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Stable and Long-Lived Trianions in the Gas Phase†

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Stable doubly charged anions have become well known over the past decade, but the knowledge about higher charged molecules is still sparse. In this article, we discuss the current status of trianions. The different species, both from experimental and theoretical work, are classified according to their bonding characteristics, that is, ionic, metallic, or covalent. Both stability with respect to electron autodetachment and with respect to dissociation is covered. New results on the currently smallest stable covalently bound trianion are also shown. Last, we outline future perspectives in the field of multiply charged anions.

1. Introduction

Almost 15 years ago, it was shown that many small multiply charged anions are not stable in the gas phase. The strong internal Coulomb repulsion leads to the spontaneous emission of one or more electrons. Even well-known anions such as SO_4^{2-},[1−3] CO_3^{2-},[1,4] and PO_4^{3-}[2] are electronically unstable without the stabilizing effect of the environment like counterions or solvent molecules. Much research went into the investigation of dianions in the following years, which led to the discovery of a number of small species that are stable in the gas phase (for reviews, see refs 5−8).

Looking at the literature, it is interesting to note that “multiply charged anion” is almost always used synonymously with “doubly charged anion”. This can be explained by the simple fact that the literature on negatively charged species with more than two excess electrons is still very sparse. Nonetheless, some metastable or even stable triply charged anions have been discovered, both experimentally and theoretically. They are summarized in Table 1, wherein representative examples are given in case of a whole “family” of trianions, and some of them are also pictured in Figure 1. But so far, the different works represent isolated islands of knowledge, which have yet to be assembled under some unifying principles. This work will thus review these results and we will also present some new results that are not published yet.

First, let us take a brief look at some stable dianions in order to propose a proper classification scheme for higher charged species. The search for the smallest dianion that is still stable with respect to electron emission resulted in the discovery of AX_3^{2-} ($A = Li, Na, K$; $X = F, Cl$)[6,9] as early as in 1992, of which LiF_3^{2-} could be verified experimentally just recently.[10] In these compounds, the atoms are bound mostly electrostatically; the strong attractive forces between the negative halogenid atoms and the positive alkali atom enables the dianions to be stable although they just consist of four atoms. Without such a clear-cut separation of charges, many more atoms are necessary to obtain a stable species. If one considers metallic bonds, then the smallest doubly charged cluster of, for instance, silver atoms, is Ag_{27}^{2-}.[11] Covalently bound dianions, however, at least allow one to partially separate the negative charges in case they possess electronegative atoms or groups at different ends of the molecule. This way, dianions as small as OC_5^{2-} can exist in the gas phase. This species was observed experimentally among a series of carbon−oxygen cluster dianions OC_n^{2-} ($n = 5{-}19$) in a mass spectrometer, whereas its geometry and electronic structure could be determined theoretically.[12]

It is obvious that the different types of bonding lead to quite different requirements for electronic stability. Accordingly, we organized this article in the following way: In Section 2, we will focus on mostly electrostatically bound trianions and will show specifically how the known AX_3^{2-} dianions can be extended to electronically stable trianions. Some triply negatively charged transition metal complexes will also be addressed there. The work done on trianionic metal clusters is the scope of Section 3. Finally, we will turn to covalently bound trianions in Section 4. This includes large oligonucleotides, the metastable, but long-lived trianion $N(BF_3)_4^{3-}$, and our most recent results on the smallest trianion of this kind known until today, which is $B(C_3O_2)_3^{3-}$. We close by outlining some future perspectives.

Before we start, a very important phenomenon occurring in multiply charged anions has yet to be described and some terminology has to be established. As already mentioned above, some multiply charged anions are not stable, but at least possess a finite lifetime; that is, they are either metastable with respect to electron autodetachment or with respect to dissociation to lesser charged fragments. Both of these kinds of metastability can be explained by a barrier, resulting from the combination of the long range Coulomb repulsion of the electron or the fragment from the remaining molecule with one negative charge less and the short range attraction caused by the positive nuclei or chemical bonds, respectively. In the case of electrons, this barrier was termed repulsive Coulomb barrier (RCB); it was observed experimentally (see, e.g., refs 13−15) as well as extensively studied theoretically.[16]

A negative electron detachment energy (EDE) corresponds to an electronically unstable species. If the absolute value of this EDE is lower than the RCB, then the electrons can tunnel only through the barrier, resulting in metastable species often with long lifetimes. A rule of thumb is that lifetimes larger than

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TABLE 1: Summary of Trianions Studied in the Literature[a]

	stability		
species/family	electronic	fragmentation	remarks
$A_2X_5^{3-}$	stable	metastable	A = Na, K; X = F, Cl
	?	metastable	A = Li; X = F
	?	unstable	A = Li; X = Cl
$E_2X_7^{3-}$	stable	metastable	E = Mg, Ca; X = F
	?	metastable	E = Be; X = F
	?	unstable	E = Be; X = Cl
			for all cases: loss of X^-
MX_6^{3-}	metastable	not studied	M = Sc, Y, La; X = F
	metastable	not studied	M = La; X = Cl
MF_6^{3-}	metastable	metastable	M = Eu, Lu; loss of F^-
	stable	metastable	M = Gd; loss of F^-
M_n^{3-}	stable	not studied	M = Na, K, Al, Cu, Ag, Au, Ti: n ≥ 205, 152, 208, 90, 90, 51, not given for Ti
C_{60}^{3-}	metastable	stable	
$C_{60}F_{47}^{3-}$	metastable	metastable	loss of F and F_2
$B(NF_3)_4^{3-}$	metastable	metastable	loss of F^-
$[CuHPc(SO_3)_4]^{3-}$	stable	not studied	Pc = phthalocyanine
$B(C_2CO_2)_3^{3-}$	stable	stable	

[a] Not included are a number of huge oligonucleotides, peptides, and polysaccharides, the stability of which can be considered as granted. A question mark means that stability could not be established beyond doubt, that is, for species with EDEs near zero. For references, see the text.

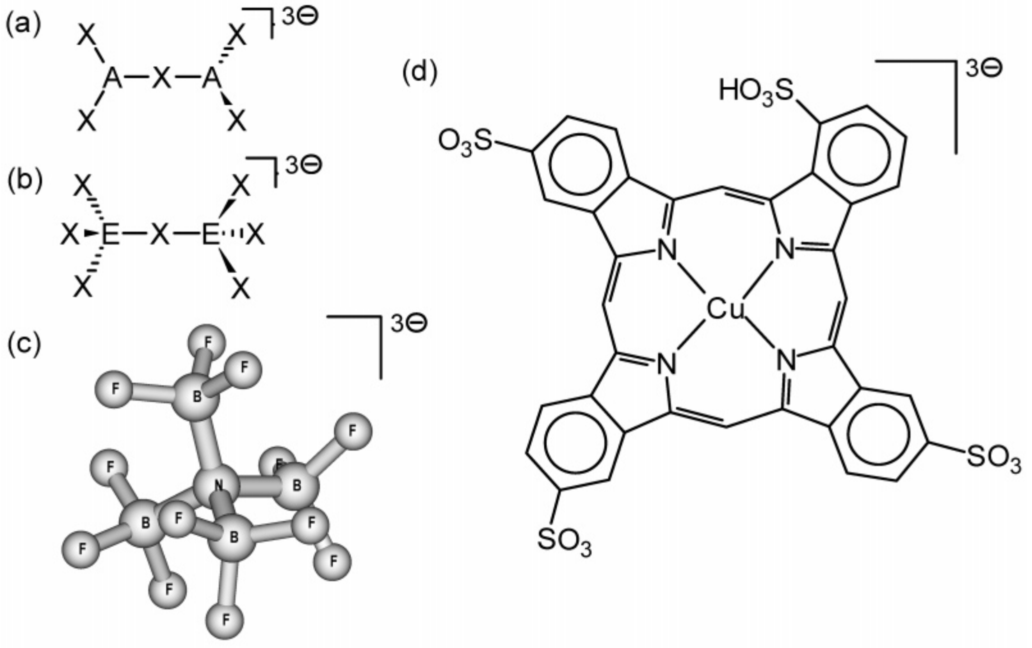

Figure 1. Structures of some stable or metastable trianions. The families represented by a and b (A = Li, Na, K; E = Be, Mg, Ca; X = F, Cl) are ionic trianions that were predicted theoretically to be observable in the gas phase. Note that the halogen atoms are in a “staggered” conformation. Trianion c also possesses a long lifetime according to ab initio calculations, but is covalently bound. The same is true for d, which was investigated by photoelectron spectroscopy in the gas phase and found to be stable with respect to electron autodetachment. For more details and references, see the text.

10^{-5} s allow the experimental observation of the anion in a mass spectrometer (for examples, see refs 14 and 15). If, however, the absolute value of the EDE is higher than the RCB, then the electrons can leave the system freely and it is truely unstable. Because the accurate determination of RCBs is nontrivial, lifetimes are usually difficult to estimate theoretically.

2. Ionic Trianions

The search for small trianions that are bound mainly by electrostatic forces started in 1993, when Scheller and Cederbaum presented a construction principle for alkali halide clusters with negative charges larger than two.[17] This principle consists of adding units of AX_2^- (A = Li, Na, K; X = F, Cl) to the stable AX_3^{2-} dianions, which were discovered theoretically by the same authors.[4,9] It is interesting to note that the smallest member of those dianions, that is, LiF_3^{2-} indeed could be detected experimentally just recently.[10] Later, it was demonstrated that in the same way, ionic trianions can be obtained by adding units of EX_3^- to the EX_4^{2-} dianions (E = Be, Mg, Ca; X as above).[18] These doubly negative alkaline earth halides were also proposed theoretically,[9,19] and some of them were verified experimentally.[20]

The first publication on these trianions[17] discussed only $K_2F_5^{3-}$, whereas the next one consisted of an extensive investigation of all possible fluorides and chlorides except for $Mg_2F_7^{3-}$ and $Ca_2Cl_7^{3-}$.[18] For the respective ground-state structures of these species, see Figure 1. At the one-particle self-consistent field (SCF) and outer-valence Green's function (OVGF)[21,22] level of theory as well as using the so-called *ionic model*,[9] strong evidence was presented that $A_2X_5^{3-}$ (A = Na, K; X = F, Cl) and $E_2F_7^{3-}$ (E = Mg, Ca) indeed represent species that are stable with respect to electron autodetachment. The analogous lithium and beryllium fluorides and chlorides are on the verge of electronic stability and can at least be expected to possess a long lifetime. But turning to the fragmentation of the molecular framework, it was observed that there is no or virtually no barrier for the decay into $LiCl_3^{2-}$ + $LiCl_2^-$ and $BeCl_4^{2-}$ + $BeCl_3^-$, respectively, making the experimental observation of the corresponding trianion very unlikely. For the other trianions studied, the dissociation is also exothermic, but hindered by broad barriers of 1.5 Å ($Li_2F_5^{3-}$) up to 5 Å ($Ca_2F_7^{3-}$). These triply negatively charged species should thus all be observable in a mass spectrometer.

The overall result of these studies was that both the electronic stability and the stability to fragmentation increases with increasing ionic character of the bonds. This manifests itself in the finding that the fluorine compounds are more stable to dissociation than the trianions in which the halogen atoms have been replaced by less electronegative chlorine atoms. Additionally, there is the trend that the trianions containing more electropositive metal atoms are more stable, the major reason for this being that the metal atoms carry a much larger positive charge. This explains the instability of $Li_2Cl_5{}^{3-}$ and $Be_2Cl_7{}^{3-}$.

Another finding was that the alkali halide trianions are less stable than the alkaline earth halide trianions because of the larger Coulomb repulsion in the former. Although there are more negatively charged halogen atoms in the alkaline earth halides, the much larger positive charge of the metal atoms compensates for this easily. When comparing the trianions to the respective dianions AX_3^{2-} and EX_4^{2-}, a markedly smaller binding energy for the third excess electron in the former is observed than for the second excess electron in the latter. This is also explained by the increased Coulomb repulsion because of a larger number of negatively charged halogen atoms.

According to the above, increased ionic character of the bonds leads to more stable compounds. Consistent with this finding is that the only known transition metal and lanthanide complexes, which are perhaps stable despite a triply negative charge, are made up of fluorine atoms and electropositive metals.

Gutowski et al. investigated some mono- and dianions and a number of trianions of the general formula MF_6^{3-} (M = Al, Ga, In, Tl, La) as well as $LaCl_6^{3-}$.[23] Most of the trianions were already unstable or only barely stable with respect to the spontaneous emission of an electron at the level of Koopmans' theorem; referring to previous experiences that correlation and relaxation decreases the stabilitiy even more, the authors did not investigate these trianions further. The only exceptions were the lanthanum halides, for which calculations at a correlated level were carried out accordingly. For $LaCl_6^{3-}$, EDEs between −0.03 and −0.77 eV were obtained, depending on the level of theory. This species is thus a candidate for a metastable trianion, but additional studies are required. The other lanthanum halide, LaF_6^{3-}, has also been found by Gutowski et al. to possess only negative EDEs when employing different orders of the Møller−Plesset pertubation theory (MPn). Alternatively, a propagator-based approach including third and infinite order terms[24] yielded a positive EDE of 0.78 eV.

A further publication[25] was expected to shed more light on the electronic stability of LaF_6^{3-}. Therein, ScF_6^{3-} and YF_6^{3-} were also studied. This time, a larger basic set was employed and additional calculations with OVGF and density functional theory (DFT) were performed. Although a trend of increasing stability from the scandium to the yttrium to the lanthanum triply negatively charged complexes was observed, the results were still inconclusive. The EDEs calculated with the B3LYP functional were below −1.7 eV for all three trianions, whereas OVGF yielded values between −0.17 and 1.07 eV. With MP2, the authors obtained EDEs about 1 eV higher than with B3LYP, which were thus still negative by at least 0.66 eV. We should mention that DFT is not able to describe the diffuse nature of multiply negatively charged anions properly (see, e.g., ref 26 and the discussion in ref 25 itself). For this review, we calculated an additional EDE value for LaF_6^{3-} using coupled cluster theory, including single and double excitations (CCSD), which turned out to be −0.42 eV. Except for OVGF, all of these results point to the conclusion that MF_6^{3-} with M = Sc, Y, and La are at most metastable with respect to electron autodetachment with only LaF_6^{3-} possibly living long enough to be observable in the gas phase.

These two studies[23,25] were extended further by Takeda et al. some years later, who investigated all of the lanthanide fluorides MF_6^{3-} with M = Ce, . . ., Lu.[27] The only trianions that are probably electronically stable turned out to be EuF_6^{3-}, GdF_6^{3-}, and LuF_6^{3-}. Even for those, only the EDEs for GdF_6^{3-} were uniformly positive at different levels of theory. Employing either unrestricted Hartree−Fock (UHF) or complete active space self-consistent field (CAS−SCF), negative EDEs of −0.38 down to −1.7 eV were obtained for EuF_6^{3-} and LuF_6^{3-}, whereas second-order multiconfiguration quasidegenerate perturbation theory (MC-QDPT) predicted them to be stable by 0.24 and 1.10 eV, respectively. The three trianionic complexes also possess energy barriers with respect to the exothermic dissociation of one fluoride anion, with heights of 0.38 (Eu), 0.43 (Gd), and 0.16 eV (Lu). Unfortunately, the widths of the barriers were not given, so estimations of their lifetimes are very difficult. But according to the results for the alkali and alkaline earth halides (see above), and bearing in mind the results at the correlated level of theory for the electronic stability, it seems to be reasonable to expect their observation in a mass spectrometer in the future.

Let us mention that Petrie and Stranger performed an extensive study of dinuclear complexes, including some trianionic ones.[26] But their aim in this work was to determine which DFT functional is best suited for reproducing experimental geometries; they did not comment at all on the electronic stability or the stability to fragmention of these trianions.

3. Metallic Trianions

With respect to their bonding characteristics, metall clusters are the "opposite" of ionic compounds. It can thus be anticipated that a much larger number of atoms is necessary to accommodate excess negative charges. Exactly this was observed, both theoretically and experimentally.

The investigations started with an extensive study of negatively charged sodium clusters in 1993.[28] Yannouleas and Landman introduced a modified liquid drop model, known from nuclear physics,[29] which treats the cluster as a droplet and corrects for shell effects using a density functional approach. However, they employed this correction only in their calculations of the first and second electron affinities and their dependence on the number of Na atoms in the cluster, and neglected it for the third and fourth electron affinities. Their estimate that Na_n^{3-} becomes stable for $n \geq 205$ thus has to be taken with some caution. Similar estimates were provided for K_n^{3-} and Al_n^{3-}; the results were $n \geq 152$ and 208, respectively.

Several years later, the first experimental observation of triply negatively charged metal clusters was reported: In the year 2000, Herlert et al. discovered Ti_n^{3-} trianions.[30] They size-selected monoanions stored in a Penning trap, which were generated by laser vaporization first, then guided an electron beam through the trap, and analyzed the resulting multiply charged ions by time-of-flight mass spectrometry. No further details were given for the titanium trianions in this publication, but the apparatus was used later for other metals. Silver[31] and gold[11] were subjected to this procedure just a year later. In these cases, the smallest trianions observed were $Ag_{\sim 100}^{3-}$ and Au_{51}^{3-}. Another result was that the yield of trianions is about 2 orders of magnitude lower than the one of dianions. For Au_n^{3-}, a general agreement with the shell-corrected liquid drop model could be established. The model also led to the conclusion that the stability of the clusters is not determined by dissociation of Au^- ions but rather by electron autodetachment. In another publication, the same group reinvestigated Ag_n^{3-} and Au_n^{3-} and completed the study of these noble metals by including Cu_n^{3-}.[32] This time, the smallest trianionic clusters observed in the experiments were Cu_{90}^{3-}, Ag_{90}^{3-}, and again Au_{51}^{3-}. The authors were able to roughly explain these appearance sizes by a charged sphere model, but only when including the RCB. They also pointed out that the effect of the RCB is much stronger in trianions than in dianions.

In contrast to these findings, Kappes et al. did not detect trianionic gold clusters Au_n^{3-} at all for n up to about 175.[33] This discrepancy is explained easily by the fact that they produced the multiply charged anions directly by laser ablation. The resulting clusters are highly exited and thus to a large part decay before the detector is reached. Additionally, the peaks of the singly and multiply charged anions were difficult to discern in the mass spectrum because there was no size selection beforehand. Consistently, the smallest *doubly* negatively charged gold cluster observed was Au_{29}^{2-}, compared to Au_{11}^{2-} in the experiment of Herlert and Schweikhard.[32] The observation of trianionic lead clusters Pb_n^{3-} with $n \geq 76$ in the same experiment[33] has thus to be considered an upper limit for the size of electronically stable triply charged lead clusters.

4. Covalent Trianions

Judging from the experiences with ionic trianions outlined in Section 2, it seems to be a difficult task to construct covalently bound trianions that are electronically stable. With decreasing ionic character, the alkali, alkaline earth, and transition metal halides become less stable. It follows that there are thus two fundamentally different approaches to covalent trianions. The first strategy is simple to distribute the charges over a large space, similar to the situation in metallic trianions. This way, the coulomb repulsion is reduced in a trivial manner. Examples are huge multiply charged DNA-fragments, consisting of at least 90 atoms (see, e.g., ref 34) or equally large proteins and polysaccharides (see, e.g., refs 35 and 36). Here it is worthwile to mention that even molecules as large as C_{60} can bind more than one electron only temporarily (see ref 37 and references therein). The lifetimes of the formed multiply charged species are at least long enough that C_{60}^{2-} [38,39] and very recently even C_{60}^{q-} ($q = 3, 4$)[40] could be observed experimentally. According to a combined theoretical and experimental study, even $C_{60}F_{47}^{3-}$ is metastable only with a lifetime long enough for this trianion to be detected by mass spectrometry.[41] The authors crudely estimated the EDE to be about -1 eV, using a model of a conduction sphere with parameters determined by DFT calculations.

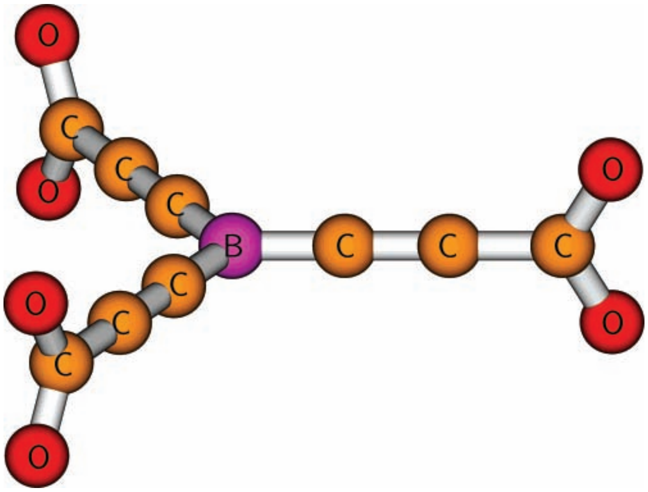

Figure 2. Smallest stable covalently bound trianion known until now. It is stable with respect to both spontaneous electron emission and fragmentation of the molecular framework. Note that both the size of the molecule and the electronegative groups at the periphery help to stabilize the three excess charges.

It is, of course, much more demanding to accommodate three excess charges in a *small* molecule. The second strategy to design trianion accordingly consists of employing strongly electronegative groups, rendering the bonds partly ionic in character. In light of the results for the large fullerenes, it is nevertheless surprising that a trianion with only 17 atoms exhibits a larger electronic stability than C_{60}^{3-}, if this conctruction principle is followed. Dreuw and Cederbaum performed an extensive ab initio investigation of the small, covalently bound trianion $B(NF_3)_4^{3-}$, and found it to be electronically metastable by just about 0.1 to 0.3 eV. This triply negatively charged system is also displayed in Figure 1. To obtain an idea about its lifetime, its RCB was calculated explicitely with the DFOSA method.[16] Using WKB theory,[42] the tunneling lifetime along the minimum energy path of the RCB was estimated to be much larger than 10^{-5} s, for an EDE of -0.1 eV even of the order of 10^{15} s. Although the calculations showed that the trianion is also unstable with respect to fragmentation, similar barriers, caused by the strong covalent bonds, are expected to lead to similar long lifetimes to dissociation. The experimental detection of this trianion should thus pose no problem, whereas the determination of its lifetime could be very difficult because on the time scale of typical experiments probably no decay would be observed at all.

The question of how small a covalent trianion can be and still bind all of its electrons is far from settled. We achieved significant progress to answer this question recently by systematically constructing a trianionic species, keeping in mind both a large extension and electronegative groups at the periphery of the molecule. A trigonal symmetry looked most promising, leading to the decision to start with a central boron atom. To this, three C_2 units were attached as spacers, followed by CO_2 groups to accommodate the negative charges, resulting in the final formula $B(C_2CO_2)_3^{3-}$. Geometry optimizations at different levels of theory revealed that the boron and carbon atoms are lying in a plane, whereas the oxygen atoms are found orthogonal to this plane. This structure is shown in Figure 2. Using MP2, CCSD, and OVGF, all vertical EDEs, that is, EDEs calculated at the geometry of the trianion, were found to be positive by at least 0.18 eV. The strong evidence for electronic stability is not restricted to these results; even when we included the relaxation of the molecular framework after electron emission, we found indication of stability. The adiabatic EDE, that is, the energy difference of the trianion to that of the corresponding dianion at its separately optimized geometry, was found to be close to zero, but still positive, at all correlated levels of theory. It is interesting that there are several geometries of the dianion lying close together in energy, caused by a very floppy potential energy surface with respect to the rotation of the CO_2 groups. We also investigated several different pathways of fragmentation, leading to either a dianion and a monoanion or to two monoanions and a free electron. At the correlated level of theory, all of these decay channels were found to be closed. In summary, $B(C_2CO_2)_3^{3-}$ is the smallest stable covalently bound trianion known until now, with just 16 nuclei and 110 electrons. More details on these findings will be published elsewhere.

To close, let us mention the experimental observation of another trianion that combines both strategies to achieve electronic stability, but is substantially larger than $B(C_2CO_2)_3^{3-}$. This is the singly protonated copper phthalocyanine-3,4′,4″,4‴-tetrasulfonate, $[\mathrm{CuHPc(SO_3)_4}]^{3-}$ [14] (see Figure 1). Apart from its large size (57 heavy atoms distributed in a plane), the sulfonate groups are predestined to separate the negative charges as far as possible. Accordingly, this trianion is stable by about 1.2 eV, as measured by photoelectron spectroscopy in the gas phase by Wang and Wang.[14]

5. Future Perspectives

A number of triply negatively charged species were discovered over the last 12 years, by both theoretical means and mass spectrometry. However, for most of them, the stability to electron autodetachment and to fragmentation is either trivial because of the very large size, examples are DNA fragments, or could not be unambiguously determined, such as for LaF_6^{3-}. It is clear that much work is left to be done to understand the properties of *small* triply charged anions. This becomes even more evident because of the fact that an order of magnitude more studies have been carried out on small dianions and there are still many unanswered questions in this field (see, e.g., ref 7). For example, little work has been done on the experimental determination of lifetimes of metastable multiply charged anions.

Keeping this in mind, it is interesting to notice that some work on tetra-anions and higher charged species already exists. Going back to the $A_2X_5^{3-}$ trianionic alkali halide clusters, which were constructed by combining the fragments AX_3^{2-} and AX_2^-, one could expect that by straightforwardly adding more AX_2^- units, higher charged clusters should be obtained. But, as already pointed out above, the triply charged clusters are less stable than their corresponding dianionic building block. By extrapolating this trend to tetraanions or even higher charged ones, it is unlikely that stable molecules of this sort can be obtained simply by this construction principle. This was already discussed in refs 17 and 43 and as a solution, the addition of AX units to increase the size of the molecule was proposed. The detection of these proposed triply or higher charged anions still poses an interesting task for experimentalists.

Turning to multiply charged metal cluster anions, so far there is no experimental evidence at all for species with more than three excess charges. Theoretical estimates by Yannouleas and Landman[28] place the onset of stability at $n = 554$, 421, 599, and 1177 for Na_n^{4-}, K_n^{4-}, Al_n^{4-}, and Na_n^{5-}, respectively. Using a different approximation scheme, Herlert and Schweikard estimated the limit to the stability of tetraanions for copper, silver, and gold at Cu_{278}^{4-}, Ag_{193}^{4-}, and Au_{128}^{4-}.[32] Note that there are interesting trends in the onset sizes of the differently charged metal cluster anions: For the main group elements, n^{2-}:n^{3-}:n^{4-} roughly follows the ratios 1:5:15, whereas for the noble metals ratios of about 1:4:9 can be calculated. Neither of these trends was pointed out by the respective authors and still awaits an explanation.

Last, let us have a look at covalently bound multiply charged anions. Apart from the DNA fragments, huge proteins, and C_{60}^{4-} mentioned above, there is to our knowledge only *one* other example for the experimental observation of species with more than three excess electrons. If the last one of the four protons of the sulfanate groups of $[\mathrm{CuHPc(SO_3)_4}]^{3-}$ is also detached, a quadruply charged species is left. Experimentally, it was shown that even though the size of the molecule and the electronegative groups were sufficient to stabilize three negative excess charges, this is no longer the case for four additonal electrons. In the photodetachment spectrum, Wang and Wang observed a *negative* EDE of −0.9 eV. This can be explained only by a high RCB, which hinders the electron from leaving the tetraanion before it gets detached by the laser.

The discovery of the rather small, covalently bound trianion $B(C_2CO_2)_3^{3-}$ reported here was certainly a step forward in the study of multiply charged species. But which consequences may possibly result from this theoretical finding? The smallest covalent *dianion* known until now, which is OC_5^{2-}, consists of 6 atoms, whereas this trianion already possesses 16. Although this ratio (6:16) is not as large as that for multiply charged metal cluster anions (see above), a crude extrapolation predicts the smallest stable covalent tetraanion to consist of about 30−50 atoms. The theoretical search for stable covalent tetraanions will thus be not straightforward. The only way up until now to treat molecules of this size on a correlated level is DFT, which is known to be unreliable for the description of multiply negatively charged anions. Hopefully, this deficit will be circumvented some day. However, we expect that the experience gathered for dianions and trianions can serve the search for higher charged anions and that fundamentally new ideas for constructing multiply charged covalent anions can be developed.

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