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

Supplementary Information

Searching for Stable Copper Borozene Complexes, CuB_7^- and CuB_8^-

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Table S1 Population sizes for each cluster employed in the CK search.

Stoichiometry	Population Size
CuB_7^- (doublet and quartet states)	2000
CuB_7 (singlet and triplet states)	1500
CuB_8^- (singlet and triplet states)	2700
CuB_8 (doublet and quartet states)	2400

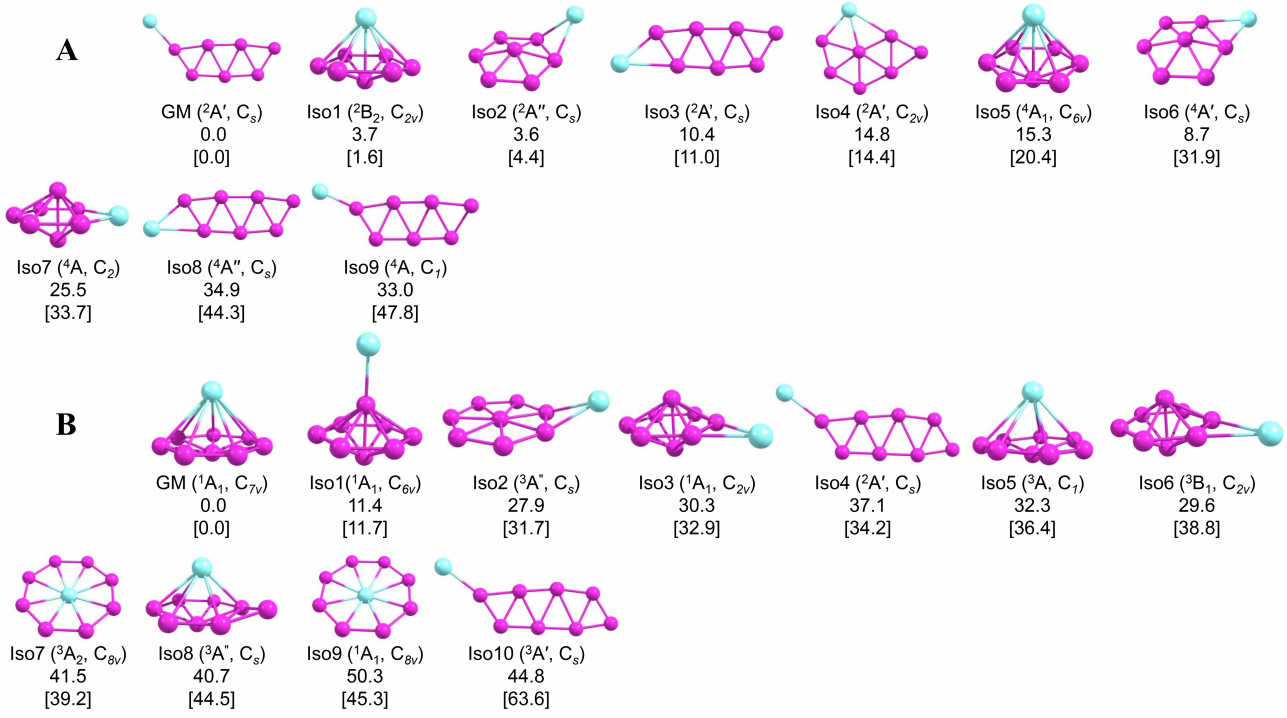

Fig. S1 Low-lying structures of (**A**) CuB_7^- and (**B**) CuB_8^- found via the CK search. Relative energies in kcal/mol are given at PBE0/def2-TZVPD with the CCSD(T)/aug-cc-pVQZ values shown in the brackets.

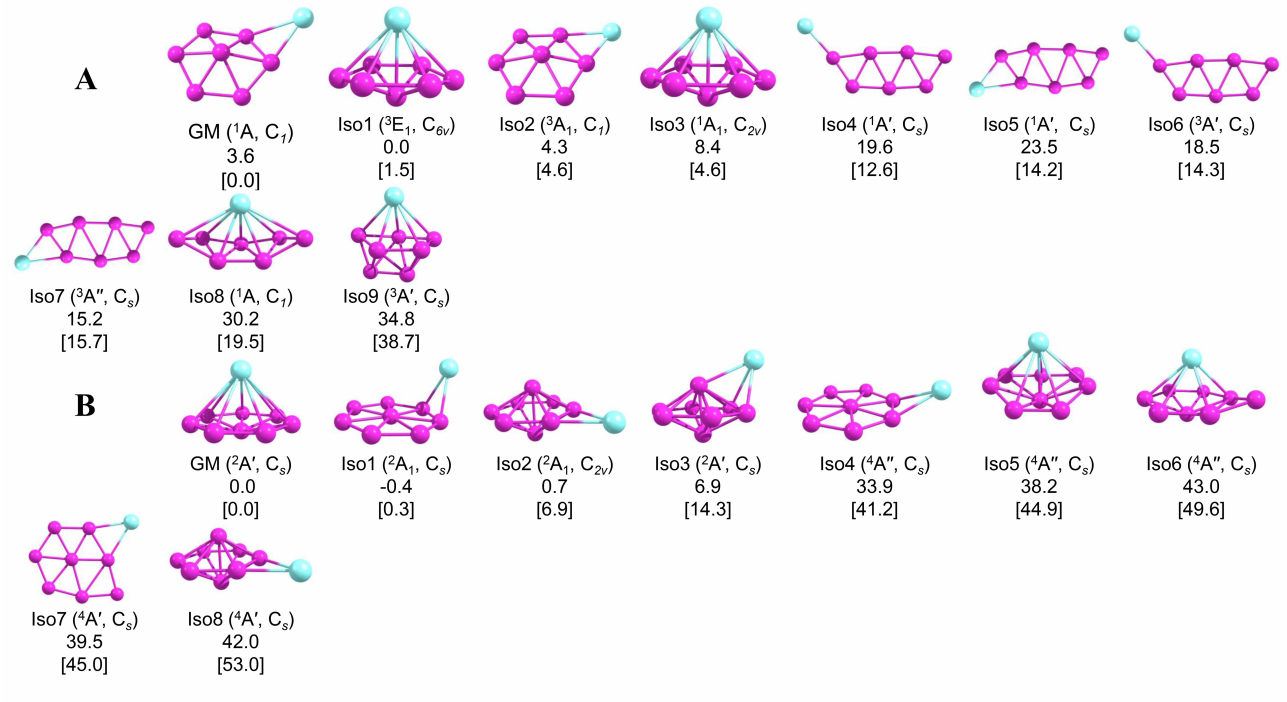

Fig. S2 Low-lying structures of (**A**) CuB_7 and (**B**) CuB_8 found via the CK search. Relative energies in kcal/mol are given at PBE0/def2-TZVPD with the CCSD(T)/aug-cc-pVQZ values shown in brackets.

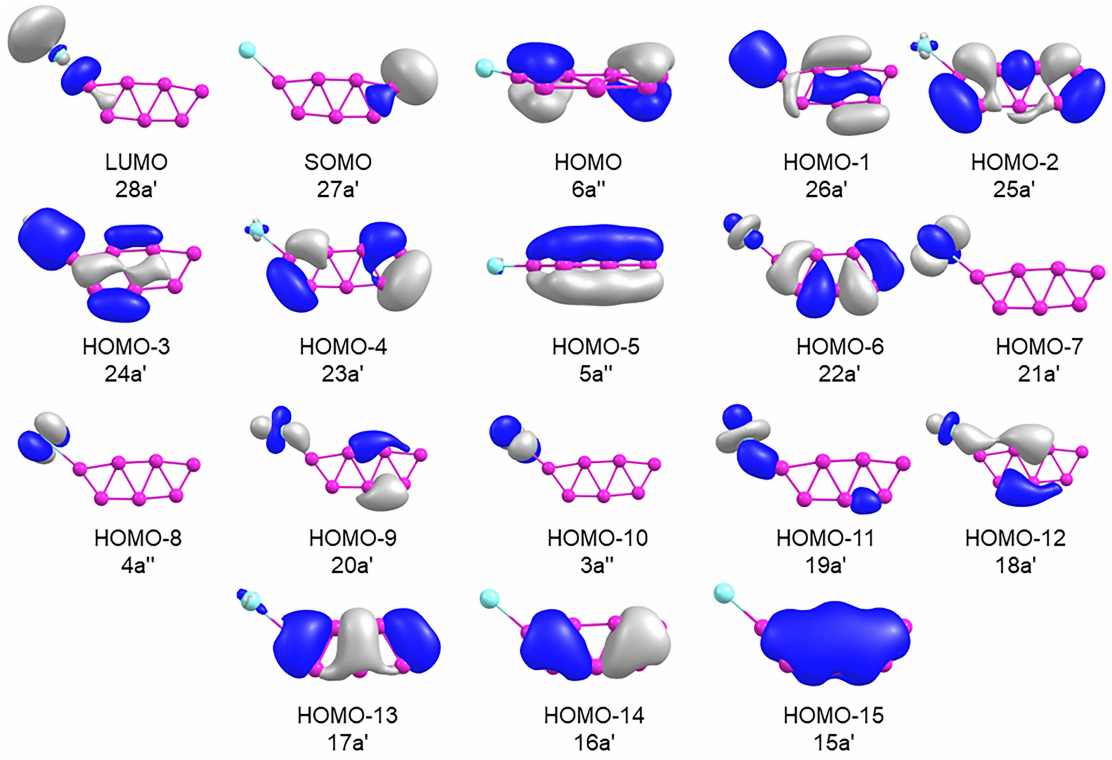

Fig. S3 The valence MOs for the GM of CuB_7^- (C_s, $^2A'$).

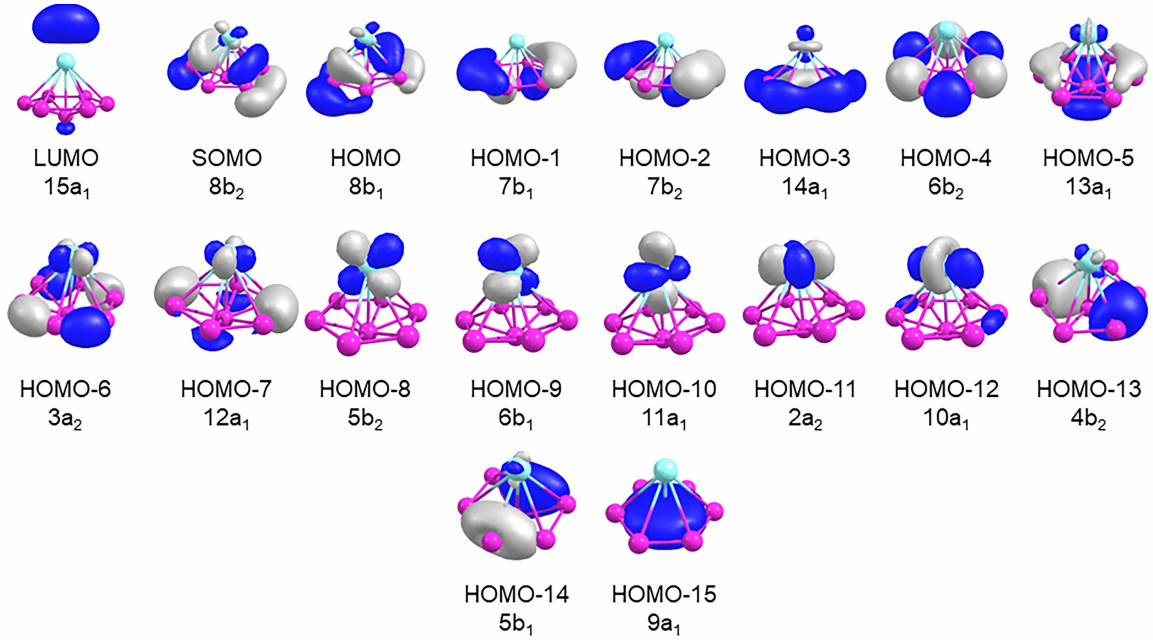

Fig. S4 The valence MOs for Iso1 of CuB_7^- (C_{2v}, $^2B_2$).

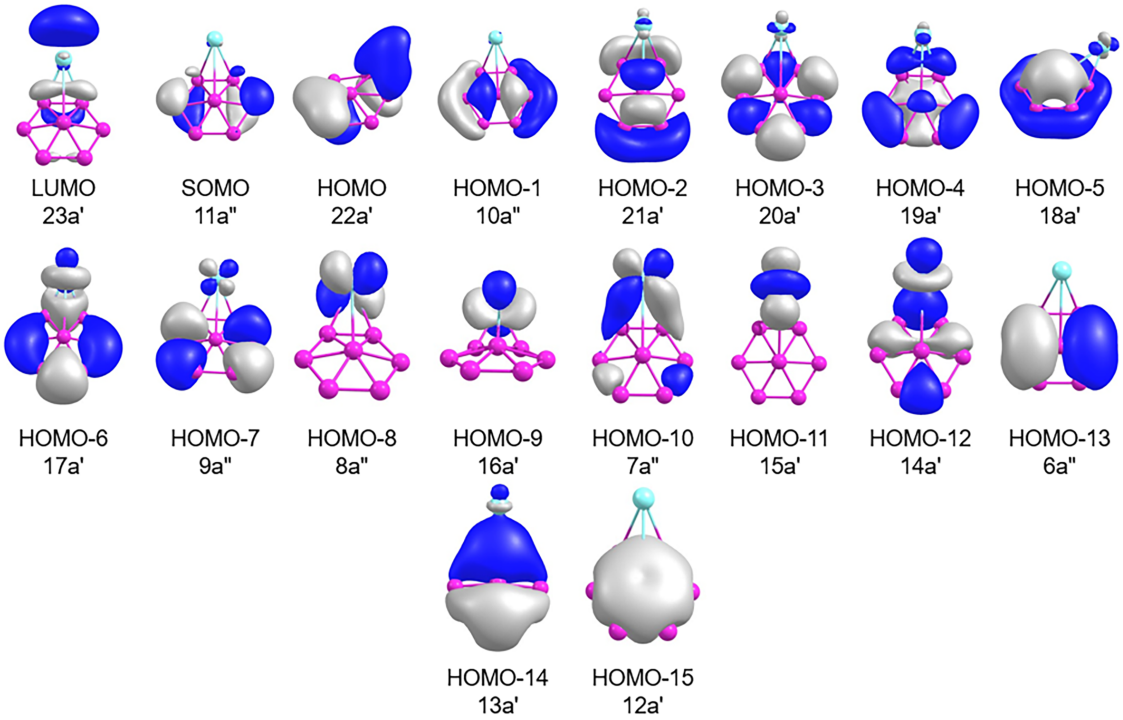

Fig. S5 The valence MOs for Iso2 of CuB_7^- (C_s, $^2A''$).

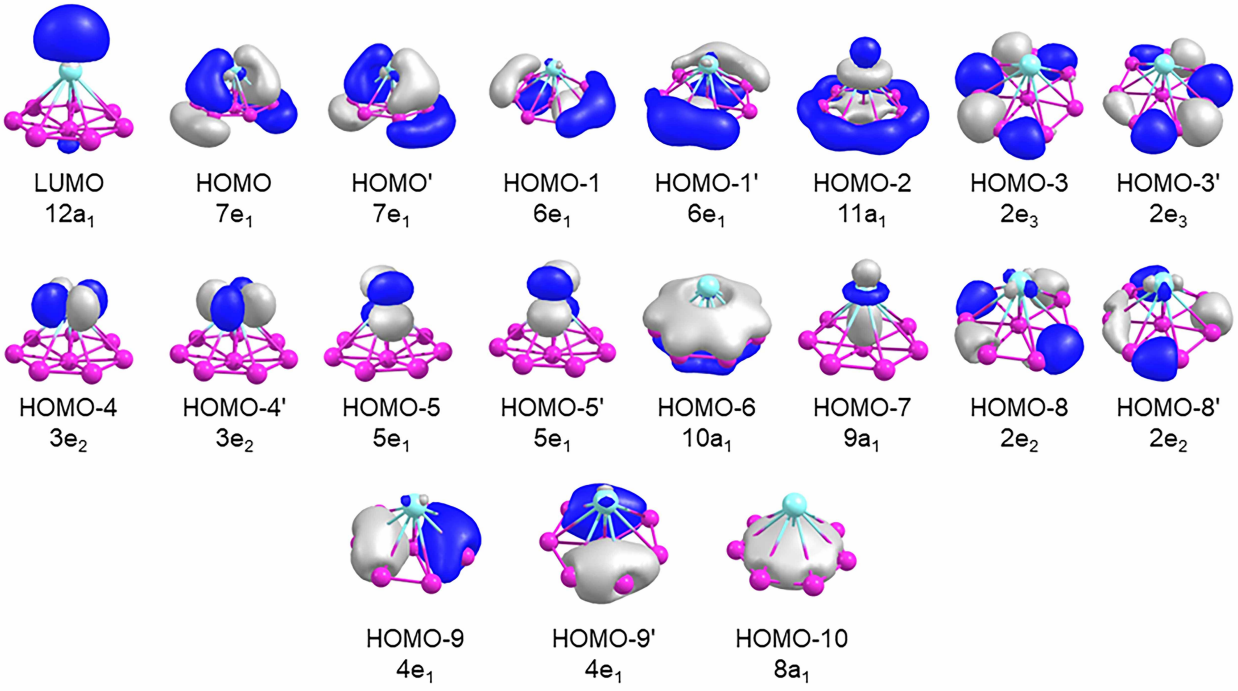

Fig. S6 The valence MOs for the GM of CuB_8^- (C_{7v}, $^1A_1$).

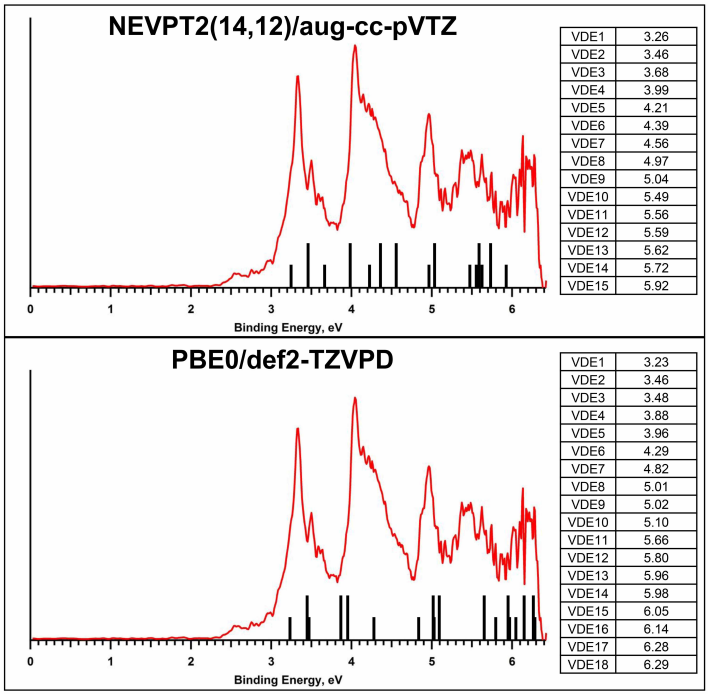

Fig. S7 Comparison of VDEs computed at the NEVPT2(14,12)/aug-cc-pVTZ and PBE0/def2-TZVPD levels of theory for the GM of CuB_7^-.

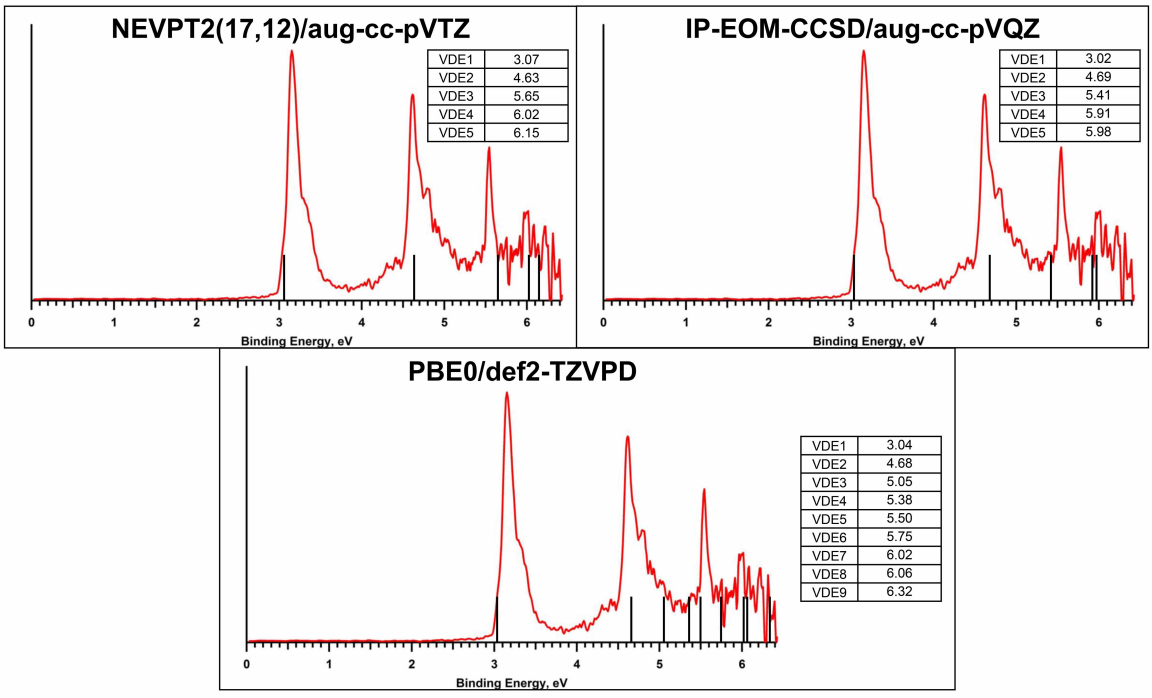

Fig. S8 Comparison of VDEs computed at the NEVPT2(17,12)/aug-cc-pVTZ, IP-EOM-CCSD/aug-cc-pVQZ, and PBE0/def2-TZVPD levels of theory for the GM of CuB_8^-.

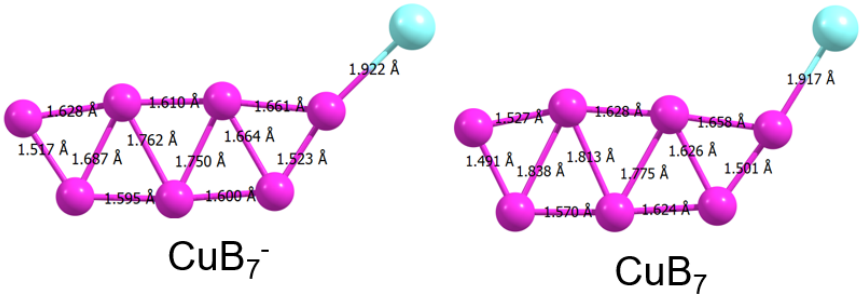

Fig. S9 Comparison of the GM structure of CuB_7^- (C_s, $^2A'$) with its corresponding neutral (C_s, $^1A'$).

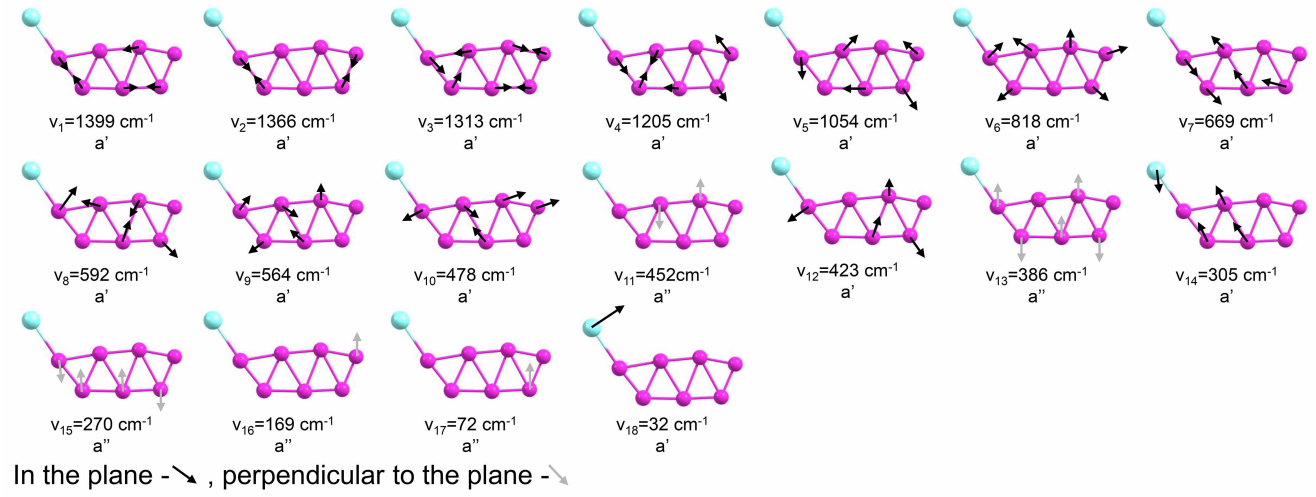

Fig. S10 The vibrational modes and their computed harmonic frequencies for CuB_7 at the PBE0/def-TZVPD level of theory.

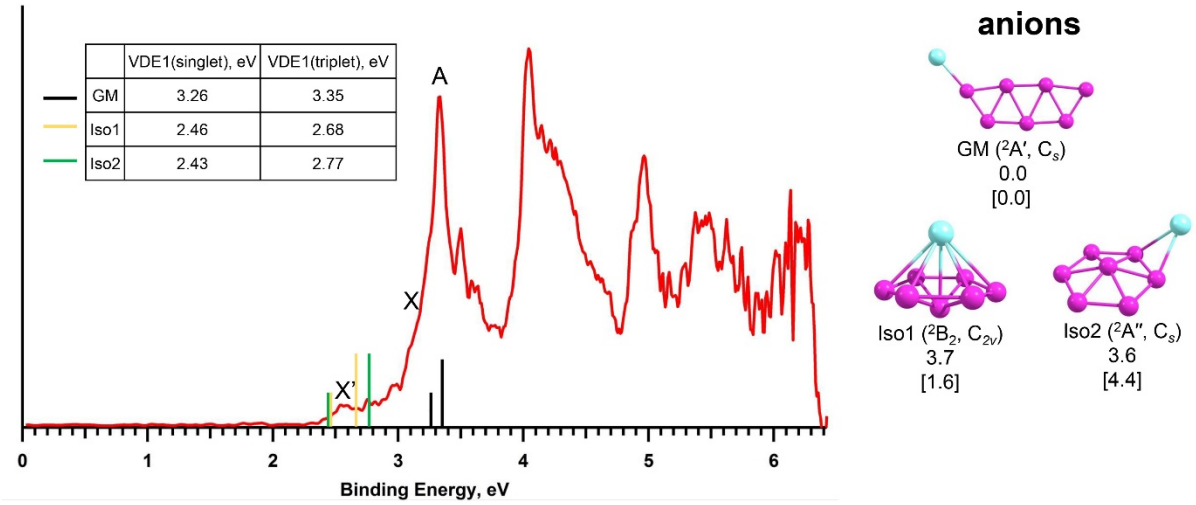

Fig. S11 Comparison of theoretical VDEs computed for the GM, Iso1, and Iso2 isomers of CuB_7^- for the X', X, A bands.

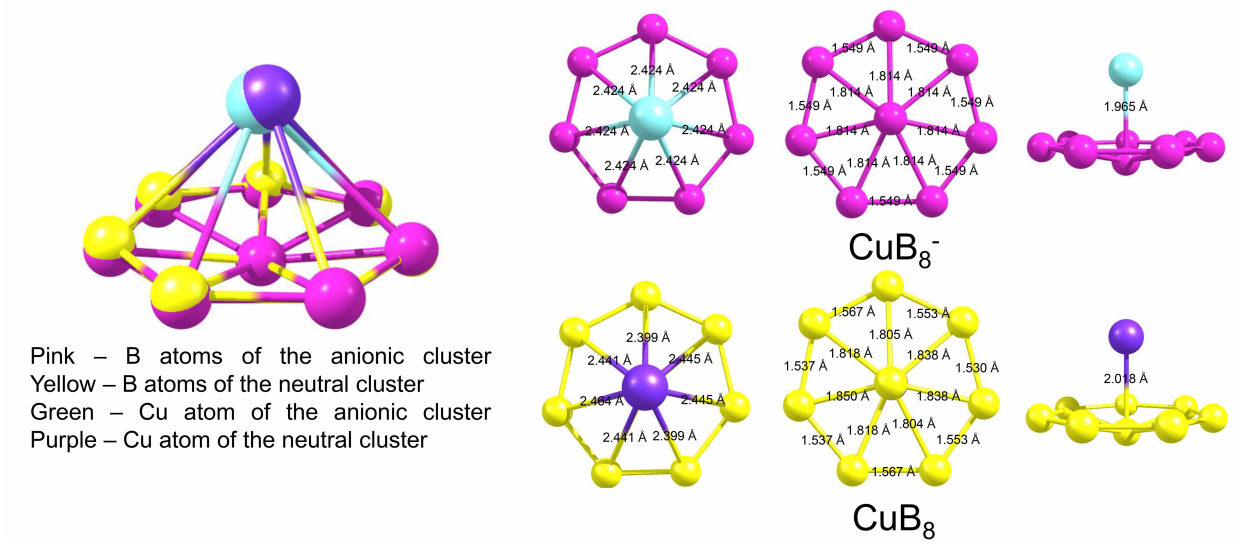

Fig. S12 Comparison of the GM structure of CuB_8^- (C_{7v}, $^1A_1$) with its corresponding neutral (C_s, $^2A'$).

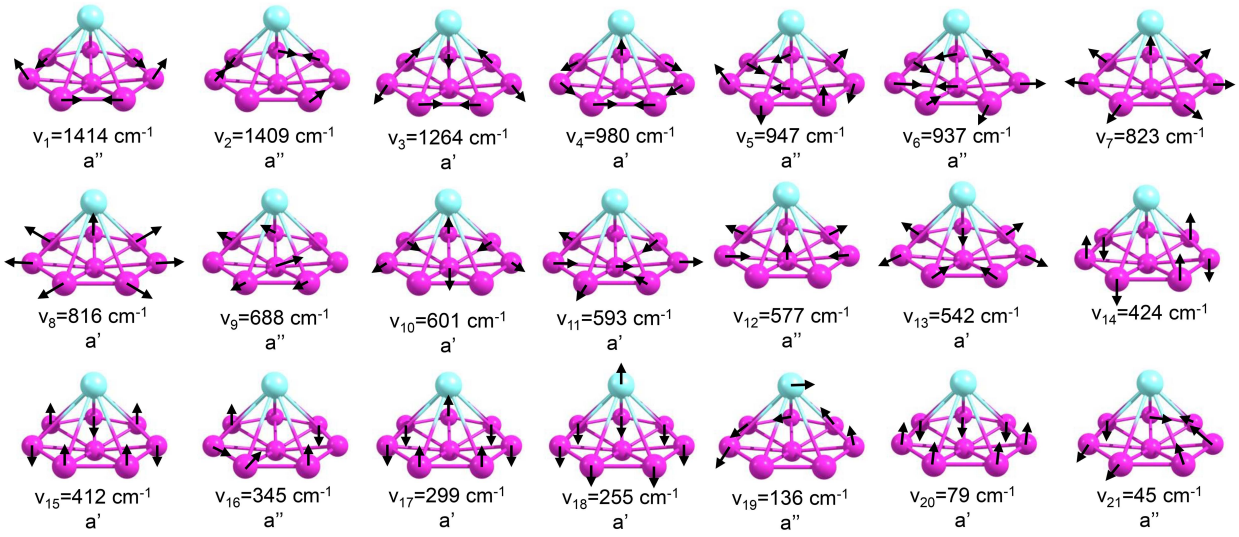

Fig. S13 The vibrational modes and their computed harmonic frequencies for CuB_8 at the PBE0/def-TZVPD level of theory.

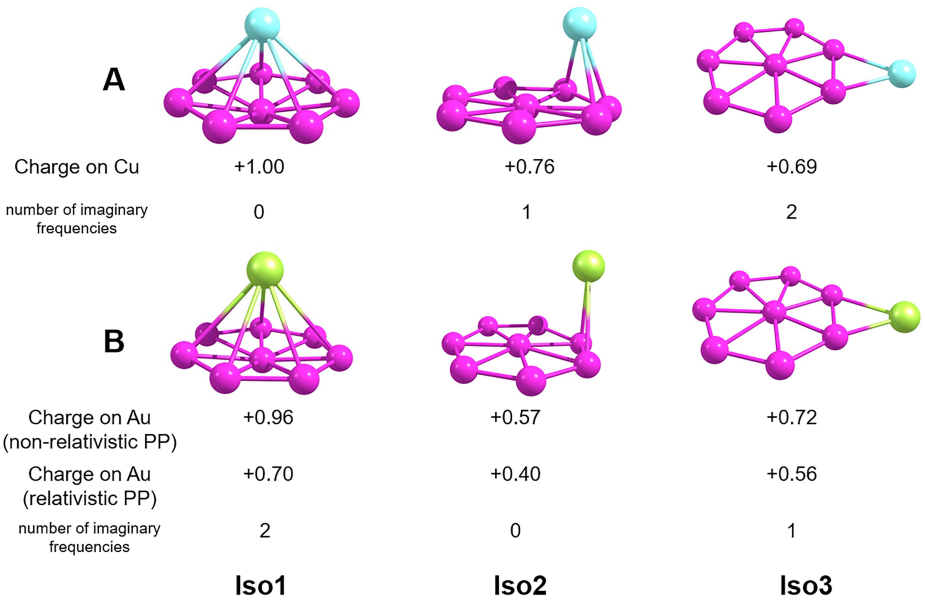

Fig. S14 Isomers with different positions of Cu/Au relative to the B_8 wheel for (**A**) CuB_8^- and (**B**) AuB_8^-. We analyzed natural charges on the Cu/Au atoms depending on their positions relative to the B_8 wheel in the singlet state of the anionic clusters. We employed the PBE0/def2-TZVPD level of theory for CuB_8^- and found +1.00 |e| on Cu in Iso1, +0.76 |e| for Iso2, and +0.69 |e| for Iso3. Only Iso1 is a local minimum for CuB_8^-, while Iso2 and Iso3 possess imaginary frequencies. For Au we employed two different energy-consistent pseudopotentials (PP) – the nonrelativistic ECP60MHF in conjunction with the ECP60MHF basis set[1] and the relativistic ECP60MDF with the AVTZ basis set.[2,3] For the nonrelativistic PP, we found +0.96 |e| charge on Au for Iso1, +0.57 |e| for Iso2, and +0.72 |e| for Iso3. Thus, Iso2 possesses the lowest charge on the Au atom, so it exhibits the most covalent interaction in this case. Both Iso1 and Iso3 have imaginary frequencies, making the edge position of Au atom in Iso2 the only stable configuration. Introduction of scalar-relativistic effects brings much lower charges on the Au atom — +0.70 |e| for Iso1, +0.40 |e| for Iso2, and +0.56 |e| for Iso3. The energy difference between Iso2 and Iso1 with the non-relativistic PP is 2.8 kcal/mol, while with the relativistic PP, it increases up to 16.4 kcal/mol. Thus, Au tends to acquire more covalent bonds than Cu in similar structures that can be attributed to the more diffuse orbitals on Au atoms and the relativistic effects, as seen from the comparison of nonrelativistic and relativistic pseudopotentials.

References

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2 D. Figgen, G. Rauhut, M. Dolg and H. Stoll, *Chem. Phys.* 2005, **311**, 227–244.

3 K. A. Peterson and C. Puzzarini, *Theor. Chem. Acc.* 2005, **114**, 283–296.