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# Investigation on the neutral and anioninc $B_xAl_yH_2$ ($x + y = 7$, 8, 9) clusters using density functional theory combined with photoelectron spectroscopy

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**Table S1** The calculated VDEs for next low-lying state of anionic $B_xAl_yH_2$ ($x + y = 7$, 8, 9) at B3LYP/6-311+G* level of theory. All energies are in eV.

| Isomers | VDE | Isomers | VDE | Isomers | VDE |
|---|---|---|---|---|---|
| $BAl_6H_2^-$ | 3.10 | $BAl_7H_2^-$ | 2.94 | $BAl_8H_2^-$ | 2.95 |
| $B_2Al_5H_2^-$ | 3.10 | $B_2Al_6H_2^-$ | 2.36 | $B_2Al_7H_2^-$ | 2.86 |
| $B_3Al_4H_2^-$ | 2.94 | $B_3Al_5H_2^-$ | 2.05 | $B_3Al_6H_2^-$ | 2.84 |
| $B_4Al_3H_2^-$ | 2.47 | $B_4Al_4H_2^-$ | 2.97 | $B_4Al_5H_2^-$ | 2.95 |
| $B_5Al_2H_2^-$ | 2.52 | $B_5Al_3H_2^-$ | 2.39 | $B_5Al_4H_2^-$ | 2.83 |
| $B_6AlH_2^-$ | 3.69 | $B_6Al_2H_2^-$ | 2.59 | | |
| | | $B_7AlH_2^-$ | 2.40 | | |

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**Table S2** Natural charge populations (NPA) for the Al, B and H atoms of the most stable neutral $B_xAl_yH_2$ ($x + y = 7$) clusters.

| $x + y = 7$ | $Al_7H_2$ | $BAl_6H_2$ | $B_2Al_5H_2$ | $B_3Al_4H_2$ | $B_4Al_3H_2$ | $B_5Al_2H_2$ | $B_6AlH_2$ | $B_7H_2$ |
|---|---|---|---|---|---|---|---|---|
| $B_1$ | | -1.682 | -0.853 | -0.255 | -0.207 | -0.553 | -0.086 | 0.050 |
| $B_2$ | | | -1.400 | -1.057 | -0.826 | 0.193 | -0.346 | 0.133 |
| $B_3$ | | | | -0.696 | -0.132 | -0.167 | -0.065 | -0.049 |
| $B_4$ | | | | | -0.645 | 0.232 | -0.133 | -0.230 |
| $B_5$ | | | | | | -0.312 | -0.346 | -0.056 |
| $B_6$ | | | | | | | -0.086 | 0.128 |
| $B_7$ | | | | | | | | 0.065 |
| $Al_1$ | 0.085 | 0.439 | 0.567 | 0.518 | 0.393 | 0.758 | 1.020 | |
| $Al_2$ | 0.246 | 0.641 | 0.018 | 0.399 | 0.655 | 0.827 | | |
| $Al_3$ | -0.011 | 0.306 | 0.455 | 0.480 | 0.692 | | | |
| $Al_4$ | 0.044 | 0.393 | 0.506 | 0.543 | | | | |
| $Al_5$ | -0.011 | 0.030 | 0.983 | | | | | |
| $Al_6$ | 0.152 | 0.149 | | | | | | |
| $Al_7$ | 0.138 | | | | | | | |
| $H_1$ | -0.333 | 0.051 | 0.046 | 0.004 | 0.064 | 0.061 | 0.021 | -0.020 |
| $H_2$ | -0.310 | -0.326 | -0.323 | 0.064 | 0.006 | -0.041 | 0.021 | -0.022 |

**Table S3** Natural charge populations (NPA) for the Al, B and H atoms of the most stable anionic $B_xAl_yH_2$ ($x + y = 7$) clusters.

| $x + y = 7$ | $Al_7H_2^-$ | $BAl_6H_2^-$ | $B_2Al_5H_2^-$ | $B_3Al_4H_2^-$ | $B_4Al_3H_2^-$ | $B_5Al_2H_2^-$ | $B_6AlH_2^-$ | $B_7H_2^-$ |
|---|---|---|---|---|---|---|---|---|
| $B_1$ | | -1.303 | -0.904 | -0.548 | -0.612 | -0.290 | -0.159 | 0.008 |
| $B_2$ | | | -1.307 | -1.106 | -0.421 | -0.479 | -0.410 | -0.207 |
| $B_3$ | | | | -0.548 | -0.905 | -0.429 | -0.163 | 0.008 |
| $B_4$ | | | | | -0.362 | -0.467 | -0.271 | -0.370 |
| $B_5$ | | | | | | -0.379 | -0.410 | -0.207 |
| $B_6$ | | | | | | | -0.159 | 0.088 |
| $B_7$ | | | | | | | | -0.260 |
| $Al_1$ | -0.077 | 0.161 | 0.461 | 0.305 | 0.524 | 0.598 | 0.594 | |
| $Al_2$ | 0.206 | 0.146 | 0.395 | 0.326 | 0.363 | 0.476 | | |
| $Al_3$ | -0.244 | -0.142 | -0.030 | 0.252 | 0.411 | | | |
| $Al_4$ | -0.165 | 0.153 | 0.423 | 0.326 | | | | |
| $Al_5$ | -0.165 | 0.462 | 0.311 | | | | | |
| $Al_6$ | 0.206 | -0.074 | | | | | | |
| $Al_7$ | -0.305 | | | | | | | |
| $H_1$ | -0.363 | -0.047 | 0.015 | -0.004 | -0.034 | -0.038 | -0.011 | -0.030 |
| $H_2$ | -0.363 | -0.355 | -0.365 | -0.004 | 0.036 | 0.006 | -0.011 | -0.030 |

**Table S4** Natural charge populations (NPA) for the Al, B and H atoms of the most stable neutral $B_xAl_yH_2$ ($x + y = 8$) clusters.

| $x + y = 8$ | $Al_8H_2$ | $BAl_7H_2$ | $B_2Al_6H_2$ | $B_3Al_5H_2$ | $B_4Al_4H_2$ | $B_5Al_3H_2$ | $B_6Al_2H_2$ | $B_7AlH_2$ | $B_8H_2$ |
|---|---|---|---|---|---|---|---|---|---|
| $B_1$ | | -1.21 | -1.089 | -0.729 | -1.244 | -0.476 | -0.234 | -0.190 | -0.104 |
| $B_2$ | | | -1.808 | -1.721 | -0.391 | -0.476 | -0.369 | -0.190 | 0.148 |
| $B_3$ | | | | -0.508 | -0.476 | -0.411 | -0.274 | 0.053 | -0.104 |
| $B_4$ | | | | | -0.341 | -0.411 | -0.370 | -0.386 | 0.092 |
| $B_5$ | | | | | | -0.752 | -0.277 | 0.032 | 0.092 |
| $B_6$ | | | | | | | -0.115 | 0.032 | 0.069 |
| $B_7$ | | | | | | | | -0.183 | 0.069 |
| $B_8$ | | | | | | | | | -0.261 |
| $Al_1$ | -0.154 | 0.454 | 0.736 | 0.748 | 0.955 | 0.930 | 0.704 | 0.743 | |
| $Al_2$ | 0.361 | 0.083 | 0.743 | 0.748 | 0.703 | 0.807 | 0.882 | | |
| $Al_3$ | -0.153 | 0.231 | 0.478 | 0.776 | 0.530 | 0.790 | | | |
| $Al_4$ | 0.388 | 0.071 | 0.763 | 0.647 | 0.567 | | | | |
| $Al_5$ | -0.148 | 0.082 | 0.614 | 0.401 | | | | | |
| $Al_6$ | 0.388 | 0.275 | 0.199 | | | | | | |
| $Al_7$ | -0.115 | 0.358 | | | | | | | |
| $Al_8$ | 0.088 | | | | | | | | |
| $H_1$ | -0.328 | -0.181 | -0.309 | -0.337 | 0.004 | -0.00002 | -0.001 | 0.045 | -0.031 |
| $H_2$ | -0.328 | -0.162 | -0.327 | -0.025 | -0.309 | -0.00002 | 0.055 | 0.045 | 0.029 |

**Table S5** Natural charge populations (NPA) for the Al, B and H atoms of the most stable anionic $B_xAl_yH_2$ ($x + y = 8$) clusters.

| $x + y = 8$ | $Al_8H_2^-$ | $BAl_7H_2^-$ | $B_2Al_6H_2^-$ | $B_3Al_5H_2^-$ | $B_4Al_4H_2^-$ | $B_5Al_3H_2^-$ | $B_6Al_2H_2^-$ | $B_7AlH_2^-$ | $B_8H_2^-$ |
|---|---|---|---|---|---|---|---|---|---|
| $B_1$ | | -2.513 | -1.190 | -0.758 | -0.365 | -0.427 | -0.290 | -0.416 | -0.071 |
| $B_2$ | | | -1.758 | -1.857 | -0.365 | -0.243 | -0.201 | -0.069 | -0.199 |
| $B_3$ | | | | -0.430 | -1.276 | -0.626 | -0.326 | -0.069 | -0.210 |
| $B_4$ | | | | | -0.972 | -0.626 | -0.558 | -0.100 | -0.048 |
| $B_5$ | | | | | | -0.791 | -0.219 | -0.462 | 0.024 |
| $B_6$ | | | | | | | -0.656 | -0.280 | -0.135 |
| $B_7$ | | | | | | | | -0.280 | -0.137 |
| $B_8$ | | | | | | | | | -0.203 |
| $Al_1$ | -0.308 | 0.456 | 0.635 | 0.583 | 0.515 | 0.569 | 0.749 | 0.705 | |
| $Al_2$ | 0.061 | 0.034 | 0.659 | 0.548 | 0.465 | 0.550 | 0.490 | | |
| $Al_3$ | -0.261 | 0.265 | 0.345 | 0.608 | 0.515 | | | | |
| $Al_4$ | 0.347 | 0.135 | 0.546 | 0.452 | 0.441 | | | | |
| $Al_5$ | -0.233 | 0.178 | 0.468 | 0.257 | | | | | |
| $Al_6$ | 0.118 | 0.545 | -0.006 | | | | | | |
| $Al_7$ | -0.314 | 0.597 | | | | | | | |
| $Al_8$ | 0.310 | | | | | | | | |
| $H_1$ | -0.363 | -0.362 | -0.344 | -0.358 | 0.020 | 0.031 | 0.018 | -0.015 | -0.008 |
| $H_2$ | -0.356 | -0.334 | -0.356 | -0.046 | 0.020 | 0.011 | -0.007 | -0.015 | -0.012 |

**Table S6** Natural charge populations (NPA) for the Al, B and H atoms of the most stable neutral $B_xAl_yH_2$ ($x + y = 9$) clusters.

| $x + y = 9$ | $Al_9H_2$ | $BAl_8H_2$ | $B_2Al_7H_2$ | $B_3Al_6H_2$ | $B_4Al_5H_2$ | $B_5Al_4H_2$ |
|---|---|---|---|---|---|---|
| $B_1$ | | -1.559 | -2.137 | -0.346 | -0.283 | -0.668 |
| $B_2$ | | | -1.984 | -0.897 | -0.654 | -0.347 |
| $B_3$ | | | | -0.892 | -0.785 | -0.668 |
| $B_4$ | | | | | -1.887 | -0.347 |
| $B_5$ | | | | | | -0.937 |
| $Al_1$ | -0.314 | 0.077 | 0.531 | 0.386 | 0.488 | 0.7561 |
| $Al_2$ | 0.135 | 0.201 | 0.850 | 0.494 | 0.766 | 0.568 |
| $Al_3$ | 0.193 | 0.077 | 0.851 | 0.350 | 0.766 | 0.869 |
| $Al_4$ | 0.263 | 0.159 | 0.530 | 0.523 | 0.708 | 0.767 |
| $Al_5$ | -0.115 | 0.158 | 0.767 | 0.010 | 0.833 | |
| $Al_6$ | 0.171 | 0.456 | 0.641 | 0.280 | | |
| $Al_7$ | 0.231 | 0.068 | 0.641 | | | |
| $Al_8$ | -0.129 | 0.643 | | | | |
| $Al_9$ | 0.160 | | | | | |
| $H_1$ | -0.304 | -0.304 | -0.344 | 0.045 | 0.030 | 0.004 |
| $H_2$ | -0.291 | 0.025 | -0.344 | 0.047 | 0.018 | 0.004 |

**Table S7** Natural charge populations (NPA) for the Al, B and H atoms of the most stable anionic $B_xAl_yH_2$ ($x + y = 9$) clusters.

| $x + y = 9$ | $Al_9H_2^-$ | $BAl_8H_2^-$ | $B_2Al_7H_2^-$ | $B_3Al_6H_2^-$ | $B_4Al_5H_2^-$ | $B_5Al_4H_2^-$ |
|---|---|---|---|---|---|---|
| $B_1$ | | -2.644 | -1.212 | -0.832 | -0.355 | -1.035 |
| $B_2$ | | | -2.076 | -0.832 | -0.717 | -0.236 |
| $B_3$ | | | | -1.010 | -0.741 | -0.234 |
| $B_4$ | | | | | -1.985 | -0.410 |
| $B_5$ | | | | | | -1.454 |
| $Al_1$ | -0.408 | 0.309 | -0.025 | 0.295 | 0.271 | 0.708 |
| $Al_2$ | 0.103 | 0.188 | 0.565 | 0.017 | 0.679 | 0.531 |
| $Al_3$ | 0.013 | 0.304 | 0.422 | 0.005 | 0.680 | 0.537 |
| $Al_4$ | 0.076 | 0.447 | 0.420 | 0.583 | 0.480 | 0.588 |
| $Al_5$ | -0.165 | 0.557 | 0.661 | 0.295 | 0.693 | |
| $Al_6$ | -0.027 | -0.047 | 0.382 | 0.465 | | |
| $Al_7$ | 0.226 | 0.0830 | 0.208 | | | |
| $Al_8$ | -0.139 | 0.448 | | | | |
| $Al_9$ | -0.017 | | | | | |
| $H_1$ | -0.344 | -0.340 | 0.008 | 0.007 | 0.014 | 0.004 |
| $H_2$ | -0.319 | -0.305 | -0.353 | 0.007 | -0.0120 | 0.001 |

**Fig. S1** Equilibrium geometries of the low-lying isomers for neutral and anionic $B_xAl_yH_2$ ($x + y = 7$) clusters at B3LYP/6-311+G* level of theory. The pink spheres stand for aluminum atoms and the cyan ones for boron atoms.

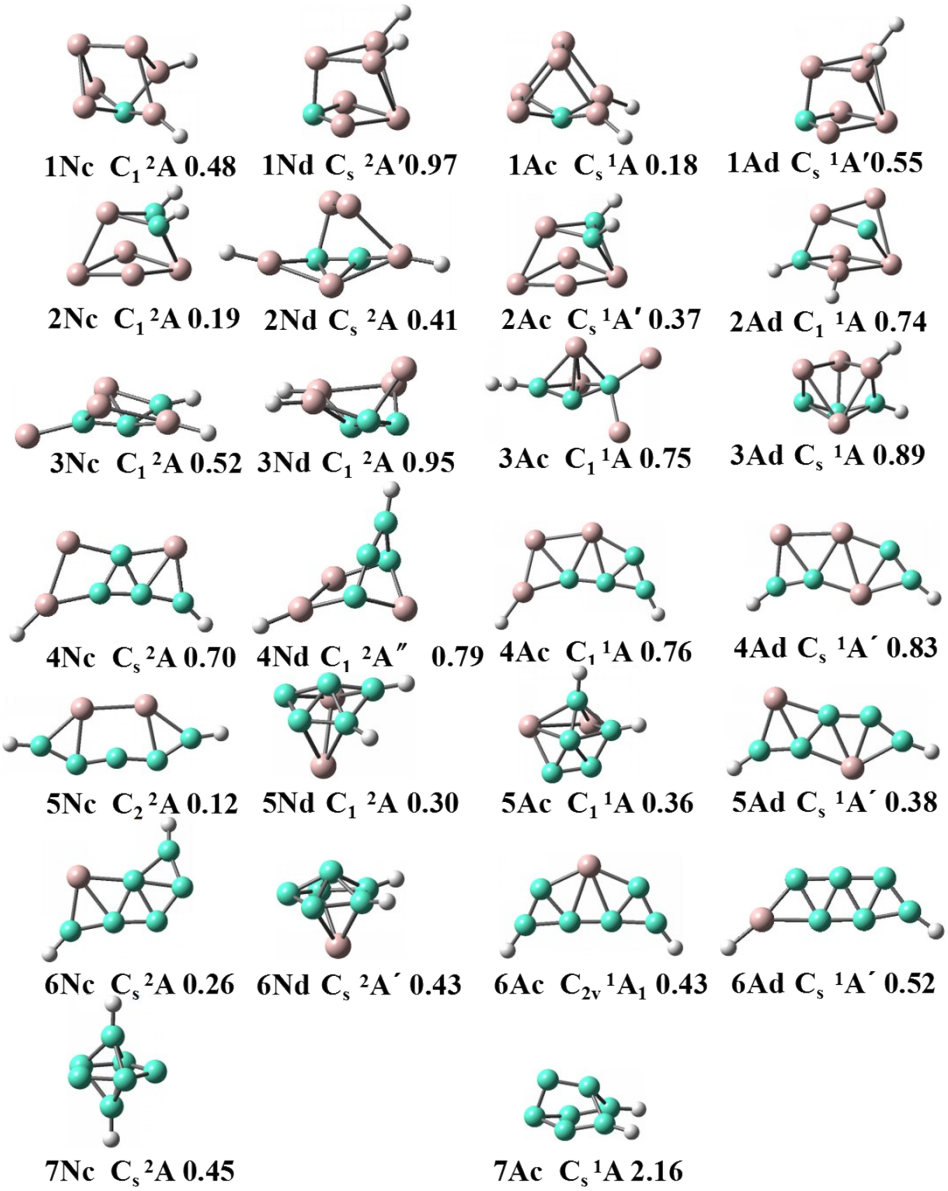

**Fig. S2** Equilibrium geometries of the low-lying isomers for neutral and anionic $B_xAl_yH_2$ ($x + y = 8$) clusters at B3LYP/6-311+G* level of theory. The pink spheres stand for aluminum atoms and the cyan ones for boron atoms.

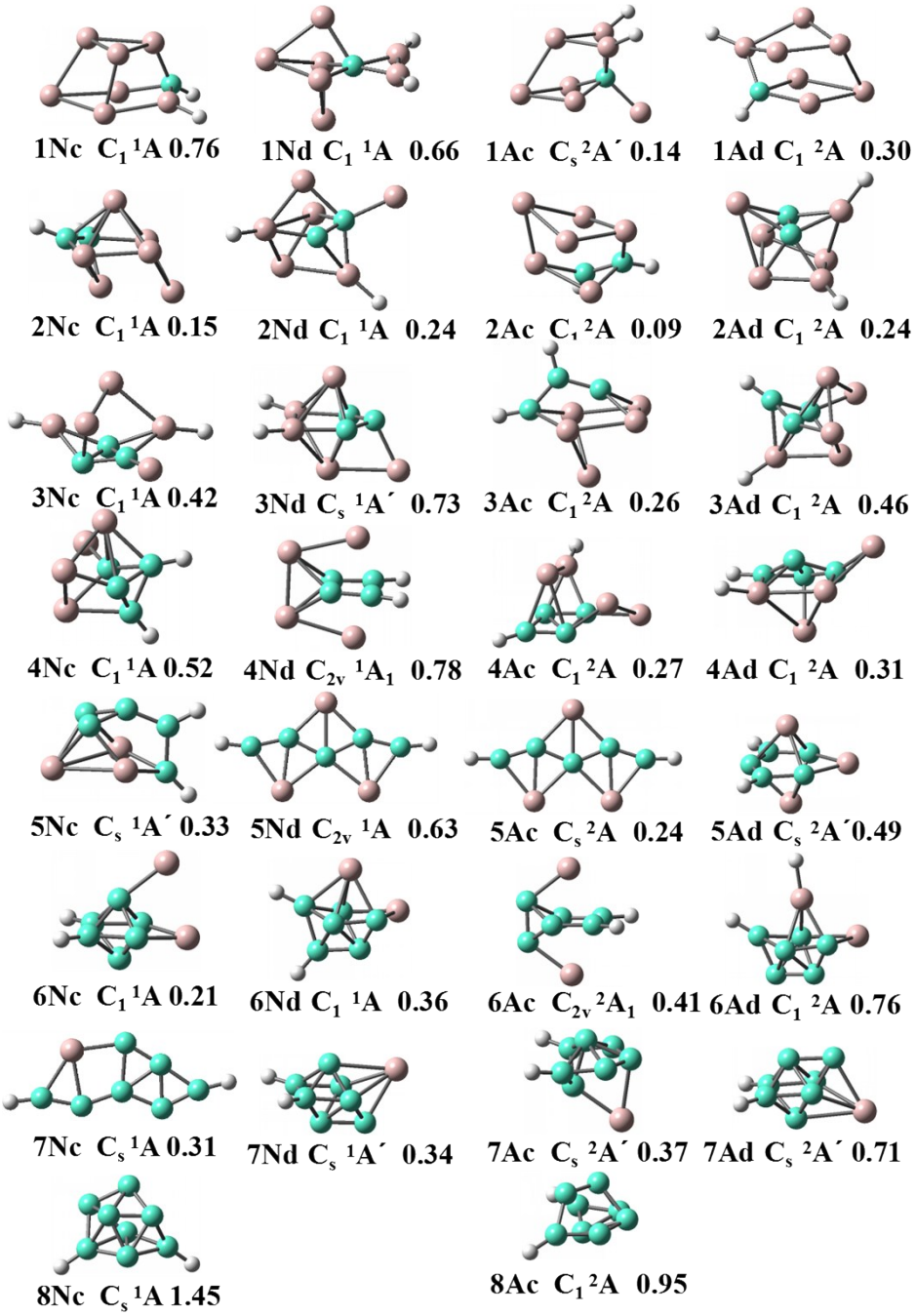

**Fig. S3** Equilibrium geometries of the low-lying isomers for neutral and anionic $B_xAl_yH_2$ ($x + y = 9$) clusters at B3LYP/6-311+G* level of theory. The pink spheres stand for aluminum atoms and the cyan ones for boron atoms.

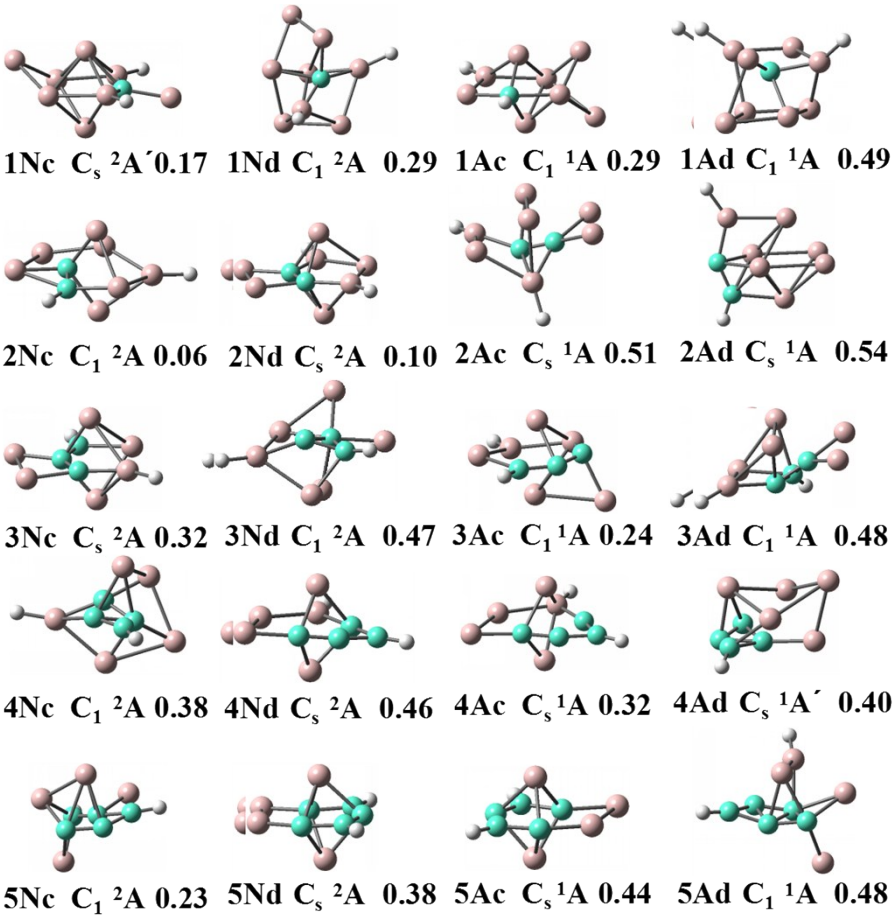

**Fig. S4** Simulated spectra for the next low-lying isomers of anionic $B_xAl_yH_2$ ($x + y$ = 7) clusters at B3LYP/6-311+G* level of theory.

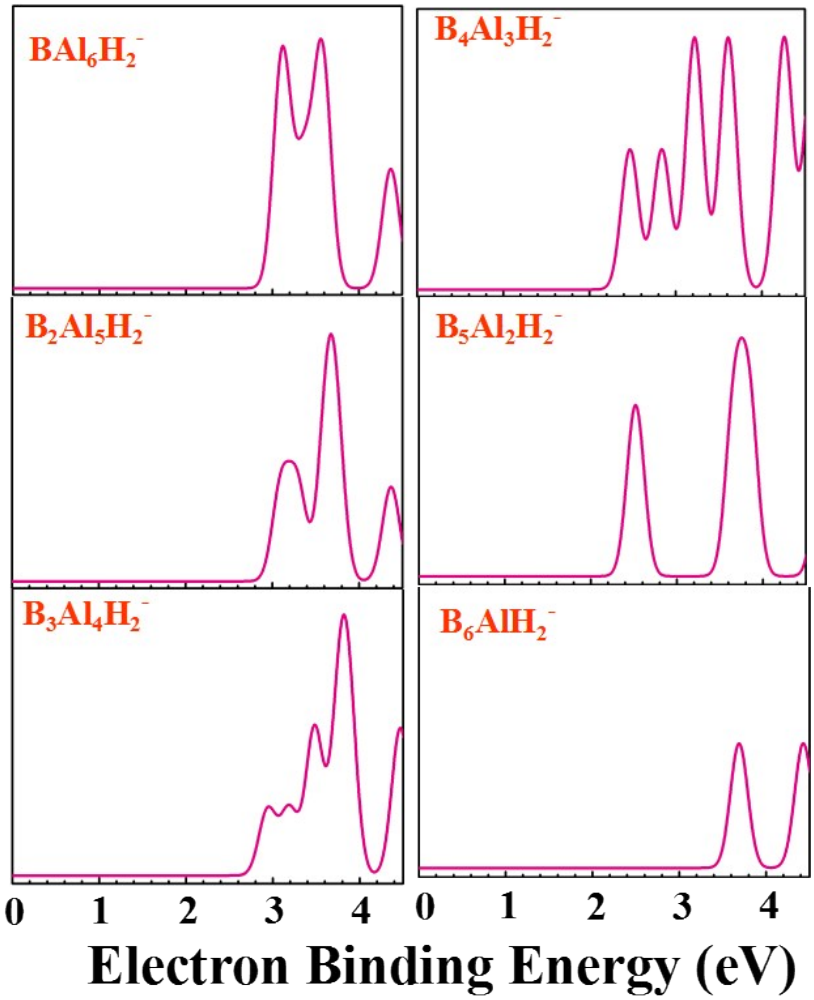

**Fig. S5** Simulated spectra for the next low-lying isomers of anionic $B_xAl_yH_2$ ($x + y$ = 8) clusters at B3LYP/6-311+G* level of theory.

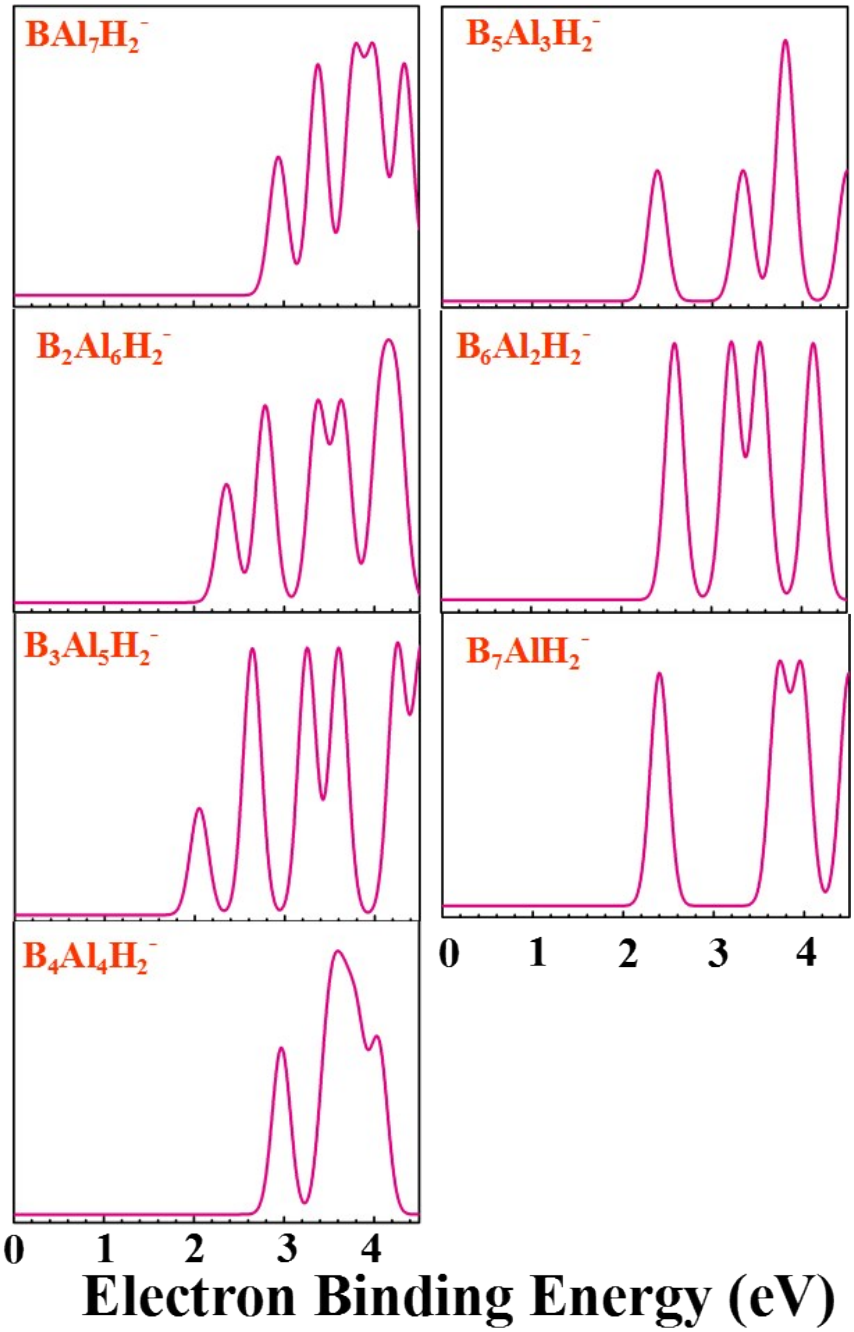

**Fig. S6** Simulated spectra for the next low-lying isomers of anionic $B_xAl_yH_2$ ($x + y$ = 9) clusters at B3LYP/6-311+G* level of theory.

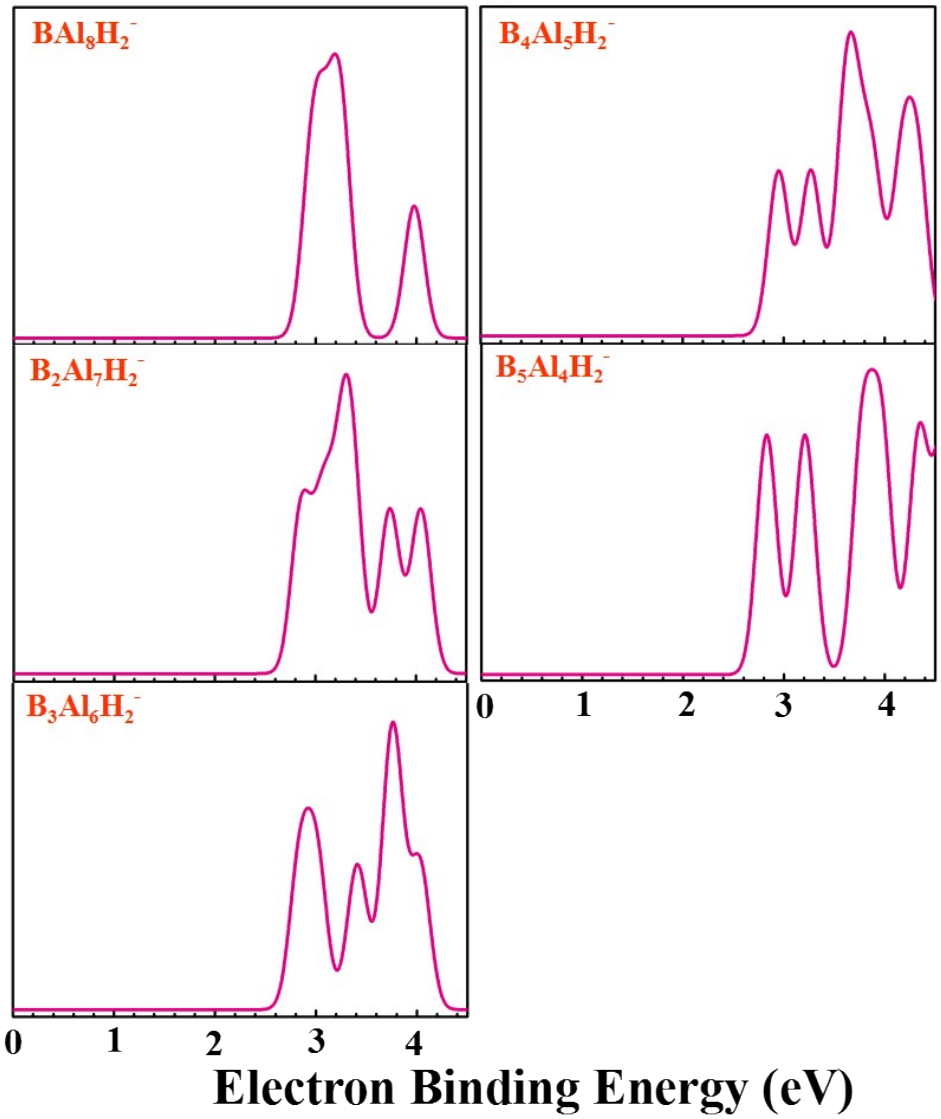

**Fig. S7** The four next highest occupied molecular orbitals of ground state anionic $B_xAl_yH_2$ ($x + y = 7$) clusters at B3LYP/6-311+G* level of theory.

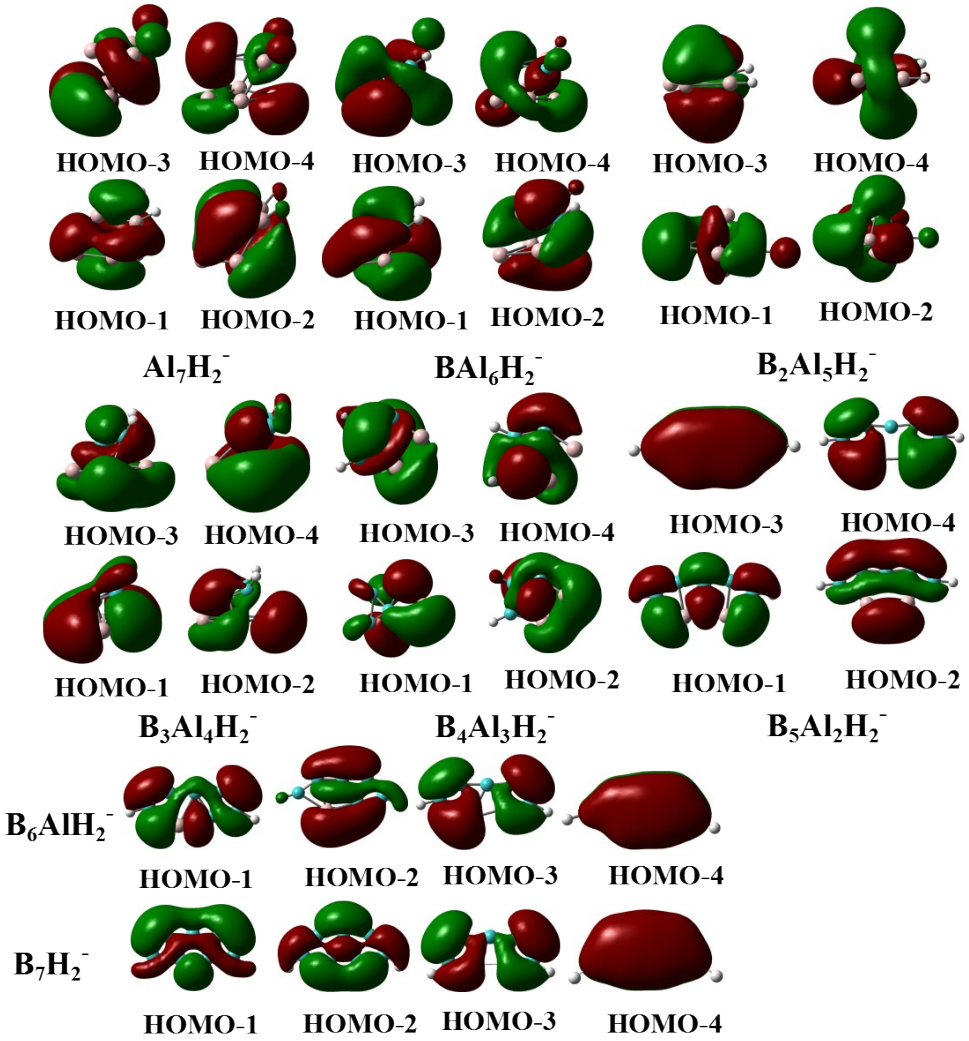

**Fig. S8** The four next highest occupied molecular orbitals of ground state anionic $B_xAl_yH_2$ ($x + y = 8$) clusters at B3LYP/6-311+G* level of theory.

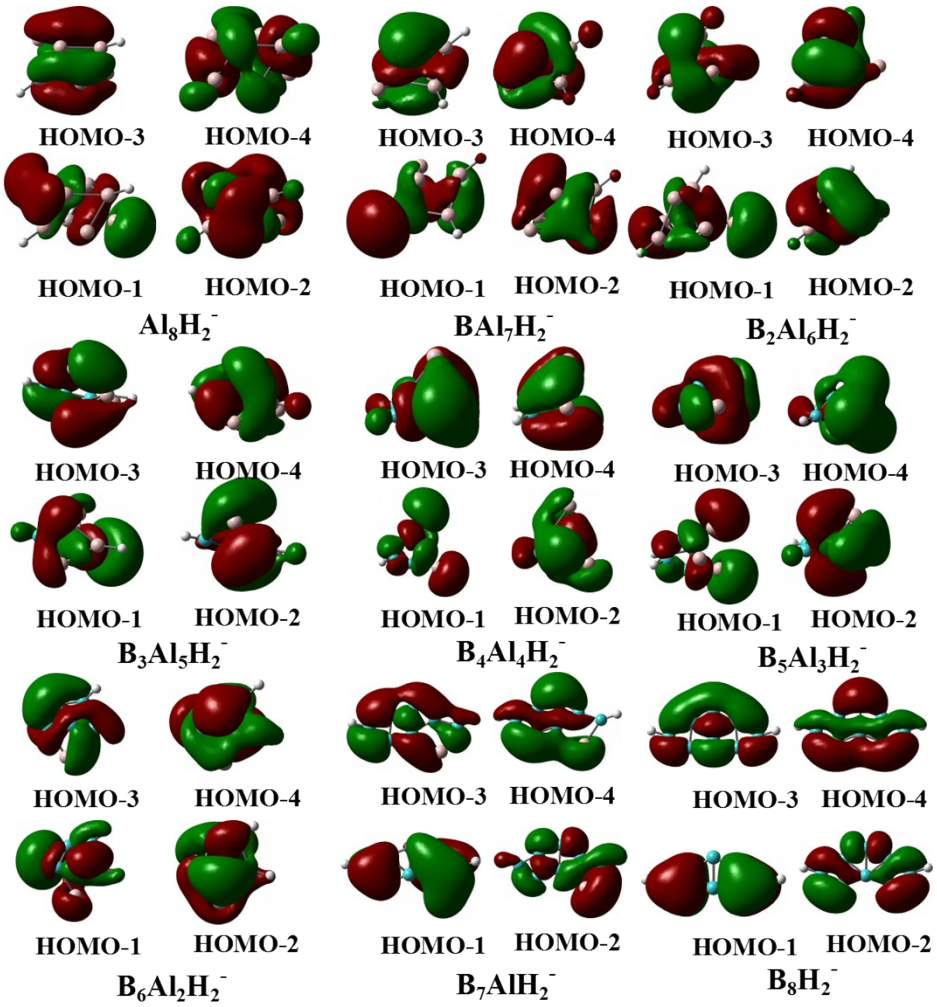

**Fig. S9** The four next highest occupied molecular orbitals of ground state anionic $B_xAl_yH_2$ ($x + y = 9$) clusters at B3LYP/6-311+G* level of theory.