

Like Charges Attract?

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Supporting Information

ABSTRACT: Using multiscale first-principles calculations, we show that two interacting negatively charged $B_{12}I_9^-$ monoanions not only attract, in defiance of the Coulomb's law, but also the energy barrier at 400 K is small enough that these two moieties combine to form a *stable* $B_{24}I_{18}^{2-}$ moiety. Ab initio molecular dynamics simulations further confirm its stability up to 1500 K. Studies of other $B_{12}X_9^-$ (X = Br, Cl, F, H, Au, CN) show that while all of these $B_{24}X_{18}^{2-}$ moieties are *stable* against dissociation, the energy barrier, with the exception of $B_{24}Au_{18}^{2-}$, is large so as to hinder their experimental observation. Our results explain the recent experimental observation of the "spontaneous" formation of $B_{24}I_{18}^{2-}$ in an ion trap. A simple model based upon electrostatics shows that this unusual behavior is due to



competition between the attractive dipole-dipole interaction caused by the aspherical shape of the particle and the repulsive interaction between the like charges.

oulomb's law,¹ first published in 1784 by French physicist Charles de Coulomb, is one of the most fundamental laws of science that describes the electrostatic interaction between electrically charged particles. According to this classical law, particles with like charges repel and those with unlike charges attract. Although violation of Coulomb's law is not seen in nature, this topic has fascinated scientists for more than a century. In 1845, William Thomson (later Lord Kelvin²) developed a theory to explain the attraction between two positively charged particles as due to the difference in the magnitude of the image charges. Study of classical electrostatic attraction between positively charged³⁻⁷ confined colloidal particles continues to attract attention today as they are relevant in physical as well as biological sciences. That two positively charged atoms can also form a "stable" state was observed by Tsong⁸ in a Mo₂²⁺ dimer whose binding energy was estimated to be at least 1.2 eV. Subsequent theoretical study by Liu et al.9 of the interaction between two positively charged transition-metal atoms brought into focus that quantum mechanics may also play a role and the interaction between two like charges may not always be repulsive at all distances. In fact, for very small distances, the potential for a Mo2²⁺ dimer was found to be attractive. However, the total energy of the Mo₂²⁺ dimer was found to be higher than that of two isolated Mo⁺ ions with its dissociation to individual Mo⁺ ions protected by a large energy barrier. Thus, Mo_2^{2+} is metastable and would dissociate into two Mo⁺ ions, once the barrier is crossed. In a similar vein, the stability of nuclei arises because the attractive strong force overtakes repulsive Coulomb forces between protons at very short distances. Attractive interaction between two negatively charged particles is rare.¹⁰

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In 1956, Cooper showed that two phonon-mediated electrons, known as a Cooper pair,¹¹ can attract to form a bound state in a superconductor. A fundamental question that remains to be answered is can two negatively charged particles spontaneously combine, without mediation, to form a stable bound state and, if so, under what condition?

In this Letter, we show that this is indeed possible if the charged particles are aspherical and the attractive interaction between the two resulting dipole moments overcomes, at some critical distance, the repulsive force due to the monopole charges. The chemical bonding that will ensue between the atoms of individual charged particles can then lead to a stable bound state of the dianion. This hypothesis is supported by a recent experiment of Warneke et al.¹² During sequential stripping of iodine from the $B_{12}I_{12}^{2-}$ icosahedral cage, the authors observed the formation of $B_{12}I_9^-$ monoanions. Spontaneous reaction between these two negatively charged $B_{12}I_9^-$ monoanions then led to the formation of $B_{24}I_{18}^{2-}$. In sharp contrast to the metastability of Mo_2^{2+} , $B_{24}I_{18}^{2-}$ was found to be stable. To quote the authors, "This is very remarkable based on the expected Coulomb repulsion". This seminal experiment raises some fundamental questions: (1) Under what conditions can two negative ions attract? (2) Is the reaction really spontaneous, or is there a small energy barrier that can be easily overcome under moderate conditions, thus making the reaction appear spontaneous? (3) Is this phenomenon generic to only an iodine-decorated B_{12} cage, or can decoration by

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Figure 1. (a) Geometries of $B_{12}I_{12}^{2-}$ dianion, $B_{12}I_{12}^{-}$ monoanion, and $B_{12}I_{12}$ neutral clusters, (b) geometries of I_n^- clusters (n = 2-12), and (c) geometries of the $B_{12}I_9^-$ anion and $B_{24}I_{18}^{2-}$ dianion with their corresponding symmetry.

other halogen atoms lead to similar results? (4) While successive deiodination of $B_{12}I_{12}^{2-}$ led to $B_{12}I_{12-x}^{-}$ (x = 1-12) species, why did the authors only observe the formation of $B_{24}I_{18}^{-2-}$? Could it be that the formation of $B_{12}I_9^{-}$ is preferred during deiodination? (5) Could the phenomenon observed in the formation of $B_{24}I_{18}^{2-}$ persist in nonhalogenated species such as two interacting $B_{12}X_9^{-}$ (X = H, Au, and CN) monoanions?

Here we address these questions using a first-principles multiscale approach based on density functional theory (DFT), Møller–Plesset perturbation theory up to second order (MP2), and quantum molecular dynamics. We show that the Coulomb repulsion between two B₁₂I₉⁻ monoanions is compensated by the chemical bonding that forms when these two monoanions approach each other due to attractive dipole-dipole interaction. Electronic shell closure in $B_{24}I_{18}^{2-}$, attributed to the Wade-Mingos rule,¹³⁻¹⁶ further contributes to its stabilization. A small energy barrier that exists when two $B_{12}I_9$ monoanions come close to each other can be easily overcome at moderate temperatures, giving the appearance of spontaneous reaction. Systematic studies of the interaction between other halogenated $B_{12}X_9^-$ (X = Br, Cl, F) and nonhalogenated (X = H, Au, and CN) species further show that all $B_{24}X_{18}^{2-}$ (X = Br, Cl, F, H, Au, and CN) moieties are stable against dissociation into $B_{12}X_9^-$ monomers. However, with the exception of B₂₄Au₁₈²⁻, the energy barriers steadily increase as iodine is replaced by Br, Cl, F, CN, and H, thus making these moieties less likely to form spontaneously under moderate thermodynamic conditions. This contrasting behavior is attributed to different electronegativity and size of the ligand atoms. A systematic study of the total energies of I_n^- as a

function of *n* further shows that I_3^- is a superhalogen and is the most stable cluster among I_n^- anions. Consequently, as $B_{12}I_{12}^{2-}$ fragments into $B_{12}I_{12-n}^- + I_n^-$, the $B_{12}I_9^-$ monoanion is a preferred byproduct because of the high stability of the I_3^- . We predict that the formation of $B_{24}Au_{18}^{2-}$ should be observable.

In the following, we discuss the interest in studying $B_{12}X_{12}^{2-1}$ anions, the experimental result showing that two negatively charged B₁₂I₉⁻ monoanions "spontaneously" attract, and our interpretation of the underlying mechanism. Polyhedral boranes with three-center-two-electron bonds¹⁷⁻²⁰ are among the most interesting cage molecules^{21–23} in chemistry. They belong to a unique class of clusters among which the *closo*-dodecaborate $B_{12}H_{12}^{2-}$ is a well-known stable dianion in the gas phase.²⁴ Here, the second electron is bound by 0.9 eV.²⁵⁻²⁷ While negative ions with multiple charges can be stable in crystals or in solvated systems due to the presence of compensating positive ions, their stability in the gas phase is hindered due to the electrostatic repulsion between the two extra electrons. The extraordinary stability of $B_{12}H_{12}^{2-}$ is attributed to the Wade-Mingos rule, which requires that for a borane polyhedron to be stable it must have (n + 1) pairs of electrons, where n is the number of vertices. Note that the structure of $B_{12}H_{12}^{2-}$ is a perfect icosahedron with 12 H atoms radially bonded to 12 B atoms occupying the vertices of the icosahedron. With each BH pair contributing two electrons to the cage bonding, there are 26 electrons in $B_{12}H_{12}^{2-}$, exactly what is needed to satisfy the Wade-Mingos rule. In addition to their unique structure and stability, the *closo*-dodecaborates play an important role in applied research. They are used for the development of new types of ionic liquids, as weakly

coordinating ions, as X-ray contrast agents, and for treatment of tumors.

Recently, a new series of perhalogenated $B_{12}X_{12}^{2-}$ (X = F, Cl, Br, I) clusters have been prepared and studied ^{12,20,28} that show unusual gas-phase reactivity when subjected to collisions in an ion trap mass spectrometer. Sequential removal of iodine from $B_{12}I_{12}^{2-}$ showed that the cage structure begins to break^{29,30} and becomes planar when seven iodine atoms are left. In the process, $B_{12}I_9^{-}$ is formed when I⁻ is removed from $B_{12}I_{10}^{2-}$. The most surprising result of this experiment is that two $B_{12}I_9^{-}$ moieties seem to attract spontaneously to form a stable $B_{24}I_{18}^{2-}$ species.¹² As mentioned earlier, this would seem to contradict Coulomb's law, which states that particles with like charges must repel. The outstanding questions that need to be answered are why do the authors observe⁴ only the formation of $B_{24}I_{18}^{2-}$ species and why do two $B_{12}I_9^{-}$ moieties appear to attract spontaneously?

To seek answers to the above questions, we first studied the structures and total energies of I_n^- clusters as well as that of $B_{12}I_9^-$ species using DFT. The interaction between two $B_{12}I_9^-$ species as a function of distance between the centers of two $B_{12}I_9^-$ icosahedra was then studied. The transition state and the binding energy of $B_{24}I_{18}^{-2-}$ species against dissociation into two $B_{12}I_9^-$ species were calculated using the nudged elastic band method. Molecular dynamics calculations were carried out to further confirm the stability of $B_{24}I_{18}^{-2-}$ species at higher temperatures. Calculations were repeated by replacing the iodine atoms with other halogen atoms such as Br, Cl, and F to see if the above phenomenon is unique only to I-containing species. The results are compared with the stability of nonhalogenated species $B_{24}X_{18}^{-2-}$ (X = H, Au, and CN) as two $B_{12}X_9^-$ monomers approach each other

In Figure 1a, we plot the equilibrium geometries of the $B_{12}I_{12}$ neutral, $B_{12}I_{12}^{-}$ monoanion, and $B_{12}I_{12}^{-2}$ dianion. The geometries of other $B_{12}X_{12}^{2-}$ (X = Br, Cl, F) species are similar to those in Figure 1 and are given in Figure S1 of the Supporting Information (SI). The $B_{12}X_{12}$ neutral and monoanion have T_h symmetry, while the $B_{12}X_{12}^{2-}$ dianion has the I_h symmetry. In $B_{12}I_{12}$, the B–B and B–I distances increase from 1.79 to 1.80 Å and from 2.17 to 2.19 Å, respectively, as one goes from the neutral to the dianion species. The B-B distances are affected very little as the I atom is replaced by Br, Cl, or F, but the B-X distances continually decrease from X = I to F, as expected due to their smaller sizes. To study the stabilities of these species with successive electron attachment, we have calculated the vertical (VDE) and adiabatic detachment energies (ADE). The former (VDE) is the energy difference between the ground state of the anion and its neutral at the anion geometry, while the latter (ADE) is the energy difference between the anion and its neutral, both at their respective ground-state geometries. In Table S1, we provide the energy gain as the first electron is attached to neutral $B_{12}X_{12}~(\Delta E^{\tilde{first})}$ and the second electron is attached to anionic $B_{12}X_{12}^{-12}$ (ΔE^{second}). These energies, defined as $\Delta E^{\text{first}} = E(B_{12}X_{12}) - E(B_{12}X_{12}^{-})$ and $\Delta E^{\text{second}} = E(B_{12}X_{12}^{-})$ $- E(B_{12}X_{12}^{2})$, are compared with the corresponding values of $B_{12}H_{12}$ and available experiments. We note that all of these species are stable. The electron binding energies of the first electron increase as the electron affinities of the halogen ligands increase. No such consistent trend is found for the second electron binding energy. These results agree with earlier theoretical calculations and available geometrical parameters from experiments.^{20,28}

To shed light on the apparent stability of B₁₂I₉⁻ species produced during sequential deiodination of $B_{12}I_{12}^{2-}$, we began with studies of the structures and relative stabilities of I_n clusters. The ground-state geometries of I_n^- clusters are given in Figure 1b. The geometries of I_n^- clusters with n = 2-4 are linear chains, while those of n = 5-7 are planar. For n > 7, the structures assume three-dimensional geometries. These results agree with previous theoretical calculations.³¹ We note that I₃⁻ is the building block of all larger I_n^- clusters. This indicates that I_3^- must be the most stable anion in the I_n^- cluster series. To confirm this, we studied the relative stability of I_n^- clusters by calculating the energy gain as successive iodine atoms are added to I_{n-1}^{-} cluster, namely, $\Delta E_n = E(I_{n-1}^{-}) + E(I) - E(I_n^{-})$. The calculated values of ΔE_n are 1.54, 2.68, 1.10, 2.37, 0.98, 2.15, 0.66, 2.38, 1.21, 1.54, and 1.19 eV for *n* = 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12, respectively. Note that the energy gains oscillate with odd ones being more stable than even ones. In particular, ΔE_n is the highest for I₃⁻, confirming that it is the most stable species in the I_n^- cluster series. The stability of I_3^- can also be seen from the point of view that it is a superhalogen, having an electron affinity of 4.02 eV, which is larger than that of any halogen atom. These results are consistent with experiment,³¹ which shows that the mass ion intensity of I_3^- is 2 orders of magnitude larger than those of the other clusters. It has been established in previous theoretical and experimental studies³²⁻³⁴ that during fragmentation the most stable cluster is always the preferred by product. Thus, $\mathrm{B}_{12}\mathrm{I}_9^-$ would be a relatively more stable cluster among the deiodinized $B_{12}I_{12-x}$ series. This may explain why experimentally the authors observed the formation of the $B_{24}I_{18}^{\ 2-}$ moiety.

We also note that during sequential deiodination it is possible that $B_{12}I_{12}^{2-}$ can dissociate along one of two different pathways; the dissociated iodine atoms can either be neutral or carry a negative charge. To confirm the preferred channel, it is, therefore, necessary to compare the energies needed in both processes, namely, $\Delta E_n^{1} = E(B_{12}I_{n-1}^{--}) + E(I^-) - E(B_{12}I_n^{2-})$ and $\Delta E_n^{2} = E(B_{12}I_{n-1}^{2-}) + E(I) - E(B_{12}I_n^{2-})$. These energies are plotted in Figure S2 of the SI. The preferred channel of dissociation is the one that requires the least energy. From Figure S2, we see that the iodine will preferably be ejected as a negative ion.

To obtain the geometries of the $B_{12}X_9^-$ anions (X = I, Br, Cl, F), it is a priori not clear which of the halogen atoms are to be removed, whether they should be random or nearest neighbors. Therefore, we studied all possible configurations and found that the equilibrium geometries are the ones where the halogen atoms are removed from nearest-neighbor sites. In Figure 1c, we give the geometry of the $B_{12}I_9^-$ anion, which agrees with previous DFT/GGA-based results obtained by using Slater-type all-electron basis (ZORA-scalar/TZP).³⁵ The geometries of other $B_{12}X_9^-$ anions (X = Br, Cl, F; H, Au, CN) are similar to that in Figure 1c and are given in Figure S3 of the SI. The energy needed to remove an X_3^- anion from the $B_{12}X_{12}^{2-}$ dianion is calculated as the energy difference, $\Delta E = E(B_{12}X_9^{-})$ $+ E(X_3^{-}) - E(B_{12}X_{12}^{-})$. The energy costs for removing I_3^{-} , Br_3^{-} , Cl_3^{-} , and F_3^{-} are 2.78, 4.03, 5.50, and 8.23 eV, respectively. Note that the energy cost increases as the size of the halogens atoms, X, decreases, and it costs the least energy to remove I_3^- . This is consistent with the electronegativity of the halogens atoms, which increase as size decreases.

To study the formation of $B_{24}X_{18}^{2-}$ as two $B_{12}X_9^{-}$ monomers are brought together, we first calculated the energy as a function of distance between the centers of two $B_{12}X_9^{-}$ (X = I, Br, Cl, F) moieties using the nudged elastic band method. At each distance, the geometries were fully optimized. The equilibrium geometry of $B_{24}I_{18}^{2-}$ is given in Figure 1c and is in agreement with previous calculation of Heine and coworkers.³⁵ The corresponding geometries for $B_{24}X_{18}^{2-}$ (X = Br, Cl, F) are given in Figure S4a of the SI, which are similar to that of $B_{24}I_{18}^{2-}$. The energies of $B_{24}X_{18}^{2-}$ measured with respect to two dissociated $B_{12}X_9^{-}$ species as a function of distance are plotted in Figure 2. We note that the energies increase very slowly as the two ions come together and at some critical distance sharply decrease to form bound dianions.



Figure 2. Energy as a function of distance between the boron cage centers of two $B_{12}X_9^-$ (X = F, Cl, Br, I; H, Au, CN) icosahedra.

The energy barrier for this recombination to occur, the binding energies of the $B_{24}X_{18}^{2-}$ dianions with respect to their two dissociated $B_{12}X_9^{-}$ units, the transition state distances between the boron cage centers of $B_{12}X_9^{-}$ monoanions, and their dipole moments are given in Table 1.

We note that the barrier for the formation of $B_{24}I_{18}^{2-}$ is the lowest among all of the halogenated species studied. Similarly,

Table 1. First and Second Electron Adiabatic Detachment Energies ($\Delta E^{1st} = E(B_{24}X_{18}) - E(B_{24}X_{18}^{-})$; $\Delta E^{2nd} = E(B_{24}X_{18}^{-}) - E(B_{24}X_{18}^{-2})$), the Transition State Distance, Barrier Height, Binding Energy against Dissociation into Two Monoanions of $B_{24}X_{18}^{-2}$, and Dipole Moment of $B_{12}X_{9}^{-2}$ (X = F, Cl, Br, I, H, CN, and Au)

	ADE (eV)					
B ₂₄ X ₁₈ ²⁻	$\Delta E^{ m first}$	$\Delta E^{ m second}$	transition state distance (Å)	barrier (eV)	binding energy (eV)	dipole (Debye)
F	5.77	2.49	8.90	1.17	2.95	130.7
Cl	5.53	2.88	9.45	0.66	5.07	143.6
Br	5.41	2.98	10.47	0.62	5.49	151.1
Ι	5.00	2.62	10.98	0.40	5.94	156.6
Н	4.92	2.37	7.54	1.29	1.98	113.5
CN	8.70	5.07	10.82	1.12	6.50	165.2
Au	3.87	1.77	11.12	0.47	5.75	153.0

the binding energy of $B_{24}I_{18}^{2-}$ with respect to two dissociated $B_{12}I_9^{-}$ species is the highest among the series, although all of these dianions are bound and hence stable. That the transition state distance between the centers of two $B_{12}X_9^{-}$ moieties is the largest for X = I is consistent with the size of the halogen atoms.

To see if the formation of $B_{24}X_{18}^{2-}$ species is possible with nonhalogen ligands, we carried out calculations for X = H, Au, and CN. Note that H and Au are both electronegative elements, although the electron affinity of H, namely, 0.75 eV, is much smaller than that of Au, namely, 2.31 eV. CN, on the other hand, is superhalogen with an electron affinity of 4.04 eV.^{36,37} We found all of the $B_{24}X_{18}^{2-}$ (X = H, Au, CN) moieties to be stable against dissociation into $B_{12}X_9^-$ (X = H, Au, and CN) monomers. In Table 1, we compare the energy barrier for this recombination to occur, the binding energies of the $B_{24}X_{18}^{2-}$ dianions with respect to their two dissociated $B_{12}X_{9}^{-}$ units, the transition state distances between the centers of $B_{12}X_9^-$ monoanions, and their dipole moments with those of the halogenated species. We note that among the nohalogentaed moieties, $B_{24}Au_{18}^{2-}$ is the only species whose energy barrier for formation, namely, 0.47 eV, is close to that encountered in $B_{24}I_{18}^{2-}$. Thus, we predict that one should be able to observe $B_{24}Au_{18}^{2-}$ in experiment. Details of the dimerization of $B_{24}X_{18}^{2-}$ (X = H, Au, CN) are given in section V of the SI.

The stability of the $B_{24}X_{18}^{2-}$ moieties can be explained by using a simple model based on electrostatics. Note that due to its aspherical structure, B12X9 has a dipole moment. The calculated dipole moments of ions, **p**, of $B_{12}X_9$ given in Table 1 are 156.6, 151.1, 143.6, 130.7, 113.5, 153.0, and 165.2 D for X = I, Br, Cl, F, H, Au, and CN, respectively. Thus, the interaction between two B₁₂X₉⁻ ions would have an attractive term due to dipole-dipole interaction and a repulsive term due to the interaction between two negative charges (monopoles) on each moiety. Because the spatial dependence of these two forces is different, it is possible that the dipole term may dominate over the monopole term at some critical distance. The attractive force provided by the dipole-dipole interaction will help reduce the energy barrier as the two $B_{12}X_9^-$ ions appraoch each other. The ensuing chemical bond that would form between the atoms of two $B_{12}X_9^-$ moieties may then lead to a thermodynamically stable $B_{24}X_{18}^{2-}$ moiety. It is difficult to derive a simple formula for the interaction energy for a realistic system due to the complex interplay among many factors such as charge polarization, charge redistribution, and attraction and repulsion of the charged particles with different shape and composition, We, therefore, demonstrate this effect by using a simple model where two B₁₂X₉⁻ moieties are replaced by two point-like objects with both electric monopole and diploe moments and by calculating the total energy as the sum of the above two attractive and repulsive energies. Details of the model are given in section VI of SI. Note that according to this model, the transition state distance should decrease from I to F, in keeping with the decreasing dipole moment. This in agreement with our first-principles results in Figure 2.

To confirm our results based upon DFT, we carried out additional calculations of the interaction energy as a function of distance between the two centers of $B_{12}X_9^-$ (X = I, Br, Cl, F, H) at the MP2 level. Because the geometries computed at the DFT level are not affected when a higher level of theory is used, we took the geometry at each distance obtained at the DFT level and calculated the single-point energy at the MP2 level. The results are plotted in Figure S9 of the SI. Our conclusions based on DFT remain unchanged, and the energy variation at

the MP2 level agrees with that obtained using DFT calculations (see Figure 2) and preivous experimental results as well.³⁵ However, the calculated energy barriers of forming $B_{24}X_{18}^{2-}$ for X = I, Br, Cl, F, and H are 0.12, 0.24, 0.26, 0.31, and 0.65 eV, respectively, and are smaller than that of the values calculated using DFT in Table 1.

To understand the electronic origin of the stability of $B_{24}X_{18}^{2-}$ (X = I, Br, Cl, F, H, Au, and CN) species in general and that of $B_{24}I_{18}^{2-}$ in particular, we examine its geometry in Figure 1c. The geometries of $B_{24}X_{18}^{2-}$ (X = Br, Cl, F, H, Au, and CN) species given in Figure S4a of the SI are similar to that in Figure 1c. Of the 18 iodine atoms in the two B_{12} icosahedra in Figure 1c, 16 remain radially bonded to the B atoms, while the remaining 2 I atoms form a bridge with B atoms belonging to each icosahedron. Four of the 24 B atoms do not have any bond with I and bind to each other. It is due to the formation of these chemical bonds that the total energy of $B_{24}I_{18}^{2-}$ moiety is lower than that of the two dissociated $B_{12}I_9^-$ clusters. This geometry is consistent with the Wade-Mingos rule that requires (n + 1) pairs of electrons. Note that of the 24 B atoms in $B_{24}I_{18}^{2-}$, 16 are radially bonded and 4 are bridge-bonded to ligands. These 20 BX pairs contribute $20 \times 2 = 40$ electrons to cage bonding. Thus, $\dot{B}_{24}I_{18}^{2-}$ has 42 electrons, which equals (*n* + 1) pairs with n = 20. We have carried out molecular dynamics simulations to further study the stability of $B_{24}I_{18}^{2-}$ species at elevated temperatues. We find $B_{24}I_{18}^{2-}$ to be stable at both 1000 and 1500 K. The results are given in Figure S8e,f of the SI. The frontier molecular orbitals are given in Figure S7a,b to illustrate the electronic structure of $B_{24}I_{18}^{2-}$. We have also calculated the Raman and infrared spectra of these species (see Figure S8a-d of the SI), which can be compared with future exeperiments to validate the accuracy of our computed structure.

In summary, we show that two $B_{12}X_9^-$ (X = I, Br, Cl, F; H, Au, CN) moieties carrying equal and like charges attract and form a bound state. This unusual behavior is attributed to the chemical bonding between B and X atoms as the two moieties come together due to attractive dipole-dipole interaction. The energy barrier to form this bound state depends on the ligands X, and for X = I, the barrier is so small that it can be overcome at 400 K, making their bonding appear spontaneous. As I is replaced by other halogens Br, Cl, and F, the energy barriers increase, but the $B_{24}X_{18}^{2-}$ moieties continue to form stable bound states. However, observation of $B_{24}X_{18}^{2-}$ moieties (X = Br, Cl, F) is hindered because of the increasingly large barrier. This is consistent with experiment where only the $B_{24}I_{18}^{2-}$ molety was observed, but not the $B_{24}Br_{18}^{2-}$ molety.¹² The above results are explained by a simple electrostatic model involving a competition between the attractive dipole-dipole and repulsive charge monopole-monopole interaction. For nonhalogen ligands such as H, Au, and CN, while all $B_{24}X_{18}^{2-}$ (X = H, Au, CN) moieties are stable, the energy barriers for this to form as two $B_{12}X_9^-$ monoanions are brought together are too high for X = H and CN. Our results suggest that only the formation of $B_{24}Au_{18}^{2-}$ is likely to be observed in an experiment. In conclusion, we have demonstrated the power of ligand engineering in synthesizing novel multiply charged species.

THEORETICAL METHODS

Atomic structure optimizations and electronic structure calculations are carried out using density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP).³⁸ The projector-augmented wave (PAW) method³⁹ and Perdew-Burke-Ernzerhof (PBE)⁴⁰ exchangecorrelation functional within generalized gradient approximation (GGA) are used. The $1s^{1}$, $2s^{2}2p^{1}$, $2s^{2}2p^{2}$, $2s^{2}2p^{3}$, $2s^{2}2p^{5}$, 3s²3p⁵, 4s²4p⁵, 5s²5p⁵, and 5d¹⁰6s¹ atomic orbitals are treated as valence states for H, B, C, N, F, Cl, Br, I, and Au, respectively. Plane waves with a kinetic energy cutoff of 500 eV are used to expand the valence electron wave functions. For all structural relaxations, the convergence criteria for total energy and Hellmann-Feynman force are set to be 10^{-4} eV and 10^{-2} eV $Å^{-1}$, respectively. A unit cell with a vacuum space of 20 Å in the x and y directions and 30 Å in the z direction is used in order to avoid virtual interactions. (We also used the unit cell with a vacuum space of 40 Å in three different directions to confirm the accuracy and convergence of our results.) The first Brillouin zone is sampled by the Γ point.⁴¹ To check the dynamical stability, we use density functional perturbation theory (DFPT) and the Phonopy code 42 to calculate the vibrational spectra. Ab initio molecular dynamics (AIMD) simulations are also performed to assess the thermal stability of the B₂₄I₁₈²⁻ dianion. The canonical (NVT) ensemble is adopted using the Nosé heat bath method.⁴³ By using the nudged elastic band method,⁴⁴ we calculate the energy as a function of distance between the centers of two $B_{12}X_9^-$ (X = I, Br, Cl, F, H, CN, Au) icosahedra as they are brought together. The dipole moment and vibrational frequency are calculated using Gaussian 09 $code^{45}$ with the LANL2DZ⁴⁶⁻⁴⁸ basis set for halogens X (X = F, Cl, Br, and I) and Au atoms and the 6-31+G* basis set⁴⁹ for H, B, C, and N atoms. We tested a number of density functionals, including BLYP, 50-52 B3LYP, 53 and PBE0.54 We found that the PBE0 functional better reproduces the electron affinity of $B_{12}H_{12}^{2-}$ (0.93 eV), which is quite close to the previous result of 0.96 eV.⁵

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b00981.

Dimerization of nonhalogenated $B_{12}X_9^-$, point-ion model of interacting monopole–dipole moments, electronic and vibrational properties, and MP2 level of theory results (PDF)

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