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Stable Tetra- and Penta-Anions in the Gas Phase

Hong Fang^[a] and Puru Jena^{*[a]}

Abstract: The quest for stable gas-phase anions in highly negative charge states has been a great challenge. While multiply charged anions are stabilized in solids and liquids by compensating cations and solvation cells, respectively, stable anions containing less than a hundred atoms in the gas phase and capable of carrying charge beyond -3 is unknown. Here, we report the discovery of thermodynamically stable tetra- and penta-anions, containing less than 50 and 80 atoms, respectively, in the gas phase. A universal model is developed that explains their stability in terms of the synergy between closed shell, high electron affinity and size and predicts new highly-charged anions by using the known charged clusters as building blocks. Synthesis of these species can open a new chapter in materials chemistry.

The enhanced stability of a closed shell atom lies in the quantum mechanical interactions between electrons. Electrons with the same spins tend to avoid each other, thereby reducing the Coulomb repulsion between them. Therefore, a closed-shell atom, i.e. an atom with every spin being paired, gains extra stability. The closed-shell model provides a good explanation for the reactivity of atoms that are only an electron away from the closed shell. For example, a halogen (Group 17) atom with a single hole tends to form a stable core by gaining one electron from another atom having a weakly bound unpaired electron, such as an alkali (Group 1). In fact, the mono-anionic state of a halogen is more stable than its neutral state, as shown by its positive electron affinity (EA) defined by

$$EA_n = E_{(n-1)} - E_{(n)}, \quad n = 1, 2, 3, \dots \quad (1)$$

which measures the energy cost of removing one electron from the ' n ' charge state. Although other groups of atoms, such as chalcogens and pnictogens tend to gain electrons to form stable ionic bonds with other atoms, they cannot form stable di-anions (chalcogen²⁻) or tri-anions (pnictogen³⁻) in the gas phase. In the periodic table, the highest number of unpaired electrons for a nonmetal element is three and element that can accept more than one electron to form a stable negative ion in the gas phase is unknown.

For extra stability of molecules or clusters, the closed-shell model can be realized by satisfying the electron counting rules, including the jellium rule [1], the octet rule [2], the eighteen electron rule [3], the aromatic rule [4], and the Wade-Mingos rule [5]. Stable anionic clusters in the gas phase [6-7] which often have larger EA (Eq.1) than those of the halogen atoms are known as superhalogens [8-11]. Many clusters as stable gas-phase di-anions have been theoretically predicted and experimentally realized [12-17]. Among them is $B_{12}(CN)_{12}^{2-}$ which is derived from *closo*-borane (e.g. $B_{12}H_{12}^{2-}$) by replacing H with CN. $B_{12}(CN)_{12}^{2-}$ was predicted to have colossal stability with an EA of 5.28 eV of its second electron [13]. *This prediction has just been validated by its synthesis and measured EA [15], making $B_{12}(CN)_{12}^{2-}$ the most stable di-anion known.* Stable gas-phase tri-anions [18-20], including $BeB_{11}(CN)_{12}^{3-}$, $BeB_{11}(BO)_{12}^{3-}$ and $BeB_{11}(SCN)_{12}^{3-}$, have also been predicted,

with the highest third-electron EA among the three being over 2.5 eV [20]. Apart from the closed-shell requirement, the ability of these clusters to stabilize at highly negative charge states also lies in their size and the high EA of the composite terminal groups (e.g. CN^- and SCN^-). It is worth mentioning that, although highly negatively charged ions have been produced by electrospray ionization [21-22], they are macromolecules containing thousands of atoms. The first small di-anion reported in mass spectroscopy studies is C_{60}^{2-} which is thermodynamically unstable, but is long-lived due to the Coulomb barrier [23]. C_{70}^{2-} , with as many as 70 atoms, only shows a tiny stability of 0.02 eV binding energy for its second electron [24]. Although a Coulomb potential model has been developed to explain the electron tunneling phenomenon observed in the long-lived dicarboxylate dianions due to the repulsive Coulomb barrier [25], a model that can directly connect the EA and the size of the multiply charged anions and has the predictive power to find new ones is still lacking. Here, we report the discovery of thermodynamically stable clusters containing less than 50 and 80 atoms in the ' -4 ' and ' -5 ' charge states, respectively, by exploiting their proximity to the closed shell and the size and high EA of their terminal groups. A universal model is established to understand as well as predict stable gas-phase multiply charged clusters.

The extra electrons in a stable multiply charged cluster must be situated in a set of bound states. For a simple finite spherical potential well, we need to solve the transcendental equation (Eq.S1 of Supporting Information, SI) for the bound-state energy levels. Given the values of the depth (V) and radius (r) of the potential well (Figure S1 of SI), there is a finite number of bound states for the equation. This number depends on a positive coefficient a (Eq.S2 in SI), where $v \geq a/r^2$. The larger the coefficient a , the greater are the number of bound states. A deeper or wider potential well can hold more bound states (see Figure S1a and b as well as the related discussion in SI).

Based on this, we construct a phenomenological model for all stable multiply-charged clusters,

$$V \geq a_n/r^2 + V_0, \quad (2)$$

where V is approximated by the energy cost to reduce the highest negative charge state to the neutral state, i.e. the sum of the EA_n for every added electron,

$$V = \sum EA_n, \quad (3)$$

with $-n$ the most stable charge state. $n = 1, 2, 3, \dots$ is the highest negative charge state that can be accommodated by a cluster with $0 < a_1 < a_2 < a_3 < \dots < a_n$. r , the radius of a cluster, is defined as half of its longest dimension. According to Eq.2, in order to achieve a higher negative charge state with a larger coefficient a_n , a cluster has to have a higher threshold of V . Given certain a_n , a cluster with larger size is more likely to reach a higher negative charge state, since Eq.2 becomes easier to fulfill. When the size of a cluster tends to infinity, the depth of the potential tends to a constant value V_0 .

For atoms in the periodic table, the trend of EA vs. ionic radius is that an elementary anion with larger ionic radius has a smaller EA. Therefore, we use the halogen anions to benchmark the threshold value of

$$V = a_1/r^2 + V_0 \quad (4)$$

for all the stable gas-phase mono-anions. Indeed, as shown by Figure S2 of SI, there is a nice linear relation between the EA of halide and the inverse square of their ionic radii. We intentionally left out the data point corresponding to F^- as shown in Figure 1 by the open circle. Due to its very small radius, F^- , with exceptionally large Coulomb repulsion and small EA, is often

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viewed as an irregularity in the group. The value of the constant $V_0 = 1.88$ eV is obtained by extrapolating the relation of Eq.4 to $1/r^2 = 0$ ($r \rightarrow \infty$), as shown by Figure 1 (black line).

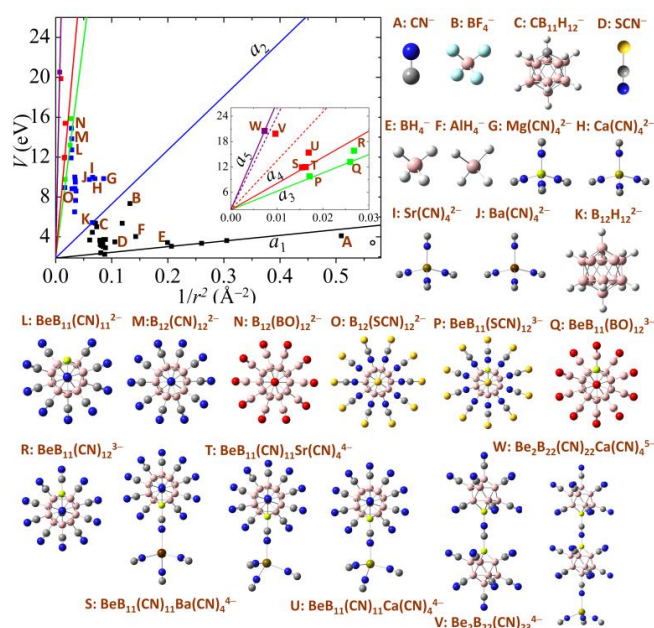


Figure 1. Calculated V vs. $1/r^2$ for the stable gas-phase mono- (black), di- (blue), tri- (green), tetra- (red) and penta- (purple) anions. The universal model in Eq.2 provides a good description for these data, with a threshold line (solid) for each category. For the mono-anion, F^- , in the open circle, is a special case with exceptionally small EA. The trend for the data points with increased negative charge state is to move to the upper-left corner of the plot. The inset shows the data points for the tri-, tetra- and penta-anions more clearly. The dashed threshold lines are estimated for the tetra- and penta-anions using the extrapolated values of a_4 and a_5 and the maximal V of tri- and tetra-anions, respectively. These lines agree well with the real solid threshold lines. Boron is in pink, beryllium in light yellow, carbon in grey, nitrogen in blue, calcium in dark yellow, strontium in green yellow, barium in brown, sulfur in yellow and oxygen in red. In some cases, the clusters with the boron cage are shown by looking down one of its five-fold axis along the radially stretched -CN branch. In other cases, the boron cages are shown by the cage configuration. The data points A to W are calculated using density functional theory. For clarity, an enlarged version of the figure (Figure S5) is also provided in the Supporting Information.

The data of V vs. $1/r^2$ for the known stable gas-phase mono-, di- and tri- anions, as given in Table I as well as Table S1, S2, and S3 of SI, agree well with the model in Eq.2. As shown in Figure 1, all the data points of each charge state are close to or above the corresponding threshold line defined by $V(1/r^2)$. The threshold line (in blue) for the stable di-anions are determined by $B_{12}H_{12}^{2-}$ which has the smallest value of V in the group and a moderate size. The threshold line (in green) for the stable tri-anions is determined by $BeB_{11}(BO)_{12}^{3-}$. The slope, a_n ($n = 1, 2, 3, \dots$), of a threshold line becomes progressively large with more negative charge state ($-n$) of the clusters, i.e. $a_1 = 5.67$ ($eV \cdot \text{\AA}^2$), $a_2 = 54.12$ ($eV \cdot \text{\AA}^2$) and $a_3 = 435.60$ ($eV \cdot \text{\AA}^2$) for mono-, di- and tri-anions, respectively. The coefficient a_n is actually a function of the number n of the allowed bound states. A simple quadratic function, $a_n = 166.52n^2 - 451.12n + 290.27$, can provide a good fit to the data of a_n (see SI). Using this equation, the values of a_4 and a_5 for stable tetra- and penta-anions are estimated to be 1155.41 ($eV \cdot \text{\AA}^2$) and 2198.89 ($eV \cdot \text{\AA}^2$), respectively. A general trend shown in Figure 1 is that the data points of more negative charge states move to the upper left corner in the V vs. $1/r^2$ plane, since a more negative charge state requires the cluster to have larger V (deeper well) and r (larger size) in order to hold more bound electrons. The increase in the maximal and averaged values of V for each charge state becomes less as the charge state becomes more negative, as shown by Figure S3 of

SI. This suggests that we can extrapolate the size (r) needed for a cluster to hold $-n$ charge state using the maximal V found for the $-(n-1)$ charge state and the estimated value of a_n . As shown in Figure 2a, the extrapolated radius of a stable tetra-anion based on the maximal V (15.85 eV) of the tri-anions is 9.09 Å. Other than looking for such size, we can combine two stable di-anions, or one stable tri-anion with one mono-anion to find a stable tetra-anion. This is actually in the spirit of the closed-shell model, where all spins should be paired to increase the stability. For example, we find $BeB_{11}(CN)_{11}^{2-}$ to be a stable gas-phase di-anion by substituting one "-B-CN" vertex in $B_{12}(CN)_{12}^{2-}$ with Be (which is closed shell in the 2s orbital). The overall closed shell of the cluster still holds, since the Wade-Mingos rule of having $2n+2$ pairs of valence electrons for a $(n+1)$ -vertex polyhedron with one vertex missing is still satisfied. n is equal to 11 for $BeB_{11}(CN)_{11}^{2-}$. There should be $2 \times 11 + 2 = 24$ pairs or 48 electrons available for bonding. Indeed, the number of valence electrons for the di-anion is $11 \times 3(B) + 1 \times 2(Be) + 11 \times 1(CN^-) + 2 = 48$. It is noted that incorporating a beryllium into a borane cage has been experimentally realized [26-27]. Such approach, using the closed-shell model as the guide line can lead us to the discovery of stable tri-anions, $BeB_{11}(CN)_{12}^{3-}$, $BeB_{11}(BO)_{12}^{3-}$ and $BeB_{11}(SCN)_{12}^{3-}$, when the stable mono-anion CN^- , BO^- or SCN^- is attached to the di-anion $BeB_{11}(CN)_{11}^{2-}$ on the Be site (see Figure 1 for these clusters).

Table 1. Calculated parameters for the key di-, tri-, tetra- and penta-anions. EA_n is the EA value as defined in Eq.1 at the negative charge state n . Units for the r , EA_n and V are Å, eV and eV, respectively. $BeB(CN)_M^{n+}$ stands for tetra-anions $BeB_{11}(CN)_{11}M(CN)_4^{n+}$ ($M = Ca, Sr, Ba$). $BeB(CN)^M^{n+}$ stands for $Be_2B_{22}(CN)_{23}^{n+}$. $BeB(CN)Ca^{n+}$ stands for penta-anion $Be_2B_{22}(CN)_{22}Ca(CN)_4^{n+}$. The value in the parenthesis corresponds to the multiplicity for each charge state. The multiplicities for the neutral states of $BeB_{11}(CN)_{11}M(CN)_4^{n+}$ are 3. For the neutral states of $Be_2B_{22}(CN)_{23}^{n+}$ and $Be_2B_{22}(CN)_{22}Ca(CN)_4^{n+}$, the multiplicities are 4 and 3, respectively.

Cluster	r	EA_1	EA_2	EA_3	EA_4	EA_5	V
$BeB_{11}(CN)_{11}^{2-}$	5.890	8.10 (2)	4.62 (1)				12.72
$BeB_{11}(CN)_{12}^{3-}$	6.111	8.44 (1)	4.76 (2)	2.65 (1)			15.85
$BeB(CN)Ca^{4+}$	7.035	7.63 (4)	5.20 (3)	1.77 (2)	0.79 (1)		15.39
$BeB(CN)Sr^{4+}$	7.184	4.21 (4)	5.16 (3)	2.41 (2)	0.20 (1)		11.98
$BeB(CN)Ba^{4+}$	7.387	4.07 (4)	5.15 (3)	2.44 (2)	0.25 (1)		11.91
$BeB(CN)^{4+}$	10.148	8.86 (3)	5.98 (4)	3.54 (3)	1.48 (2)		19.86
$BeB(CN)Ca^{5-}$	11.662	8.37 (4)	5.98 (3)	4.25 (4)	1.88 (3)	0.03 (2) 0.18 (2)	20.51

^aVertical detachment energy.

For a tetra-anion, we should find a stable di-anion that can be attached to the Be site of the stable $BeB_{11}(CN)_{11}^{2-}$. Since $BeB_{11}(CN)_{11}^{2-}$ has a radius of 5.89 Å (Table 1), the targeted di-anion should have a radius of at least 3.20 Å, according to the required radius 9.09 Å ($3.20 = 9.09 - 5.89$) estimated earlier for a tetra-anion. We find a series of stable gas-phase di-anions, $M(CN)_4^{2-}$ ($M = Mg, Ca, Sr, Ba$) [6] (Figure 1) that can satisfy the above conditions (see their radii in Table S3 of SI). The ground states of these di-anions are characterized by tetrahedrally coordinated -CN stretching radially with the carbon sites outside. This can lead to a proper attachment to the Be site of $BeB_{11}(CN)_{11}^{2-}$, since the ground state is formed when C is attached to Be, as seen in the tri-anion $BeB_{11}(CN)_{12}^{3-}$ (Figure 1) [20]. Indeed, $BeB_{11}(CN)_{11}M(CN)_4^{n+}$ ($M = Ca, Sr, Ba$) are found to be stable gas-phase tetra-anions, as shown in Figure 2b, with EA of the fourth electron being 0.79, 0.20 and 0.25 eV, respectively. By using the stable tri-anion $BeB_{11}(CN)_{12}^{3-}$, whose radius is 6.11 Å (Table 1), to attach to $BeB_{11}(CN)_{11}^{2-}$, we find another stable gas-phase tetra-anion $Be_2B_{22}(CN)_{23}^{4-}$, as shown

in Figure 2b. The fourth-electron EA of this tetra-anion is as large as 1.48 eV! It is interesting to note that the cluster's supposedly stable '-5' charge state (a direct sum of the charge states between $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ and $\text{BeB}_{11}(\text{CN})_{11}^{2-}$) has a higher energy than the '-4' charge state and the tetra-anion $\text{Be}_2\text{B}_{22}(\text{CN})_{23}^{4-}$, therefore, has a magnetic momentum of $1 \mu_B$. The optimized size, EAs, multiplicities, and the value of V (Eq.3) for the tetra-anions are summarized in Table 1. The threshold line with a modified $a_4 = 619.82 \text{ (eV}\cdot\text{\AA}^2)$ for the tetra-anions, as shown in the inset of Figure 1, is determined by $\text{BeB}_{11}(\text{CN})_{11}\text{Sr}(\text{CN})_4^{4-}$ which has the lowest V value of the series. We can further extrapolate the radius for a stable penta-anion using the maximal V (19.86 eV) of the tetra-anions and the previously estimated value of a_5 . As shown by Figure 2c, the extrapolated radius is 11.04 Å. This suggests that, to make a stable penta-anion, we can either combine $\text{Be}_2\text{B}_{22}(\text{CN})_{23}^{4-}$ ($r = 10.11 \text{ \AA}$) with $\text{Ca}(\text{CN})_4^{2-}$ ($r = 3.77 \text{ \AA}$), or $\text{BeB}_{11}(\text{CN})_{11}\text{Ca}(\text{CN})_4^{4-}$ ($r = 7.03 \text{ \AA}$) with $\text{BeB}_{11}(\text{CN})_{11}^{2-}$ (5.89 Å) or $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ (6.11 Å). From these combinations, a stable gas-phase penta-anion $\text{Be}_2\text{B}_{22}(\text{CN})_{23}\text{Ca}(\text{CN})_4^{5-}$ is found, as shown in Figure 2b. The penta-anion has a fifth-electron EA of 30 meV and a vertical detachment energy of 180 meV. The optimized size, EAs, multiplicities and the value of V are summarized in Table 1.

Similar to the case of $\text{Be}_2\text{B}_{22}(\text{CN})_{23}^{4-}$, $\text{Be}_2\text{B}_{22}(\text{CN})_{23}\text{Ca}(\text{CN})_4^{5-}$ has a lower energy than its '-6' charge state and, therefore, has a magnetic momentum of $1 \mu_B$. Note that, as shown in Figure 2b, to form the ground state of $\text{Be}_2\text{B}_{22}(\text{CN})_{23}\text{Ca}(\text{CN})_4^{5-}$, an isomer of $\text{BeB}_{11}(\text{CN})_{11}\text{Ca}(\text{CN})_4^{4-}$ with $\text{Ca}(\text{CN})_4^{2-}$ attached to the B site instead of the Be site must be used. The energy of the isomer is 0.25 eV higher than that of the ground state, as shown in Figure S6a of SI. If the ground state of $\text{BeB}_{11}(\text{CN})_{11}\text{Ca}(\text{CN})_4^{4-}$ is combined with $\text{BeB}_{11}(\text{CN})_{12}^{3-}$, the resulting isomer of $\text{Be}_2\text{B}_{22}(\text{CN})_{23}\text{Ca}(\text{CN})_4^{5-}$ is 0.25 eV higher in energy than that of its ground state, as shown in Figure S6b of SI. There is also a subtle difference between the combinations of $\text{BeB}_{11}(\text{CN})_{11}\text{Ca}(\text{CN})_4^{4-} + \text{BeB}_{11}(\text{CN})_{11}^{2-}$ and $\text{BeB}_{11}(\text{CN})_{11}\text{Ca}(\text{CN})_4^{4-} + \text{BeB}_{11}(\text{CN})_{12}^{3-}$ to form a penta-anion. As shown in Figure S6b of SI, the former combination results in an isomer having a reversed -C-N- sequence between the two cages. This isomer has a slightly higher energy, +24 meV, than that of the ground state. Another observation is that, to form $\text{Be}_2\text{B}_{22}(\text{CN})_{23}\text{Ca}(\text{CN})_4^{5-}$, certain CN^- terminal group in a stable tri- or tetra-anion needs to be knocked off, as shown in Figure 2b. This is achievable in practice, as was nicely demonstrated by the most recent experiments [15, 28], where a CN^- terminal group was removed from $\text{B}_{12}(\text{CN})_{12}^{2-}$ or stepwisely added in $\text{B}_{12}\text{H}_{12}^{2-}$. When the terminal group is removed, the cluster becomes more reactive on the exposed boron, making it readily bind to other moieties.

We use the di-anion $\text{B}_6\text{H}_6^{2-}$ as a model system to understand the bonding of the newly-found tetra- and penta-anions. This di-anion is stabilized according to the Wade-Mingos rule which states that a n -vertex *closo*-polyhedron should have $2n+1$ pairs of bonding electrons. There are indeed $6 \times 3(\text{B}) + 6 \times 1(\text{H}) + 2 = 26$, i.e. 13 pairs of, electrons in this *closo*-borane. They form either $\text{H}(s)$ and $\text{B}(p)$ hybridized orbitals called 'radial orbitals' which are lopsided, or un-hybridized $\text{B}(p)$ orbitals called 'tangential orbitals', as shown in Figure S7. Seven pairs of valence electrons are involved in the cage bonding. Among them, one pair resides on a molecular orbital (MO) formed by six radial orbitals pointing their heavy ends to the center of the cage, while six other pairs reside on MOs formed by tangential orbitals. The remaining six pairs of valence electrons are involved in the radial bonding between boron and the terminal groups (hydrogen).

As shown in Figure S7, the calculated MOs for the tetra- and penta-anions can be also characterized by the radial and tangential orbitals. Similar to the case of $\text{B}_6\text{H}_6^{2-}$, in each case, the MO at the center of cage formed by the radial orbitals have the lowest energy. Tangential orbitals form the bonding around

the cage skeleton with higher energy. Up next in energy are MOs formed by radial bonding between the boron at vertices and the terminal groups. The highest occupied MOs (HOMO) of $\text{BeB}_{11}(\text{CN})_{11}\text{Ca}(\text{CN})_4^{4-}$ and $\text{Be}_2\text{B}_{22}(\text{CN})_{23}\text{Ca}(\text{CN})_4^{5-}$ are on the $\text{Ca}(\text{CN})_4^{2-}$ group, formed by the radial bonding between Ca and CN^- . On the other hand, the HOMO of $\text{Be}_2\text{B}_{22}(\text{CN})_{23}^{4-}$ is formed by both the tangential orbitals on the cage skeleton and the radial bonding between boron and CN^- groups. It is much more spatially spread than the HOMO of $\text{BeB}_{11}(\text{CN})_{11}\text{Ca}(\text{CN})_4^{4-}$ and $\text{Be}_2\text{B}_{22}(\text{CN})_{23}\text{Ca}(\text{CN})_4^{5-}$ and, therefore, entails the high EA of $\text{Be}_2\text{B}_{22}(\text{CN})_{23}^{4-}$. The closed shell $\text{BeB}_{11}(\text{CN})_{11}\text{Ca}(\text{CN})_4^{4-}$ entails a much larger HOMO-LUMO (the lowest unoccupied MO) gap of 4.56 eV than those of $\text{Be}_2\text{B}_{22}(\text{CN})_{23}^{4-}$ and $\text{Be}_2\text{B}_{22}(\text{CN})_{23}\text{Ca}(\text{CN})_4^{5-}$, which are 0.50 and 0.26 eV, respectively.

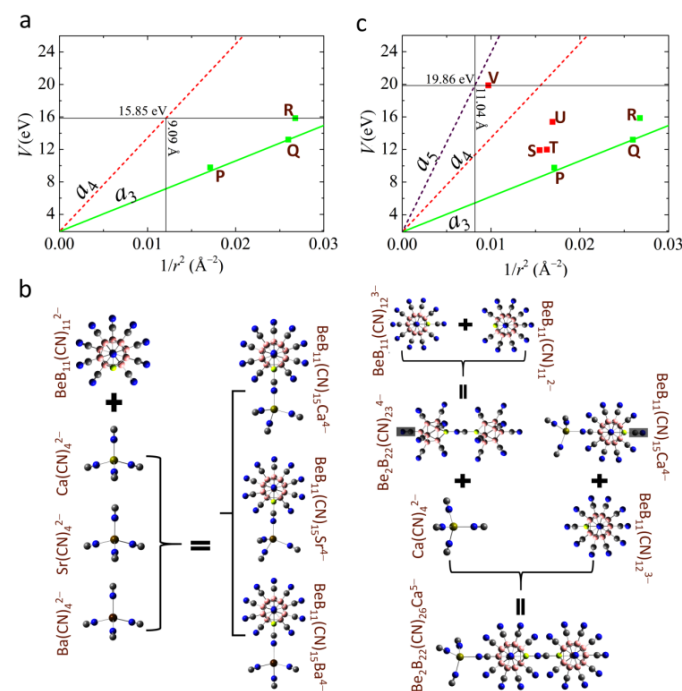


Figure 2. (a) Evaluation of the size ($r = 9.09 \text{ \AA}$) needed for a stable tetra-anion using the estimated a_4 and the maximal V (15.85 eV) of the known tri-anions (in green). The red dashed-line is the estimated threshold line for tetra-anions. The green solid line is the threshold line for tri-anions. (b) Demonstration of using the known multiply-charged clusters with proper sizes to form new clusters with higher negative charge states. To form the penta-anion, certain CN^- terminal group, as indicated under shades, needs to be knocked off. (c) Evaluation of the size ($r = 11.04 \text{ \AA}$) needed for a stable penta-anion using the estimated a_5 and the maximal V (19.86 eV) of the newly-found tetra-anions (in red). The purple dashed-line is the estimated threshold line for penta-anions. Boron is in pink, beryllium in light yellow, carbon in gray, nitrogen in blue, calcium in dark yellow, strontium in green yellow and barium in brown.

In summary, the requirement from the closed-shell model serves as a powerful guide for the discovery of the stable gas-phase tetra- and penta-anions, since the ground states with '-4' and '-5' charges do have the lowest multiplicities among all the charge states, as shown in Table 1. The multiply charged cluster can be treated as a general case of bound states in a finite 3D potential well. High EA of the terminal group (related to the depth of the potential well) and the size of the cluster (related to the width of the potential well) also play key roles to stabilize a highly negative charge state. Therefore, a viable route to find new stable multiply charged clusters, beyond the '-3' charge state, relies on using the known charged cluster as building blocks and forging a synergy between the closed-shell model, high EA, and proper size. Experimental synthesis of these predicted tetra- and penta-anions could lead to new class of weakly coordinating anions and energy materials.

Experimental Section

Method please refer to supporting information.

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Keywords: superatomic cluster • charged clusters • tetra-anions • penta-anions • universal model

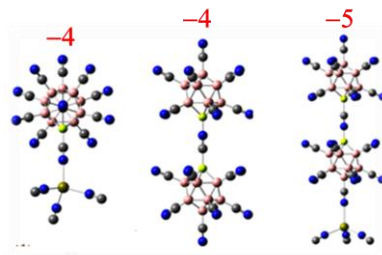
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Entry for the Table of Contents

Layout 1:

COMMUNICATION

Tetra- and penta-anions containing less than a hundred atoms with -4 and -5 charge states that are stable in the gas phase are proposed. A universal model is established to explain their large stability and predict new ones.

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