.000000000	0.000000000	0.862296000
B	0.000000000	1.573301000	0.000000000
B	0.000000000	0.000000000	-0.862296000
B	0.000000000	-1.573301000	0.000000000
B	-1.362518000	-0.786650000	0.000000000
B	-1.362518000	0.786650000	0.000000000
B	1.362518000	0.786650000	0.000000000
B	1.362518000	-0.786650000	0.000000000
Hg	0.000000000	0.000000000	-3.123224000
Hg	0.000000000	0.000000000	3.123224000

B_8Hg_2 19.1 kcal·mol^{-1}

B	0.000000000	0.000000000	3.664947000
B	0.000000000	0.000000000	1.896161000
B	-1.261216000	-0.591603000	2.990910000
B	0.633246000	0.471654000	0.255159000
B	-0.633246000	-0.471654000	0.255159000
B	1.261216000	0.591603000	2.990910000
B	-1.567839000	-0.742211000	1.476858000
B	1.567839000	0.742211000	1.476858000
Hg	-0.050393000	2.735033000	-0.468782000
Hg	0.050393000	-2.735033000	-0.468782000