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Record-High Stability and Compactness of Multiply-Charged Clusters Aided by Selected Terminal Groups

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Abstract

Multiply-charged clusters with compact sizes that are stable in the gas phase are important due to their potential applications as weakly-coordinating ions and building blocks of bulk materials. However, the number of these clusters, especially those with high charge states beyond two, is limited. In this work, we show that gas-phase di- and tri-anions with record high stability and compactness can be developed by utilizing a series of stable mono-anions with linear configurations as ligands. A stable di-anion with a record high second electron binding energy of 6.26 eV and the smallest tri-anion with a record low radius of 4.85 Å has been identified. The study demonstrates that multiply-charged clusters with highly charged state and compact sizes can be stabilized solely by selected terminal groups in the structure. This finding significantly enriches the database of the stable multiply charged gas-phase clusters and provides a path towards rational design of further multiply-charged species.

Clusters, a structured collection of atoms, which are stabilized in the gas phase at single or higher charge states and yet with compact sizes have attracted considerable attention [1-5], especially in recent years [6-11]. Individual charged clusters can serve as weakly-coordinating anions to hold counter-ions such as metal cations in liquid electrolytes, or as powerful catalytic centers for binding inert molecules [12-17]. With acceptable sizes, charged clusters can also substitute elementary ions as building blocks of bulk materials, resulting in enhanced properties [18-21]. The first small di-anion reported in mass spectroscopy studies is the long-lived C_{60}^{2-} [2]. Although the electron affinity (EA) of the di-anion is negative, it can live for many microseconds due to tunneling through the coulomb barrier which effectively increases the EA by about 1.5 eV. Adding more electrons can increase the coulomb barrier even more, making the anions more stable to electron loss. A model has been developed to explain the electron tunneling phenomenon observed in the long-lived dicarboxylate dianions due to the Coulomb barrier [5]. It is found that more cluster anions can be bound together to form a bound state. Recently, a number of charged clusters as stable mono-, di-, tri-, tetra- and penta- anions with positive EAs have been theoretically predicted [6-10] and some of their existence and properties have been experimentally verified [10-11, 13-14]. It is found that the stability of these clusters is determined by their closeness to the closed-shell model (all-paired electrons), the electron holding ability of the terminal groups in their structures, as well as their sizes [9]. For an n-charged cluster, its stability can be measured by sum of the EAs,

$$V = \sum_{i=1}^{n} EA_i, \qquad (1)$$

where

$$EA_i = E_{i-1} - E_i \qquad (2)$$

E_i is the energy of its i-charge state. However, the number of multiply-charged clusters that are stable in the gas phase at moderate sizes is rather limited, especially for clusters that can hold charges beyond two. Many of the di-anions are based on boranes as backbones with hydrogen atoms replaced by certain mono-anions,

including halogen$^-$, CN$^-$, SCN$^-$ and BO$^-$, as terminal groups (see for example Fig. S1 of the Supporting Information, SI). Among them, $B_{12}(BO)_{12}^{2-}$ is found to be the most stable one with the highest value of calculated EA_2 = 5.73 eV [7]. Only a few of stable tri-anions are known so far, including $BeB_{11}(CN)_{12}^{3-}$, $BeB_{11}(SCN)_{12}^{3-}$ and $BeB_{11}(BO)_{12}^{3-}$ [8], which all involve the insertion of one beryllium (Be) atoms in the boron-cage skeleton. Among them, $BeB_{11}(CN)_{12}^{3-}$ is the most stable one with the highest EA_3 = 2.65 eV.

Realizing that replacing B and H in $B_{12}H_{12}^{2-}$ simultaneously may be difficult experimentally, in this work, we explore the possibility of stabilizing di- and tri-anions in the gas phase by only replacing H atoms with a new class of mono-anions other than the above mentioned CN$^-$, SCN$^-$ and BO$^-$. Stable gas-phase di-anions with record-high stability surpassing that of $B_{12}(BO)_{12}^{2-}$ are found. We also show that tri-anions can be stabilized without the insertion of Be by solely utilizing selected terminal groups. This has led to the discovery of stable gas-phase tri-anions with the smallest size known so far.

To understand how to stabilize a multiply-charged cluster, we first take a look at $B_{12}(CN)_{12}^{2-}$ and $BeB_{11}(CN)_{12}^{3-}$ as examples. $B_{12}(CN)_{12}^{2-}$ was theoretically predicted [8] and later successfully synthesized [11]. This di-anion has an EA_2 of 5.55 eV [11] and a V (Eq. 1) value of 13.84 eV [9]. Its great stability comes from the fulfillment of the Wade-Mingos rule [22] (an electron counting rule suggested by the closed-shell model) and the strong electron-holding ability of the CN$^-$ terminal groups in the structure (Fig. S1 of SI). In fact, CN$^-$ itself is known as a 'super-halogen' due to its significantly large EA_1 (4.10 eV) compared to that of Cl$^-$ (3.62 eV). Therefore, $B_{12}(CN)_{12}^{2-}$ can be viewed as a combination of two stable mono-anions (Fig. S1 of SI), $B_{12}(CN)_{11}^-$ and CN$^-$. Similarly, the tri-anion $BeB_{11}(CN)_{12}^{3-}$ with EA_3 = 2.65 eV and V =15.85 eV [8], can be viewed as a combination of a stable di-anion $BeB_{11}(CN)_{11}^{2-}$ and a stable mono-anion CN$^-$ (Fig. S1 of SI). $BeB_{11}(CN)_{11}^{2-}$ is again stabilized according to the Wade-Mingos rule with EA_2 = 4.62 eV [9]. *Therefore, to stabilize a new multiply-charged cluster, the key is to select a mono-anion with large*

stability as the terminal group other than CN⁻ and combine that with B₁₂(CN)₁₁⁻. If such a mono-anion has stronger electron-holding ability compared to CN⁻, then it may also be able to stabilize tri-anions by replacing multiple CN⁻ in the structure.

To avoid steric hindrance, we choose a series of clusters with linear configurations (Fig. S2 of SI) [23]. Although the closed shell of these clusters correspond to a '−2' charge state, they are only stable as gas-phase mono-anions with $EA_1 > 0$ and $EA_2 < 0$ (Table S1 of SI). Therefore, each of them has a magnetic moment of 1 μ_B in the ground state (Table S1 of SI). Among these mono-anions, many of them, including C_2^-, SBN^-, $OBeO^-$, $SBeO^-$, $OMgO^-$, NB_2N^-, $O_3Be_2^-$ and $O_3Mg_2^-$, have larger EA_1 than that of CN^- (4.10 eV) (Table S1 of SI). $O_3Be_2^-$ is the most stable one with the largest $EA_1 = 5.90$ eV of all (Table S1 of SI). It is then expected that these mono-anions can form di-anions with higher stability than that of $B_{12}(CN)_{12}^{2-}$ and even $B_{12}(BO)_{12}^{2-}$.

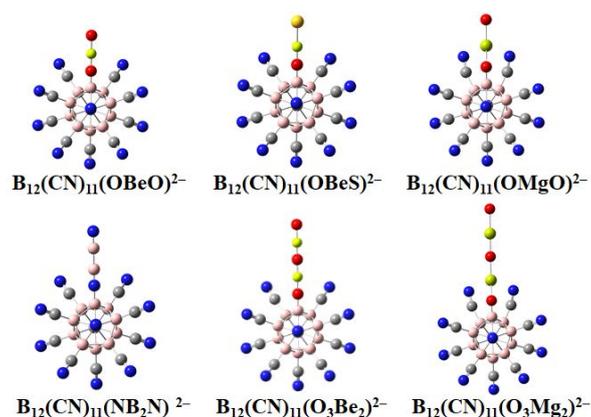$B_{12}(CN)_{11}(OBeO)^{2-}$ $B_{12}(CN)_{11}(OBeS)^{2-}$ $B_{12}(CN)_{11}(OMgO)^{2-}$

$B_{12}(CN)_{11}(NB_2N)^{2-}$ $B_{12}(CN)_{11}(O_3Be_2)^{2-}$ $B_{12}(CN)_{11}(O_3Mg_2)^{2-}$

Fig. 1 Structures of the gas-phase di-anions that are more stable (with higher EA_2) than $B_{12}(CN)_{12}^{2-}$. $B_{12}(CN)_{11}(O_3Be_2)^{2-}$ has the highest EA_2 (6.26 eV) of all. The terminal groups used are shown in Fig. S2 of SI. A complete list of stable di-anions of this study are shown in Fig. S3 and Table S3 of SI.

Indeed, new stable di-anions in the gas phase were developed based on the mono-anions, as shown in Fig. 1 and Table 1 (with the complete list in Fig. S1 and Table S1 of SI). It is found that $B_{12}(CN)_{11}(C_2)^{2-}$ is as stable as $B_{12}(CN)_{12}^{2-}$ according

to their very similar EA_2 (5.28 eV), yet is significantly smaller (r = 5.04 Å) than the latter (r = 5.88 Å). Other di-anions that exhibit high EA_2 include $B_{12}(CN)_{11}(OBeO)^{2-}$, $B_{12}(CN)_{11}(OBeS)^{2-}$, $B_{12}(CN)_{11}(OMgO)^{2-}$, $B_{12}(CN)_{11}(NB_2N)^{2-}$, $B_{12}(CN)_{11}(O_3Be_2)^{2-}$ and $B_{12}(CN)_{11}(O_3Mg_2)^{2-}$. $B_{12}(CN)_{11}(O_3Be_2)^{2-}$ has the highest EA_2 (6.26 eV) of all, surpassing that of the previous record-holder $B_{12}(BO)_{12}^{2-}$ (with EA_2 = 5.73 eV). Note that, as discussed before, all these di-anions with high stabilities resulted from the terminal groups corresponding to the mono-anions that have stronger electron-holding ability than that of CN^-. Whenever p-electrons are the main contributor to the bonding, the terminal groups are tilted when attaching to the boron site [12], as shown in the cases of $B_{12}(CN)_{11}(SBe)^{2-}$, $B_{12}(CN)_{11}(OMg)^{2-}$, $B_{12}(CN)_{11}(SMg)^{2-}$, $B_{12}(CN)_{11}(S_2)^{2-}$, $B_{12}(CN)_{11}(SBeS)^{2-}$, $B_{12}(CN)_{11}(SMgS)^{2-}$ and $B_{12}(CN)_{11}(SC_2S)^{2-}$ (Fig. S3). It is worth mentioning that, due to different atoms appearing at the two ends of many of the used mono-anions, there will be linkage isomers when they are used as terminal groups in the di-anions. The relative energy of a linkage isomer against the ground state is given in Table S3 for each case. No general rule is found for which element would preferably connect to the boron site in the ground state.

Table 1. Calculated parameters for the most stable di-anions in this study, including the length along the longest dimension (LLD), the molecular volume (MV), the radius (r), the multiplicity (M), the electron affinities (EA) and the V (Eq. 1) values. A complete list of all the di-anions in the study is given in Table S2 of SI. Also given are the calculated parameters for the stable gas-phase tri-anions found in the study. The parameters of $BeB_{11}(CN)_{12}^{3-}$, the smallest stable gas-phase tri-anion previously known [8], are also given for comparison. $B_{12}(CN)_{10}(C_2)_2^{3-}$ in this study shows significantly smaller radius (by $ca.$ 20%) than that of $BeB_{11}(CN)_{12}^{3-}$.

Di-/ Tri-anion	LLD (Å)	MV (cm³/mol)	r (Å)	M	EA_1 (eV)	EA_2 (eV)	EA_3 (eV)	V (eV)
$B_{12}(CN)_{11}(OBeO)^{2-}$	10.42	282.310	6.32	2	7.03	6.03	-	13.06
$B_{12}(CN)_{11}(OBeS)^{2-}$	10.86	393.660	6.78	2	7.18	4.96	-	12.14
$B_{12}(CN)_{11}(OMgO)^{2-}$	10.56	342.256	6.39	2	6.08	5.76	-	11.84
$B_{12}(CN)_{11}(NB_2N)^{2-}$	11.76	377.079	6.74	2	7.47	5.60	-	13.07
$B_{12}(CN)_{11}(O_3Be_2)^{2-}$	13.27	357.163	7.74	2	6.61	6.26	-	12.87
$B_{12}(CN)_{11}(O_3Mg_2)^{2-}$	14.17	310.665	8.19	2	5.62	5.74	-	11.38
$BeB_{11}(CN)_{12}^{3-}$	12.22	317.125	6.11	1	8.44	4.76	2.65	15.85

$B_{12}(CN)_{10}(C_2)_2^{3-}$	9.11	270.540	4.85	2	8.11	4.40	0.92	13.43
$B_{12}(CN)_{10}(OBeS)_2^{3-}$	10.97	375.475	7.33	2	9.09	2.87	1.43	13.39

As already discussed, given that some of the mono-anions have high electron-holding ability (Table S1 of SI), they may also be able to stabilize tri-anions upon replacing multiple CN^- groups without the insertion of Be in the boron skeleton. Stable gas-phase tri-anions are indeed found, including $B_{12}(CN)_{10}(C_2)_2^{3-}$ and $B_{12}(CN)_{10}(OBeS)_2^{3-}$, where two CN^- groups are replaced, as shown in Fig. 2. Their EAs and V values are given in Table 1. $B_{12}(CN)_{10}(C_2)_2^{3-}$ has the smallest size ($r = 4.85$ Å) among all the known tri-anions so far -- significantly smaller than that of the smallest tri-anions (6.11 Å) $BeB_{11}(CN)_{12}^{3-}$ known thus far [8-9].
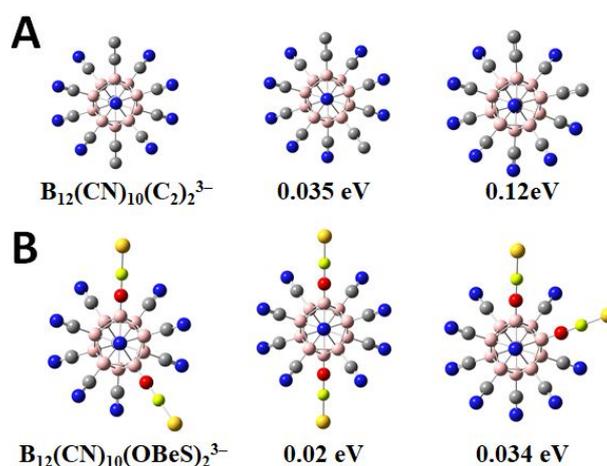

Fig. 2 Structures of the stable gas-phase tri-anions: (**A**) $B_{12}(CN)_{10}(C_2)_2^{3-}$ and its two low-lying isomers; (**B**) $B_{12}(CN)_{10}(OBeS)_2^{3-}$ and its two low-lying isomers.

All the data (Table S2 of SI and Table 1) of the di- and tri-anions found in this study can be well described by a physical model in which each additional electron is in a bound state of a general 3D potential well [9]. According to this model, the key quantities to stabilize a multiply-charged cluster are the V value and the radius (r). If we draw V *vs.* $1/r^2$ for the clusters, as shown in Fig. 3, it is found that all the data points will lie above the threshold lines

$$V_n = a_n/r^2 + V_0 \qquad (3)$$

with $n = 2$ and 3 for di- and tri-anions, respectively. The threshold line of di-anions is determined by $B_{12}H_{12}{}^{2-}$ [9] and the threshold line of tri-anions is determined by $B_{12}(CN)_{10}(C_2)_2{}^{3-}$. Data points of previously found stable di- and tri-anions are also included in the figure for comparison.

The electronic structures of the di- and tri-anions can be understood by drawing their molecular orbitals (MOs). As shown in Fig. S4 of SI, we choose $B_{12}(CN)_{11}(OBeO)^{2-}$ and $B_{12}(CN)_{11}(O_3Be_2)^{2-}$ as examples, which have the highest value of EA_2 of the di-anions studied (Table 1). The MOs of the two tri-anions (Table 1) are also studied. Since the ground states of these multiply-charged clusters are all magnetic (with 1 μ_B magnetic moment), we draw the MOs for two spins, separately. As a prototype, the MOs of $B_{12}(CN)_{12}{}^{2-}$ are given for comparison. In each case, there exists a low-lying MO formed by radial orbitals pointing their heavy ends towards the center of the boron cage. Up next in energy are the tangential orbitals around the cage skeleton and radial bonding between the boron at vertices and the terminal groups. The HOMOs and LUMOs are all concentrated on the terminal groups, suggesting their important role in stabilizing the multiply-charged clusters.
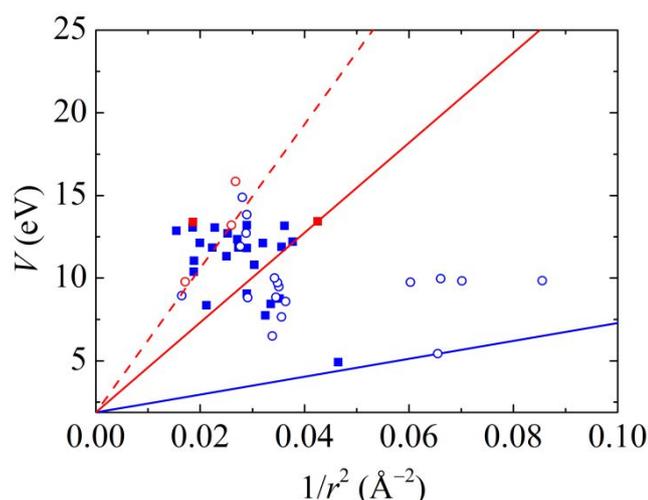

Fig. 3 Calculated V (Eq.1) vs. $1/r^2$ data (Table S2 of SI and Table 1) for the stable gas-phase di- (blue) and tri- (red) anions developed in this study (solid square) and from previous studies in Ref. 8. (open circle). The threshold lines (Eq. 3) for the di- (blue) and tri- (red)

anions are also given.

In conclusion, we have shown that many more multiply-charged clusters with compact size that are stable in the gas phase can be developed by merely using selected mono-anions with linear configurations. The electron-holding ability quantified by V in Eq.1 and the size quantified by radii (r) of these cluster anions are consistent with the physical model of electronic bound states in a general 3D potential well [9]. The di-anion $B_{12}(CN)_{11}(O_3Be_2)^{2-}$ with a record-high stability is discovered. Also found is the smallest stable gas-phase tri-anion known thus far -- $B_{12}(CN)_{10}(C_2)_2^{3-}$.

Computational Methods

The calculations are carried out using density functional theory (DFT) with the B3LYP hybrid exchange-correlation functional [24-25]. We used the Gaussian 03 with 6-31+G(d,p) basis sets for all atoms [26]. The exchange-correlation energy functional functional and basis sets used in this paper have been proven to be capable of providing reliable results in previous works. In all cases, structures are fully optimized without any symmetry constraints. All considered structures have real vibrational frequencies and therefore correspond to the potential energy minima. The convergence in the total energy and force are set at 1×10^{-6} eV and 1×10^{-2} eV/Å, respectively. The molecular orbitals are analyzed by the natural bond orbital (NBO) method.

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