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Colossal Stability of Gas Phase Tri-anions: The Concept of Super-pnictogens

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Abstract: Multiply charged negative ions are ubiquitous in nature. In crystals, they are stable due to charge compensating cations while in solutions, solvent molecules protect them; but they are rarely stable in the gas phase due to strong electrostatic repulsion between the extra electrons. Understanding their stability without the influence of the environment, therefore, has been of great interest to scientists for decades. While much of the past work has focused on the di-anions, work on triply charged negative ions is sparse and the search for the smallest stable tri-anion against spontaneous electron emission or fragmentation continues. We show here that $\text{BeB}_{11}(\text{X})_{12}^{3-}$ ($\text{X}=\text{CN}, \text{SCN}, \text{BO}$) tri-anions are all stable in the gas phase, with $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ exhibiting colossal stability against electron emission by 2.65 eV and against its neutral by 15.85 eV! The unusual stability of these tri-anions opens the door to a new class of super-pnictogens with potential applications in Al-ion batteries.

The study of multiply charged negative ions has a long history due to their importance in chemistry^[1] as the building blocks of ionic compounds. In crystals, multiply charged anions are stabilized by charge compensating cations while in solutions they are protected by the solvent molecules.^[2] However, their stability in the gas phase poses great challenge. Due to the electrostatic repulsion between the extra electrons, the molecules either fragment or auto-eject the added electron(s). Because the repulsion is greater as the size gets smaller, multiply charged anions in the gas phase are possible mostly for large biomolecules. However, small multiply charged anions^[3] can exist in metastable state due to the repulsive Coulomb barrier (RCB)^[4] that results from the short-range attraction between electrons and the positive charge on the nuclei and long-range repulsion between the electrons.^[5] Most of the studies of multiply charged anions in the gas phase has concentrated on di-anions^[6] and the experimental observation of C_{60}^{2-} and higher fullerenes is one of the early examples of a metastable di-anion in the gas phase.

There have been very few studies of the stability of tri-anions in the gas phase. Compton and coworkers have reported the mass spectra of $(\text{C}_{60})_2(\text{CN})_5^{3-}$ and $(\text{C}_{60})_2(\text{CN})_7^{3-}$.^[5] However, the observation of a species in mass spectrometry does not always guarantee its thermodynamic stability. It only suggests that such species may exist within the experimental conditions. Indeed, $(\text{C}_{60})_2(\text{CN})_5^{3-}$ is *metastable* against auto-detachment of an electron

and the search for tri-anions in the gas phase continues. In this paper, we show that CN ligands indeed can be used to stabilize a tri-anion. The system we have studied is $\text{BeB}_{11}(\text{CN})_{12}^{3-}$. It is stable against electron emission by 2.65 eV!

In the past, stability of a multiply charged anion was often interpreted within the context of the octet rule. For example, K_2SO_4 salt is composed of K^+ cations and SO_4^{2-} anions, within which a constituent atoms possess full octets of valence electrons. Cederbaum and coworkers^[7] have examined the stability of a number of tri-anions within this context and found that the best candidate, $\text{B}(\text{C}_2\text{CO}_2)_3^{3-}$ is thermodynamically unstable by -0.4 eV against electron emission. Gutsev *et al.*^[8] also predicted a large $(\text{GaAs})_n$ ($n > 48$) trianion cluster that can be stable against its di-anion state by 0.16 eV.

We followed a different strategy to design a multiply charged anion. Instead of using only the octet rule, we use multiple electron counting rules, namely the octet and Wade-Mingos rule simultaneously.^[9] The latter rule was developed to explain the stability of *closo*-borane, $\text{B}_{12}\text{H}_{12}^{2-}$ which is stable by 0.9 eV against ejection of the second electron.^[10] According to the Wade-Mingos rule, $(n+1)$ pairs of electrons are required to stabilize a borane cage where n is the number of vertices in the boron polyhedron. $\text{B}_{12}\text{H}_{12}^{2-}$ has an icosahedral symmetry where $n=12$. Of the 48 electron available for bonding, 24 electrons occupy 12 B-H covalent bonds leaving the remaining 24 electrons for cage bonding. However according to the Wade-Mingos rule $26 [= (12+1) \times 2]$ electrons are needed for the stability of $\text{B}_{12}\text{H}_{12}^{2-}$. Indeed, $\text{B}_{12}\text{H}_{12}^{2-}$ is thermodynamically stable as a di-anion.

The di-anion stability of $\text{B}_{12}\text{H}_{12}^{2-}$ can be enhanced when the ligand H atoms are replaced by a more electronegative CN moiety. Recently, Zhao *et al.*^[11] showed that $\text{B}_{12}(\text{CN})_{12}^{2-}$ is more stable than its mono-anion and it takes 5.3 eV to eject the second electron! To date $\text{B}_{12}(\text{CN})_{12}^{2-}$ is the most stable di-anion known. The author noted that this unusual stability is due to fulfilling simultaneously the Wade-Mingos rule of the boron polyhedron and the octet rule of the CN moiety. In fact, the electron affinity (EA) of CN is 3.86 eV which makes it a super-halogen.^[12] On the other hand, $\text{B}_{12}(\text{CN})_{12}$ is not stable against electron emission.

Here we show that a similar strategy can lead to an unusual stable tri-anion in the gas phase. We begin with $\text{BeB}_{11}(\text{CN})_{12}$. Note that this molecule would require three electrons to satisfy both the Wade-Mingos rule of the modified boron-cage and the octet rule of CN. Thus, $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ could be a stable molecule. Indeed, our calculations confirm this hypothesis; $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ is *stable* against auto-ejection of the third electron by 2.65 eV. To the best of our knowledge, no other cluster exists whose gas-phase stability as a tri-anion is larger than that of $\text{BeB}_{11}(\text{CN})_{12}^{3-}$. By replacing CN with SCN or BO, we also find that $\text{BeB}_{11}(\text{SCN})_{12}^{3-}$ and $\text{BeB}_{11}(\text{BO})_{12}^{3-}$ are thermodynamically stable against spontaneous electron emission by 0.59 and 1.30 eV, respectively.

The implication of the extraordinary stability of the above tri-anions is that one can regard this class of clusters as super-pnictogens, analogous to super-halogens^[12] discovered more than 30 years ago. A super-halogen is a cluster composed of

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heteroatomic species that not only mimic the chemistry of halogens but also their electron affinities exceed those of halogen atoms. In a similar vein, $\text{BeB}_{11}(\text{X})_{12}^{3-}$ ($\text{X}=\text{CN}$, SCN , and BO) not only mimic the chemistry of group 15 elements, but they are stable as tri-anions. We show that these clusters can be used to design electrolytes for Al ion batteries as well as for engaging noble gas atoms such as Xe in chemical reaction.

Our first task was to obtain the equilibrium geometries and corresponding total energies of $\text{BeB}_{11}(\text{CN})_{12}^{j-}$ ($j=0, 1, 2, 3$) for which we used both density functional theory (DFT) with hybrid B3LYP form for exchange correlation potential and the MP2 level of theory embedded in the Gaussian09 suite of programs (see the Methods section). We first optimized the geometries without any symmetry constraint at the DFT/B3LYP level of theory and then calculated the total energies using the MP2 method. We allowed CN to bind to Boron cage either with its C or N atom. The $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ structure with C bound to B atoms is found to be 5.48 eV more stable than that when N binds to B, as shown in Figure S1 of the Supporting Information (SI). In Figure 1a we show the optimized geometry corresponding to the lowest energy isomer of $\text{BeB}_{11}(\text{CN})_{12}^{3-}$. It has C_{5v} point group symmetry. The average Be-B, B-B, Be-C, B-C, and C-N bond lengths are 1.96, 1.80, 1.96, 1.45, and 1.17 Å, respectively. The energy gains in adding successive electrons are calculated in terms of the first electron affinity (FEA), second electron affinity (SEA), and third electron affinity (TEA) of $\text{BeB}_{11}(\text{CN})_{12}$ defined as,

$$\Delta E_{\text{FEA}} = E(\text{Neutral}) - E(\text{Anion}) \quad (1)$$

$$\Delta E_{\text{SEA}} = E(\text{Anion}) - E(\text{Dianion}) \quad (2)$$

$$\Delta E_{\text{TEA}} = E(\text{Dianion}) - E(\text{Trianion}) \quad (3)$$

Here E is the total energy corresponding to the ground state structure. The FEA, SEA, and TEA for $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ are, 8.44 eV, 4.76 eV, and 2.65 eV, respectively. Note that $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ is strongly stable against its di-anion, while the previously studied trianion $\text{B}(\text{C}_3\text{O}_2)_3^{3-}$ was thermodynamically unstable by -0.40 eV.^[7]

To validate our numerical method, we computed the structure and energetics of $\text{B}(\text{C}_3\text{O}_2)_3^{3-}$ using the same level of theory as used for the study of $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ (details are given in SI text 1). Our optimized geometry of $\text{B}(\text{C}_3\text{O}_2)_3^{3-}$ agrees very well with that computed by Feuerbacher and Cederbaum.^[7] Our computed adiabatic detachment energy (TEA in Eq. 3) at the MP2 Level is -0.84 eV. The corresponding value obtained by Feuerbacher and Cederbaum is -0.40 eV.^[7] Note that these authors used CCSD level of theory. This level of theory is computationally demanding and it was not possible for us to use it for a large cluster such as $\text{BeB}_{11}(\text{CN})_{12}^{3-}$. Nevertheless, what we can conclude from this comparison is that the MP2 level of theory may underestimate the stability of the tri-anion. In other words, the TEA of $\text{BeB}_{11}(\text{CN})_{12}^{3-}$, 2.65 eV, may be an underestimate.

This extraordinary stability of $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ results from three factors: First, as pointed out before, in contrast to previously studied tri-anions, $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ satisfies the Wade-Mingos and octet rule, simultaneously. Second, CN, with an EA of 3.86 eV acts as a super-halogen, and is more electronegative than either H or any other halogen atom. Recall that the metastability of $\text{Fe}(\text{CN})_6^{3-}$ (H_2O)₁₀,^[13] $(\text{C}_{60})_2(\text{CN})_5^{3-}$ and $(\text{C}_{60})_2(\text{CN})_7^{3-}$ observed experimentally could be due to the use of this more electronegative CN.^[5] Third, the size of $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ is larger than that of $\text{B}(\text{C}_3\text{O}_2)_3^{3-}$, thus permitting the added electrons to spread over a larger space. This reduces electrostatic repulsion.

We also computed the vertical detachment energy (VDE) which measures the energy difference between the ground state of the trianion and that of its dianion at the trianion geometry. This is defined as,

$$\Delta E_{\text{TEA}} = E(\text{Dianion}) - E(\text{Trianion}) \quad (4)$$

Comparison of results obtained from Eqs. (3) and (4) is a measure of the energy gained as the tri-anion relaxes when the electron is detached. We see from Table 1 that one gains about 0.4 eV in this process.

Table 1. Table Caption. The first, second, and third electron affinity (FEA), (SEA), (TEA) and vertical detachment energy (VDE) of $\text{BeB}_{11}(\text{CN})_{12}$, $\text{BeB}_{11}(\text{BO})_{12}$, and $\text{BeB}_{11}(\text{SCN})_{12}$.

| | $\$ E_{\text{FEA}}$ (eV) | $\$ E_{\text{SEA}}$ (eV) | $\$ E_{\text{TEA}}$ (eV) | $\$ E_{\text{VDE}}$ (eV) |
|------------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| $\text{BeB}_{11}(\text{CN})_{12}$ | 8.44 | 4.76 | 2.65 | 3.07 |
| $\text{BeB}_{11}(\text{BO})_{12}$ | 7.42 | 4.48 | 1.30 | 2.52 |
| $\text{BeB}_{11}(\text{SCN})_{12}$ | 5.28 | 3.19 | 0.59 | 0.97 |

To further confirm the thermal stability of $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ we performed *ab initio* molecular dynamics (AIMD) simulation t employing Nosé-Hoover heat bath^[14] at 800 K for 10 ps at 1 interval. For this calculation, we used DFT with PBE exchange correlation functional to reduce computational cost. Only small structural distortions are found during the simulation, but the bonding, over-all shape, and stability remain unaffected, as given in Figure 1b. In addition, we have calculated the Raman and IR simulated spectra of $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ for comparison with future experiments. With regard to the Raman spectroscopy, we found that the vibrational frequencies are mainly distributed in the 111 and 2300 cm^{-1} region while the infrared (IR) peaks were found at 100, 375, 680, 900, 1119 and 2300 cm^{-1} .

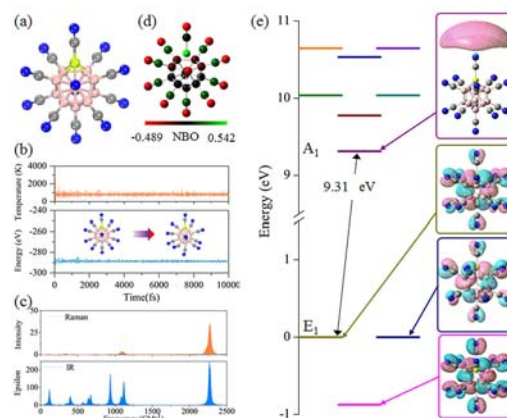


Figure 1. a) Geometry, b) AIMD simulation as a function of temperature at total energy fluctuation, c) Raman and IR simulation spectra, d) NBO charge distribution, e) energy diagram and frontier orbitals of $\text{BeB}_{11}(\text{CN})_{12}^{3-}$.

The electronic structure is analyzed by carrying out the natural bond orbital (NBO) analysis. For the $\text{BeB}_{11}(\text{CN})_{12}^{2-}$ di-anion, the α (β) spin electron configurations of Be, B, C, and N are $2s^{0.15}2p^{0.53}$, $2s^{0.28}2p^{1.26}$, $2s^{0.46}2p^{1.33}$, and $2s^{0.79}2p^{1.98}$ ($2s^{0.14}2p^{0.46}$, $2s^{0.28}2p^{1.20}$, $2s^{0.48}2p^{1.55}$, and $2s^{0.78}2p^{1.73}$), respectively. When the third electron is attached, the electron configurations of Be, B, C, and N in $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ tri-anion are $2s^{0.28}2p^{1.17}$, $2s^{0.55}2p^{2.51}$, $2s^{0.96}2p^{2.86}$, and $2s^{1.58}2p^{3.82}$, respectively. These data suggest that each B and CN

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pair gain 0.06 and 0.09 electrons on average. The NBO charge distribution of $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ is given in Figure 1d.

An analysis of the frontier molecular orbitals of $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ provides further information on its electronic structure. Due to the C_{5v} point group symmetry, we found that the highest occupied molecular orbital (HOMO) and HOMO-1 are degenerate and are delocalized as E_1 . Besides, the charge densities in HOMO, HOMO-1, and HOMO-2 are distributed on the boron cage and have π character (Wade–Mingos rule). The π character of CN is composed of C-2p and N-2p orbitals (octet rule) (see Figure 1e). The umbrella shaped lowest unoccupied molecular orbital (LUMO) is completely localized around CN which links with Be atom. The 9.31 eV HOMO-LUMO gap of $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ further confirms its unusual stability in the gas phase.

We have examined the potential of such a stable tri-anion for technological application and for promoting unusual chemistry. For the former, we have examined the role of $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ as a building block of electrolytes in Al-ion battery and for the latter, we have studied its role in enabling noble gas atoms to form chemical bonds.

Motivated by the recent prediction and subsequent experimental confirmation^[15] that $\text{CB}_{11}\text{H}_{12}$ can serve as the negative ion component of Li, Na, and Mg ion batteries,^[15] we explored the potential of using $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ as the negative ion component of an electrolyte for Al-ion battery.^[16] It is important to consider the energy needed to dissociate the electrolyte salt into individual ionic components. To compute the dissociation energy, we first optimized the geometry of $\text{Al}[\text{BeB}_{11}(\text{CN})_{12}]$. We determined the preferred geometry of this salt by considering three possible binding sites for aluminum. The resulting geometries are given in Figure 2a, 2c and 2d. The energetic stability of the higher energy isomers is given with respect to the ground state geometry in Figure 2a. In the lowest energy configuration, Al atom prefers to adsorb on the center of the islands formed by the three CN ligands linking with one Be and two B atoms. The average bond lengths of Be-B, B-B, Be-C, B-C, C-N and Al-N are 1.97, 1.80, 1.73, 1.51, 1.18, and 1.91 Å, respectively, as given in Figure 2a.

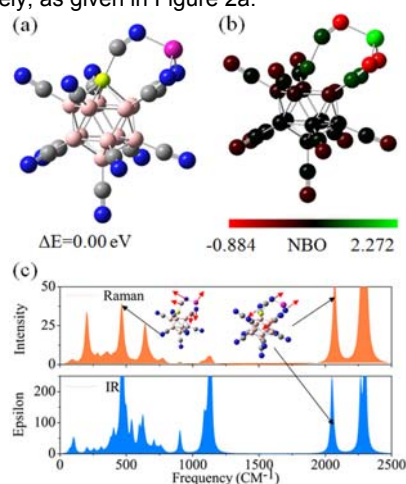


Figure 2. a) Optimized geometry and b) NBO charge distribution of $\text{Al}[\text{BeB}_{11}(\text{CN})_{12}]$; c) Simulated Raman and IR spectra of $\text{Al}[\text{BeB}_{11}(\text{CN})_{12}]$.

An NBO charge analysis yields the orbital occupation of Be, B, C, N, and Al as $2s^{0.26}2p^{1.16}$, $2s^{0.55}2p^{2.48}$, $2s^{0.95}2p^{2.83}$, $2s^{1.56}2p^{3.83}$, and

$3s^{0.37}3p^{0.36}$, respectively. This amounts to a charge transfer of 2.27 electrons from Al to $\text{BeB}_{11}(\text{CN})_{12}$. The NBO total charge distribution of $\text{Al}[\text{BeB}_{11}(\text{CN})_{12}]$ is given in Figure 2b. This analysis establishes the ionic character of $\text{Al}[\text{BeB}_{11}(\text{CN})_{12}]$. We also computed the dissociation pathway of $\text{Al}[\text{BeB}_{11}(\text{CN})_{12}]$ into Al cation and $\text{BeB}_{11}(\text{CN})_{12}$ anion. The preferred path leads to Al^+ and $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ with a dissociation energy (DE) of 5.44 eV.

In addition, we have calculated the Raman and IR spectra of $\text{Al}[\text{BeB}_{11}(\text{CN})_{12}]$ for comparison with those of $\text{BeB}_{11}(\text{CN})_{12}^{3-}$. In the Raman spectra, the vibrational frequencies are at 202, 284, 464, 639, and 2073 cm^{-1} , while in the IR spectra, the peaks occur around 476 and 2049 cm^{-1} regions. These results are given in Figure 2c.

Noble gas atoms, due to their closed electronic shell, generally do not react. However, the oxidation of Xe by AuF_6 proved^[17] that with the right reactant noble gas atoms can form chemical compounds. Note that AuF_6 is a superhalogen with a large EA of 9.56 eV.^[15a] Since AuF_6 could not oxidize smaller noble gas atom such as Ar, we conclude that both the size of the noble gas atom as well as the magnitude of the EA of the ligand are important in promoting noble gas chemistry. We note that the observation of an insertion compound involving Ar and HF opened the door to this novel chemistry where HAr^+ acts as a cation and F acts as an anion. Samanta^[18] carried this analogy a step further to see superhalogens can similarly be used to form insertion compound involving noble gas atoms. Using BO_2 and BF_4 superhalogens, the author studied the energetics of HXBO_2 and HXBF_4 ($X=\text{Ar}, \text{Kr}$) and concluded that “superhalogen (Y)-containing noble gas hydrides HXY , are more stable compared to their halogenated counterparts. Since the electron affinities of BO_2 and BF_4 , namely, 4.46 eV and 6.86 eV, are smaller than that of $\text{BeB}_{11}(\text{CN})_{12}$ (8.44 eV), we wondered if this moiety can further stabilize a noble gas insertion compound. We computed the energetics and reaction path of $\text{H}[\text{BeB}_{11}(\text{CN})_{12}]$ interacting with noble gas atoms, $X=\text{Ar}, \text{Kr},$ and Xe . We began with a geometry where the noble gas atom was inserted between H and $\text{BeB}_{11}(\text{CN})_{12}$ and calculated the resulting geometry by carrying out full geometry optimization. At the end of the simulation, all noble gas atoms, with the exception of Xe, did not insert into the ionic bond between H and $\text{BeB}_{11}(\text{CN})_{12}$. Instead, they formed an association compound where the noble gas atoms are weakly bonded to $\text{HBeB}_{11}(\text{CN})_{12}$. Note that unlike HXBO_2 and HXBF_4 ($X=\text{Ar}, \text{Kr}$) where the compounds are metastable with an energy barrier that prevents their dissociation into HBO_2 and X, we found no barrier for the dissociation in the case of $\text{HX}[\text{BeB}_{11}(\text{CN})_{12}]$ ($X=\text{Ar}, \text{Kr}$). We note that in the case studied by Samanta,^[18] the energy barrier with superhalogens was less than that with a halogen. This is where two factors compete, the size of anion and its EA. As the size of the anion increases, the binding energy decreases while reverse is the case with increasing EA. The size of $\text{BeB}_{11}(\text{CN})_{12}$ is significantly larger than that of BO_2 or BF_4 . Thus in the case of $\text{HX}[\text{BeB}_{11}(\text{CN})_{12}]$ ($X=\text{Ar}, \text{Kr}$) the size effect wins. However, this is not the case when one uses Xe. Here, because Xe is much more polarizable than its smaller cousins, it does form an insertion compound.

To study if the tri-anion stability of the $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ can be generalized, we have calculated the equilibrium geometries $\text{BeB}_{11}(\text{SCN})_{12}^{3-}$. Because SCN is twice as long as CN, we expected that $\text{BeB}_{11}(\text{SCN})_{12}^{3-}$ could be even more stable against spontaneous electron emission than $\text{BeB}_{11}(\text{CN})_{12}^{3-}$. We optimized the structure of $\text{BeB}_{11}(\text{SCN})_{12}^{3-}$ by allowing SCN to bind to the B

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cage with its S or N atom. We found that the structure with N bonding to the cage is 15.78 eV more favorable than when S is bound to the cage, as shown in Figure S2 of SI. The details of equilibrium geometry parameters, NBO analysis, thermodynamic stability, spectra and frontier molecular orbitals are given in SI text 2 and shown in Figure S3a-e. Counter to our expectation, the electron detachment energy of $\text{BeB}_{11}(\text{SCN})_{12}^{3-}$ is 0.59 eV, lower than that in $\text{BeB}_{11}(\text{CN})_{12}^{3-}$. The primary reason is that the EA of CN, namely, 3.86 eV, is larger than 3.61 eV of SCN, which more than makes up for its smaller size. Next we studied the potential of $\text{Al}[\text{BeB}_{11}(\text{SCN})_{12}]$ as an electrolyte in aluminum ion batteries. Since the diameter of $\text{BeB}_{11}(\text{SCN})_{12}$ (12.30 Å) is one and half times larger than that of $\text{BeB}_{11}(\text{CN})_{12}$ (8.91 Å), and the EA of SCN is smaller than that of CN, we expected the binding energy of Al in $\text{AlBeB}_{11}(\text{SCN})_{12}$ to be smaller than that in $\text{Al}[\text{BeB}_{11}(\text{CN})_{12}]$. Indeed, we find that the dissociation energy of this salt into Al^+ and $\text{BeB}_{11}(\text{CN})_{12}^{3-}$ is 4.43 eV, which is comparable to that of $\text{Al}[\text{BeB}_{11}(\text{CN})_{12}]$ and is better than values in commercial electrolytes used in LIBs.^[15a]

We also studied the effect of a third ligand, boronyl (BO). Note that BO^- is isoelectronic with CO. With a robust $\text{B}\equiv\text{O}$ triple bond, BO^- is a stable anion.^[19] However, its EA, namely, 2.51 eV, is smaller than that of CN. We optimized the geometries of $\text{BeB}_{11}(\text{BO})_{12}^{3-}$. Details are given in SI Text 4 and Figure S4, S5a-e. We find the tri-anion to be stable against spontaneous electron emission by 1.30 eV, which is smaller than that in $\text{BeB}_{11}(\text{CN})_{12}^{3-}$.

To examine the potential of $\text{BeB}_{11}(\text{BO})_{12}^{3-}$ as a negative ion component of an electrolyte for Al-ion battery we computed the geometry of $\text{Al}[\text{BeB}_{11}(\text{BO})_{12}]$ (see Figure S5f in SI). The dissociation energy of 5.50 eV is comparable with other borane derivatives.

In summary, we show that unusually stable trianions can be created by simultaneously using multiple electron counting rules. $\text{BeB}_{11}(\text{CN})_{12}^{3-}$, $\text{BeB}_{11}(\text{BO})_{12}^{3-}$ and $\text{BeB}_{11}(\text{SCN})_{12}^{3-}$ are all stable against spontaneous electron emission in the gas phase by 2.65, 1.30, and 0.59 eV, respectively. We are not aware of any tri-anion that exhibits this kind of stability in the gas phase. Ab-initio molecular dynamics simulations carried out for 10 ps further show that all these tri-anions are dynamically stable at 800 K. These unusually stable tri-anions can not only be used in the design of halogen-free electrolytes in aluminum ion batteries, but also can promote novel chemistry of large noble gas atoms, such as Xe. In addition, we suggest that one can view these stable tri-anions as super-atoms mimicking the chemistry of Group 15 elements. In analogy with super-halogens that mimic the chemistry of halogens, we term these very stable tri-anions as super-pnictogens.

Experimental Section

The optimized geometries and IR and Raman spectra are performed at DFT/B3LYP level of theory.^[20] We note that geometries computed at the B3LYP level of theory agree well with those computed at a higher level of theory.^[21] Therefore, we computed the total energies, molecular orbitals, HOMO-LUMO gaps, and NBO charges at the MP2 level of theory^[22] using the geometries obtained at the B3LYP level. All calculations were done using Gaussian 09 code.^[23] We used 6-311+G basis set for all atoms.^[24] Frequency analysis was performed to ensure that there are no imaginary frequencies. AIMD simulation was carried out, within the canonical (NVT)

scheme, using the gradient corrected DFT as implemented in the VASP code.^[25] The PAW method^[26] and PBE^[27] exchange correlation functional are used. Plane waves with 500 eV energy cutoff are used to expand the valence electron wave functions, with total energy convergence set to 10^{-4} eV. A unit cell with 30 Å vacuum space in three directions is used, with first Brillouin zone sampled by the Γ -point.^[28]

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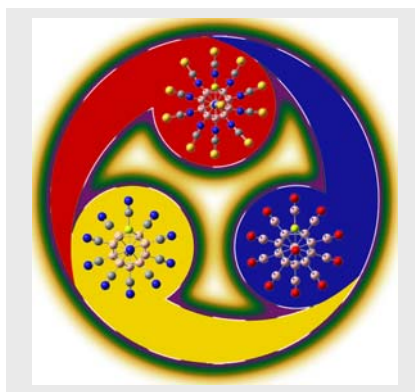
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