

Polynuclear $\text{Li}_{12}\text{F}_{13}^-$ anion as a steric shielding agent with respect to selected metal ions

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Abstract Polynuclear superhalogen anion $\text{Li}_{12}\text{F}_{13}^-$ and its ionic complexes formed by the interaction with selected metal ions (i.e., $\text{Li}_{12}\text{F}_{13}^-\text{Na}^+$, $\text{Li}_{12}\text{F}_{13}^-\text{K}^+$, $\text{Li}_{12}\text{F}_{13}^-\text{Mg}^{2+}$, and $\text{Li}_{12}\text{F}_{13}^-\text{Zn}^{2+}$) are proposed and investigated on the basis of ab initio calculations. The thermodynamic stability, vertical excess electron detachment energy, and binding energies between ionic components were examined and discussed. The $\text{Li}_{12}\text{F}_{13}^-$ anion has been proved stable against fragmentation and its vertical electronic stability was found to approach 10 eV. Due to its specific equilibrium structure that resembles a molecular basket, the $\text{Li}_{12}\text{F}_{13}^-$ anion was found capable of trapping positively charged metal ions inside to form strongly bound ionic complexes. The large values of binding energies predicted for the $\text{Li}_{12}\text{F}_{13}^-\text{Na}^+$, $\text{Li}_{12}\text{F}_{13}^-\text{K}^+$, $\text{Li}_{12}\text{F}_{13}^-\text{Mg}^{2+}$, and $\text{Li}_{12}\text{F}_{13}^-\text{Zn}^{2+}$ systems and their specific equilibrium structures indicate that the $\text{Li}_{12}\text{F}_{13}^-$ anion can be useful as a steric shielding system which protect the metal ions from the interaction with the surroundings.

Keywords Superhalogens · Anions · Steric shielding · Metal cations · Calculations

1 Introduction

Strong electron acceptors commonly called “superhalogens” were originally proposed and studied by Gutsev and

Boldyrev [1]. In general, the superhalogens were defined as a group of compounds matching the MX_{k+1} formula (where M is a metal atom having the maximal formal valence k , while X corresponds to the halogen atom) and characterized by the electron affinity (EA) higher than that of the chlorine atom (EA = 3.62 eV) [2]. It implies that superhalogens form very strongly bound and thermodynamically stable molecular anions [3–5] which are characterized by the enormous values of vertical electron detachment energies (VDEs) approaching 14 eV in certain cases [6, 7]. The very first experimental evidence of the superhalogen existence was provided in 1999 by the Wang’s group who reported the photoelectron spectra of the selected triatomic MX_2^- superhalogen anions (M = Li, Na; X = Cl, Br, I) [8]. Since then, many other superhalogen anions [e.g., $\text{Na}_k\text{Cl}_{k+1}^-$ ($k = 1-4$) and MX_3^- (where M = Be, Mg, Ca; X = Cl, Br)] have also been identified experimentally [9, 10]. As indicated by both theoretical predictions and experimental measurements, the original superhalogen formula (MX_{k+1}) can be extended to include the polynuclear $\text{M}_n\text{X}_{nk+1}$ neutral superhalogen compounds (containing n central atoms) whose corresponding polynuclear $\text{M}_n\text{X}_{nk+1}^-$ anions exhibit even larger electron binding energies than their mononuclear counterparts [11–17]. In addition to numerous applications of superhalogens, we have recently pointed out their possible usage as strong oxidizing agents [18–21] and Lewis–Brønsted superacid precursors [7, 22, 23]. It should also be mentioned that some recent works revealed novel superhalogen applications in Li-ion batteries, solar cells, and hydrogen storage materials [24–27].

It was also established that one of the important features characterizing superhalogen anions is their tendency to adopt high-symmetry compact structures [10]. Recent report concerning the properties of the $\text{Li}_n\text{F}_{n+1}^-$ ($n = 2-5$) superhalogen anions confirmed that observation, as the

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most stable isomers of the $\text{Li}_n\text{F}_{n+1}^-$ anions were found to correspond to relatively high-symmetry structures [28]. Hence, one may anticipate the formation of even larger high-symmetry $\text{Li}_n\text{F}_{n+1}^-$ anions whose stability and properties are yet to be determined. Since the positively and negatively charged $(\text{LiF})_n$ clusters and their neutral parents are well-known systems [29–33], the knowledge of their equilibrium structures might be of great help while designing the anions containing an additional fluorine atom. The preliminary considerations of the shape and size that one might expect of the $\text{Li}_n\text{F}_{n+1}^-$ structures for $n > 5$ led us to the $\text{Li}_{12}\text{F}_{13}^-$ anion that we initially predicted to be large enough to form a high-symmetry negatively charged molecular basket [34]. If such predictions were confirmed, the $\text{Li}_{12}\text{F}_{13}^-$ anion could be considered useful as a steric shielding agent (enabling the introducing of selected metal ions into various solutions). Since the steric shielding occurs when molecules or molecular clusters are large enough to protect other reactive groups (or atoms) from contact with the chemical environment, this technique remains very common and useful in chemistry [35, 36], e.g., particularly with reference to certain complexes formed by crown ethers [37–40]. Taking into account both the anticipated cage-like equilibrium structure of the $\text{Li}_{12}\text{F}_{13}^-$ system and its excess negative charge, one might expect an analogous ability regarding this polynuclear superhalogen anion.

In this contribution, we demonstrate the possible use of the $\text{Li}_{12}\text{F}_{13}^-$ anion as a steric shielding compound with respect to certain metal cations. We believe that the ability of trapping selected positively charged ions by the polynuclear superhalogen anions will turn out to be a general feature of many other high-symmetry superhalogen clusters and will inspire experimental investigations in this direction.

2 Methods

The equilibrium geometries and the harmonic vibrational frequencies of the $\text{Li}_{12}\text{F}_{13}^-$ superhalogen anion, its corresponding neutral parent ($\text{Li}_{12}\text{F}_{13}$), the ionic complexes ($\text{Li}_{12}\text{F}_{13}^-\text{Na}^+$, $\text{Li}_{12}\text{F}_{13}^-\text{K}^+$, $\text{Li}_{12}\text{F}_{13}^-\text{Mg}^{2+}$, $\text{Li}_{12}\text{F}_{13}^-\text{Zn}^{2+}$), and $\text{Li}_{12}\text{F}_{13}^-$ fragmentation products were calculated using the second-order Møller–Plesset ab initio perturbational method (MP2) [41, 42] and the 6-311+G(*d*) basis set [43, 44]. The fourth-order Møller–Plesset method with single, double, and quadruple substitutions employing analytic gradients (MP4(SDQ) [45–47]) with the same 6-311+G(*d*) basis set were used to estimate binding energies (BEs) in the $\text{Li}_{12}\text{F}_{13}^-\text{Na}^+$, $\text{Li}_{12}\text{F}_{13}^-\text{K}^+$, $\text{Li}_{12}\text{F}_{13}^-\text{Mg}^{2+}$, and $\text{Li}_{12}\text{F}_{13}^-\text{Zn}^{2+}$ ionic complexes.

Thermodynamic stability of the superhalogen anion $\text{Li}_{12}\text{F}_{13}^-$ was verified through the analysis of the Gibbs free

energies of the most probable fragmentation reactions. The Gibbs free energies (ΔG_s) were evaluated by using electronic energies calculated employing the quadratic configuration interaction method including single and double substitutions (QCISD [48–50]) and the 6-311+G(*d*) basis set together with the zero-point energy corrections, thermal corrections (at $T = 298.15$ K), and entropy contributions estimated with the MP2 method and 6-311+G(*d*) basis set.

To test the reliability of the MP4(SDQ) and QCISD methods in estimating electronic energies of the species investigated in this work, the additional calculations using the coupled-cluster method with single, double, and non-iterative triple excitations (CCSD(T) [48, 51]) were performed. It was verified that the reaction energies calculated using the CCSD(T) method for two selected $\text{Li}_{12}\text{F}_{13}^-$ fragmentation processes leading to relatively structurally simple products (i.e., LiF , Li_2F_2 , and Li_4F_5^-) differ by less than 2–3 % in comparison with those assessed with either MP4(SDQ) or QCISD approaches. Hence, we assumed that employing both the QCISD and MP4(SDQ) methods should result in reproducing proper electronic energy values for the systems studied in this contribution.

The vertical electron detachment energy (VDE) of the $\text{Li}_{12}\text{F}_{13}^-$ was calculated by applying the outer valence Green function OVGf method (*B* approximation) [52–60] together with the 6-311+G(3*df*) basis set. Analogous methods and basis sets have been used for superhalogen anions before and provided an excellent agreement with the experimentally measured VDE values [10, 61]. Due to a fact that the OVGf remains valid only for outer valence ionization for which the pole strengths (PS) are greater than 0.80–0.85 [62], we verified that the PS value obtained for the $\text{Li}_{12}\text{F}_{13}^-$ anion (0.93) was sufficiently large to justify the use of the OVGf method.

The partial atomic charges were fitted to the electrostatic potential according to the Merz–Singh–Kollman scheme [63]. All calculations were performed with the GAUSSIAN09 (Rev.A.02) package [64].

3 Results

3.1 $\text{Li}_{12}\text{F}_{13}^-$ superhalogen anion

The equilibrium geometry of the $\text{Li}_{12}\text{F}_{13}^-$ superhalogen anion is presented in Fig. 1. The initial structure for the geometry optimization was assumed to resemble a typical cubic cage $(\text{LiF})_{13}$ neutral cluster but having one lithium atom detached. The minimum energy structure of the $\text{Li}_{12}\text{F}_{13}^-$ was found to resemble a C_{4v} -symmetry molecular basket with almost quadratic base (the Li–F–Li valence angles are nearly equal to 90°) and four equivalent walls extended outward (the Li–F–Li valence angles that involve

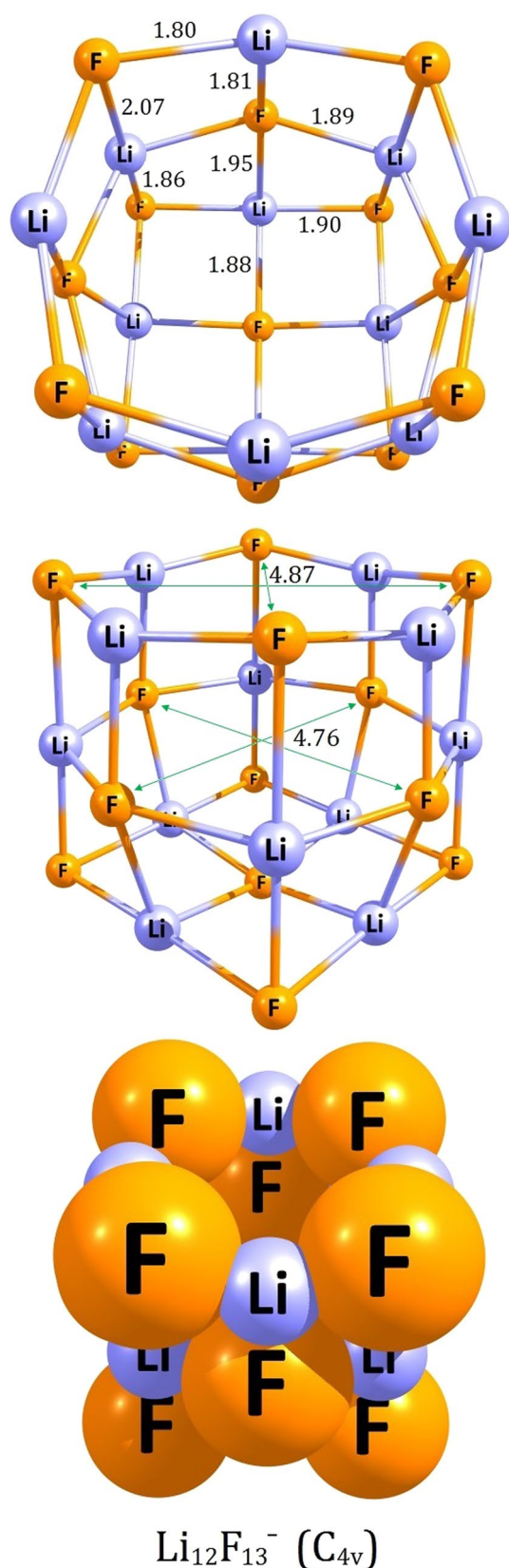


Fig. 1 Equilibrium structure of the C_{4v} -symmetry $\text{Li}_{12}\text{F}_{13}^-$ anion. The *bottom* view shows the Li and F nodes depicted as spheres representing the Li^+ and F^- ionic radii. Selected interatomic distances are given in Å

the central F atom are equal to 144.1° and 158.8°). The Li–F bond lengths involving the atoms constituting the base of the molecular basket were found to be in the 1.88–1.90 Å range, while the remaining Li–F bonds span the 1.80–2.07 Å range (see the detailed bond lengths in Fig. 1). Since the $\text{Li}_{12}\text{F}_{13}^-$ system holds an excess negative charge, one may assume the presence of a negatively charged cavity inside of its structure, which in turn might allow for an effective cation capturing. The cavity size depends on the distance between two central fluorine atoms belonging to the opposite walls of the $\text{Li}_{12}\text{F}_{13}^-$ equilibrium structure (see the lower part of Fig. 1 where the actual cavity size is shown by presenting the ionic radii of the lithium and fluorine nodes). According to our findings, the mentioned F–F distance is equal to 4.87 Å which indicates that only selected cations (i.e., characterized by the appropriate size) can be placed into the $\text{Li}_{12}\text{F}_{13}^-$ molecular cavity.

Since any prospective applications involving the $\text{Li}_{12}\text{F}_{13}^-$ anion require its thermodynamic stability against fragmentation processes, we verified its susceptibility to a few arbitrarily chosen (yet likely most probable) fragmentation reactions. In particular, we chose those routes that lead to the products considered as the most stable and characterized by the highest possible symmetry. The Gibbs free energy (ΔG) values obtained for such selected fragmentation paths span the 57.8–98.1 kcal/mol range which in turn indicates the thermodynamic stability of the $\text{Li}_{12}\text{F}_{13}^-$ anion against the corresponding reactions; see Table 1. It was also verified that other isomeric structures of the $\text{Li}_{12}\text{F}_{13}^-$ anion possess higher electronic energies which supports the conclusion that the basket-like structure presented in Fig. 1 indeed corresponds to the global minimum. Namely, the following $\text{Li}_{12}\text{F}_{13}^-$ isomers were found by testing various initial structures: (1) the quasi-planar layer (consisting of 12 lithium and 13 fluorine atoms) whose electronic energy turned out to be much larger (by 15 kcal/mol) than that of the global minimum structure, (2) the system resembling a regular primitive (simple) crystal structure (with the additional fluorine atom connected to it) whose energy was found to exceed that of the C_{4v} -symmetry molecular basket by ca. 5 kcal/mol (these

Table 1 Gibbs free energies (ΔG in kcal/mol) calculated for the selected fragmentation reactions of $\text{Li}_{12}\text{F}_{13}^-$ anion at the QCISD/6-311+G(d)//MP2/6-311+G(d) level (at $T = 298.15$ K)

Fragmentation reaction	ΔG (kcal/mol)
$\text{Li}_{12}\text{F}_{13}^- \rightarrow \text{Li}_{12}\text{F}_{12} + \text{F}^-$	74.9
$\text{Li}_{12}\text{F}_{13}^- \rightarrow \text{Li}_{11}\text{F}_{12}^- + \text{LiF}$	66.6
$\text{Li}_{12}\text{F}_{13}^- \rightarrow \text{Li}_{11}\text{F}_{11} + \text{LiF}_2^-$	62.8
$\text{Li}_{12}\text{F}_{13}^- \rightarrow \text{Li}_8\text{F}_9^- + \text{Li}_4\text{F}_4$	57.8
$\text{Li}_{12}\text{F}_{13}^- \rightarrow \text{Li}_8\text{F}_9^- + 2\text{Li}_2\text{F}_2$	98.1
$\text{Li}_{12}\text{F}_{13}^- \rightarrow \text{Li}_8\text{F}_8 + \text{Li}_4\text{F}_5^-$	60.4

Fig. 2 Local minima of $\text{Li}_{12}\text{F}_{13}^-$ superhalogen anion with their relative energy values (ΔE in kcal/mol)

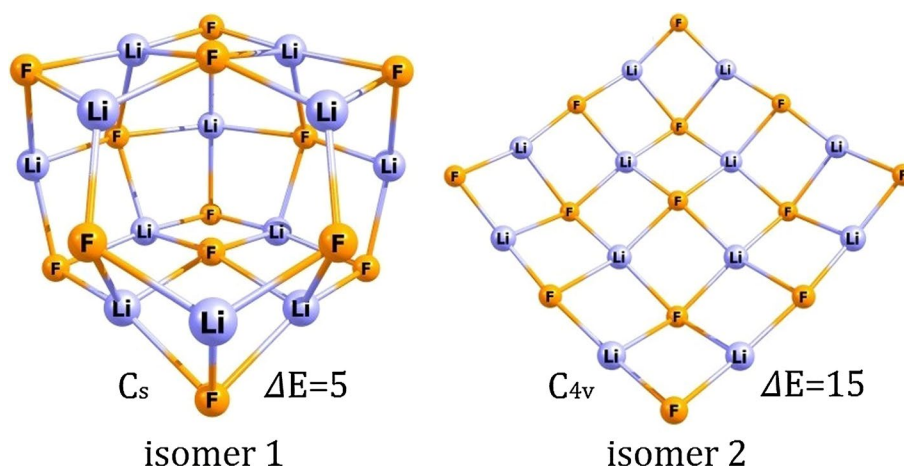


Table 2 Vertical electron detachment energies (in eV) of all $\text{Li}_{12}\text{F}_{13}^-$ anionic minima calculated at OVGF/6-311+G(3df) level

Species	VDE (eV)
$\text{Li}_{12}\text{F}_{13}^-$ global minimum	9.85
$\text{Li}_{12}\text{F}_{13}^-$ isomer 1 ($\Delta E = 5$ kcal/mol)	10.01
$\text{Li}_{12}\text{F}_{13}^-$ isomer 2 ($\Delta E = 15$ kcal/mol)	10.64

local minima are presented in Fig. 2). It seems also important to mention that many other attempts of locating different competitive structural isomers of the $\text{Li}_{12}\text{F}_{13}^-$ anion (performed by starting the geometry optimization process using various initial structures and by using Coalescence Kick (CK) method with the structure-generating algorithm [65]) led to the global minimum structure or to the local minima whose energies exceed that of the global minimum by over 20 kcal/mol.

Even though the evaluation of the electronic stability of the $\text{Li}_{12}\text{F}_{13}^-$ anion was not the main goal of this work, we provide it here for the reason of completeness. The VDE of the $\text{Li}_{12}\text{F}_{13}^-$ system was calculated to be 9.85 eV, thus indicating its superhalogen nature. As expected, the vertical electronic stability of $\text{Li}_{12}\text{F}_{13}^-$ is larger than the VDEs obtained for the $\text{Li}_n\text{F}_{n+1}^-$ ($n = 1-4$) systems, although slightly smaller than the VDE calculated for the Li_5F_6^- anion (VDE = 10.18) [28]. One may also notice that the vertical excess electron detachment energy of the $\text{Li}_{12}\text{F}_{13}^-$ anion is comparable to that of the well-known tetrahedral superhalogen AlF_4^- anion (VDE = 9.79 eV, as calculated at the same level of theory) [11]. VDEs of all $\text{Li}_{12}\text{F}_{13}^-$ minima described in this section are presented in Table 2.

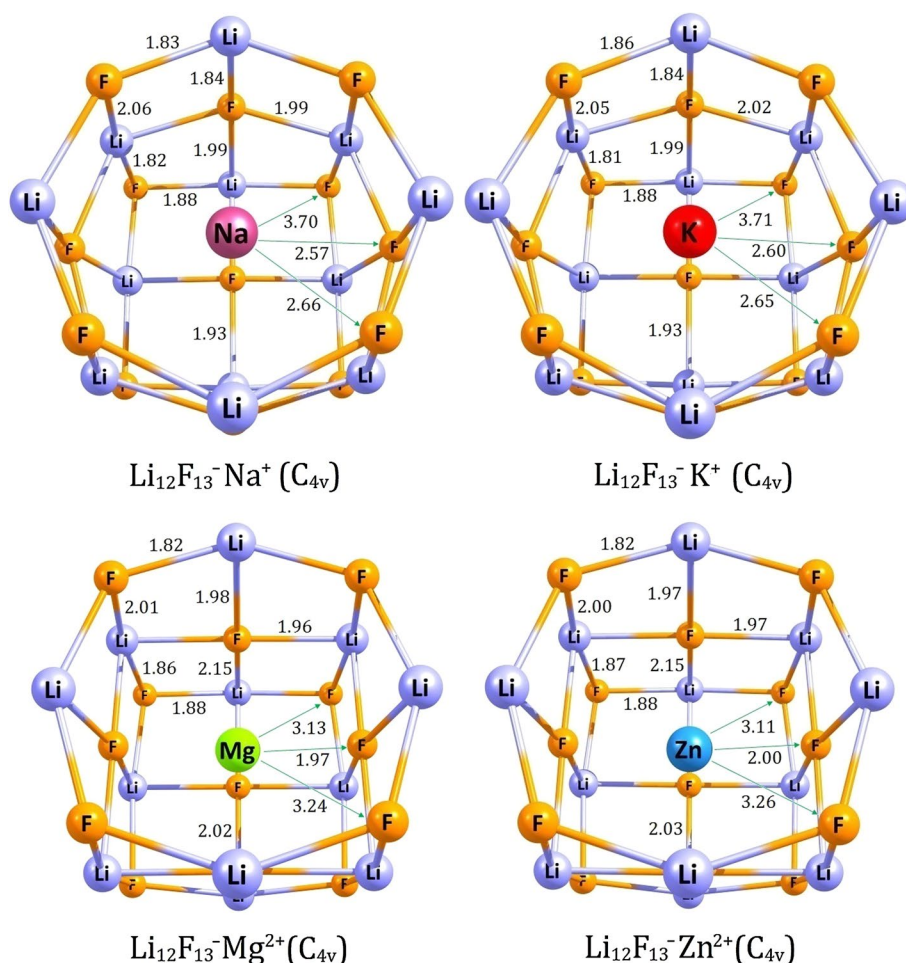
3.2 Ionic complexes with selected metal ions

After the description of the $\text{Li}_{12}\text{F}_{13}^-$ superhalogen anion we now present and discuss the results of our investigation

concerning its potential capability to act as an effective steric shielding agent. As indicated in the preceding section, the size of the cavity formed inside the $\text{Li}_{12}\text{F}_{13}^-$ structure (given by the separation between the F atoms located in the centers of the opposite walls of the molecular cage) can be estimated as equal to 4.87 Å; however, taking into account the radii of fluorine atoms constituting the structure, the actual size of the cavity should be considered as not exceeding 3 Å; see Fig. 1. Hence, it might be expected that certain metal cations whose radii are small enough to fit, can be embedded into the $\text{Li}_{12}\text{F}_{13}^-$ system. In order to verify this hypothesis we selected four cations having different ionic radii, i.e., Na^+ ($r = 1.02$ Å), K^+ ($r = 1.51$ Å), Mg^{2+} ($r = 0.72$ Å), and Zn^{2+} ($r = 0.74$ Å), to examine the steric shielding ability of the $\text{Li}_{12}\text{F}_{13}^-$ anion.

The equilibrium geometries of the $\text{Li}_{12}\text{F}_{13}^- \text{Na}^+$, $\text{Li}_{12}\text{F}_{13}^- \text{K}^+$, $\text{Li}_{12}\text{F}_{13}^- \text{Mg}^{2+}$, and $\text{Li}_{12}\text{F}_{13}^- \text{Zn}^{2+}$ ionic complexes are depicted in Fig. 3. Alike the isolated $\text{Li}_{12}\text{F}_{13}^-$ superhalogen anion, all these minimum energy structures correspond to C_{4v} -symmetry. Each cation is located inside the cavity formed by the $\text{Li}_{12}\text{F}_{13}^-$ structure; however, the monocations (Na^+ and K^+) are situated closer to its edge, whereas the dications (Mg^{2+} and Zn^{2+}) are embedded deeper (see the interatomic distances between metal ions and selected fluorine atoms presented in Fig. 2). The partial atomic charges localized on the Na, K, Mg, and Zn atoms are equal to +0.5, +0.7, +0.7, and +1.3 a.u., respectively, thus indicating that their excess positive charge is preserved. The structure of the $\text{Li}_{12}\text{F}_{13}^-$ moiety in each complex is only slightly deformed in comparison with the basket-like structure of the $\text{Li}_{12}\text{F}_{13}^-$ isolated anion. Namely, the lengths of the Li–F bonds change by less than 0.2 Å when the $\text{Li}_{12}\text{F}_{13}^-$ relaxes its structure while interacting with any of the cations studied (see Figs. 1, 2 for the details). The largest structural effect of the cation insertion is observed for both Mg^{2+} and Zn^{2+} dications whose interactions with the $\text{Li}_{12}\text{F}_{13}^-$ lead to the spatial extension

Fig. 3 Equilibrium structures of the $\text{Li}_{12}\text{F}_{13}^- \text{Na}^+$, $\text{Li}_{12}\text{F}_{13}^- \text{K}^+$, $\text{Li}_{12}\text{F}_{13}^- \text{Mg}^{2+}$, and $\text{Li}_{12}\text{F}_{13}^- \text{Zn}^{2+}$ ionic complexes. Selected interatomic distances are given in Å



of the anionic basket. This extension is clearly visible when the Li–F bond lengths between the nodes constituting the quasi-square cavity base are concerned; namely, the distance between the central F atom and any of the Li atoms is elongated to 2.02 and 2.03 Å in $\text{Li}_{12}\text{F}_{13}^- \text{Mg}^{2+}$ and $\text{Li}_{12}\text{F}_{13}^- \text{Zn}^{2+}$, respectively, whereas the analogous distance is shorter for both $\text{Li}_{12}\text{F}_{13}^- \text{Na}^+$ and $\text{Li}_{12}\text{F}_{13}^- \text{K}^+$ (1.93 Å); see Fig. 3. Clearly, these effects are caused by the deeper location of the Mg^{2+} and Zn^{2+} dications in the $\text{Li}_{12}\text{F}_{13}^-$ cavity in comparison with the Na^+ and K^+ monocations.

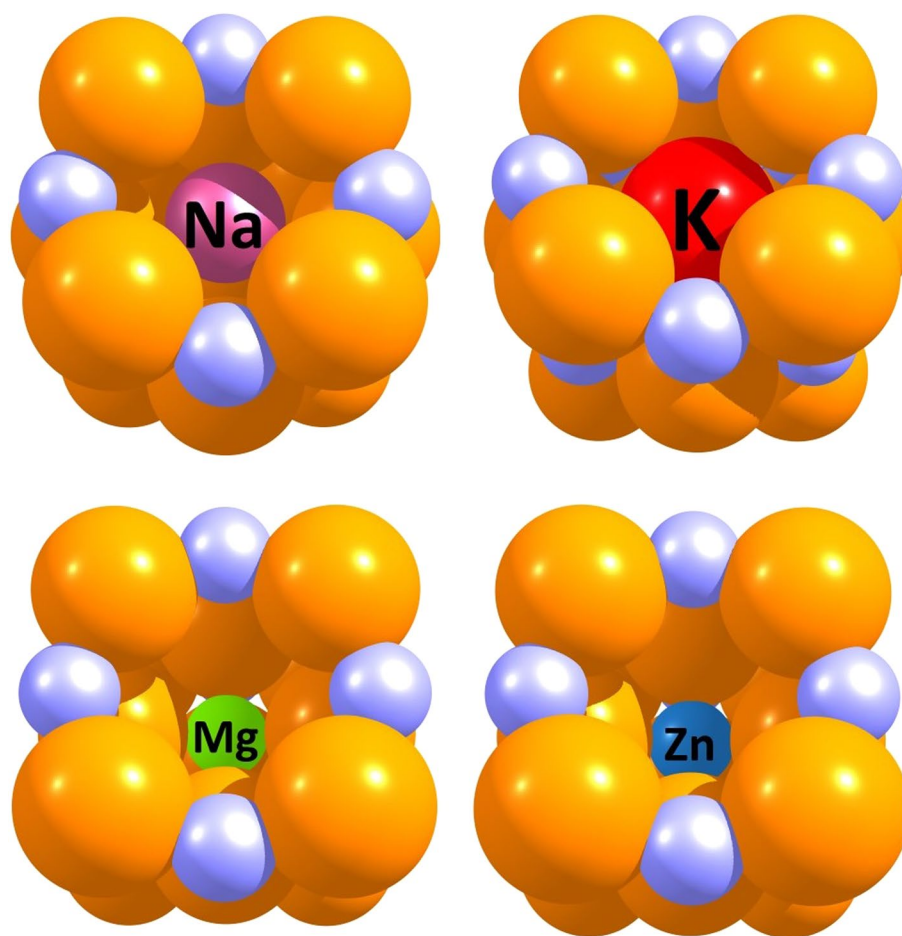
The equilibrium structures of the $\text{Li}_{12}\text{F}_{13}^- \text{Na}^+$, $\text{Li}_{12}\text{F}_{13}^- \text{K}^+$, $\text{Li}_{12}\text{F}_{13}^- \text{Mg}^{2+}$, and $\text{Li}_{12}\text{F}_{13}^- \text{Zn}^{2+}$ ionic complexes indicate that the $\text{Li}_{12}\text{F}_{13}^-$ superhalogen anion can bind selected metal ions inside its basket-like structure and form geometrically stable ionic complexes. Hence, the $\text{Li}_{12}\text{F}_{13}^-$ anion might be expected to play an important role in the steric shielding process. It should be stressed that not only cations from the first and second groups of the periodic table but even the transition metals (e.g., Zn^{2+}) can be inserted inside the $\text{Li}_{12}\text{F}_{13}^-$ cage; see Fig. 3. These

Table 3 Binding energies (BE in kcal/mol) between the $\text{Li}_{12}\text{F}_{13}^-$ superhalogen anion and selected metal ions placed inside its cavity

Species	Symmetry	BE (kcal/mol)
$\text{Li}_{12}\text{F}_{13}^- \text{Na}^+$	C_{4v}	105.4
$\text{Li}_{12}\text{F}_{13}^- \text{K}^+$	C_{4v}	83.5
$\text{Li}_{12}\text{F}_{13}^- \text{Mg}^{2+}$	C_{4v}	406.4
$\text{Li}_{12}\text{F}_{13}^- \text{Zn}^{2+}$	C_{4v}	426.5

conclusions are also supported by the analysis of the calculated binding energies between the ionic complex subunits. The BE values (calculated as the difference between the energy of the complex and those of isolated ions) are in the range of 83.5–426.5 kcal/mol; see Table 3. It needs to be emphasized that all examined complexes are very strongly bound ionic compounds (binding energies exceed 83 kcal/mol), but those involving dications are obviously more strongly bound systems than the complexes formed by trapping either sodium or potassium ions. The difference

Fig. 4 Equilibrium geometries of the $\text{Li}_{12}\text{F}_{13}^{-}\text{Na}^{+}$, $\text{Li}_{12}\text{F}_{13}^{-}\text{K}^{+}$, $\text{Li}_{12}\text{F}_{13}^{-}\text{Mg}^{2+}$, and $\text{Li}_{12}\text{F}_{13}^{-}\text{Zn}^{2+}$ ionic complexes (the Li and F nodes and the embedded cations are depicted as spheres representing their ionic radii)



between binding energies of $\text{Li}_{12}\text{F}_{13}^{-}\text{Na}^{+}$ and $\text{Li}_{12}\text{F}_{13}^{-}\text{K}^{+}$ systems (ca. 22 kcal/mol) is likely caused by the larger size of potassium cation as the tight packing of atoms in the case of $\text{Li}_{12}\text{F}_{13}^{-}\text{K}^{+}$ structure may result in destabilizing valence repulsion effects which reduce the BE value; see Fig. 4. In contrast, analogous difference in binding energy between $\text{Li}_{12}\text{F}_{13}^{-}\text{Mg}^{2+}$ and $\text{Li}_{12}\text{F}_{13}^{-}\text{Zn}^{2+}$ compounds (ca. 20 kcal/mol) may be caused by the larger positive partial atomic charge located on the Zn atom (+1.3 a.u.) in comparison with the Mg atom (+0.7 a.u.).

Due to the fact that each of the $\text{Li}_{12}\text{F}_{13}^{-}\text{Na}^{+}$, $\text{Li}_{12}\text{F}_{13}^{-}\text{K}^{+}$, $\text{Li}_{12}\text{F}_{13}^{-}\text{Mg}^{2+}$, and $\text{Li}_{12}\text{F}_{13}^{-}\text{Zn}^{2+}$ represents a strongly bound ionic complex whose equilibrium structure consists of a cation hidden inside the $\text{Li}_{12}\text{F}_{13}^{-}$ trap, none of these metal ions can directly react with molecular species in the surrounding area. Therefore, the $\text{Li}_{12}\text{F}_{13}^{-}$ anion itself can be treated as a promising steric shielding agent with respect to selected metal ions (whose ionic radius does not exceed that of K^{+}). This novel property of the polynuclear high-symmetry superhalogen anions (which the $\text{Li}_{12}\text{F}_{13}^{-}$ anion is a representative example of) might be utilized in the future and, analogously to crown ethers, could enable the entering of metal ions into various solutions.

4 Conclusions

The electronic and thermodynamic stability of the polynuclear $\text{Li}_{12}\text{F}_{13}^{-}$ anion and its possible application as an effective steric shielding system embedding selected metal cations (Na^{+} , K^{+} , Mg^{2+} , and Zn^{2+}) were investigated on the basis of the ab initio calculations carried out at the MP2/6-311+G(*d*) level (for equilibrium geometries and force constants) and the QCISD/6-311+G(*d*) and MP4(SDQ)/6-311+G(*d*) levels (for electronic energies). The analysis of the results led us to the following conclusions:

1. The $\text{Li}_{12}\text{F}_{13}^{-}$ system is a strongly bound and thermodynamically stable polynuclear superhalogen anion whose vertical excess electron detachment energy was evaluated as equal to 9.85 eV.
2. The equilibrium geometry of the $\text{Li}_{12}\text{F}_{13}^{-}$ anion corresponds to the high-symmetry (C_{4v}) compact structure and resembles a molecular basket with the negatively charged cavity inside. The size of the cavity (about 3 Å) allows for trapping selected metal ions (Na^{+} , K^{+} , Mg^{2+} , and Zn^{2+}).

- The ionic $\text{Li}_{12}\text{F}_{13}^{-}\text{Na}^{+}$, $\text{Li}_{12}\text{F}_{13}^{-}\text{K}^{+}$, $\text{Li}_{12}\text{F}_{13}^{-}\text{Mg}^{2+}$, and $\text{Li}_{12}\text{F}_{13}^{-}\text{Zn}^{2+}$ are characterized by the large binding energies (83.5–426.5 kcal/mol) between the $\text{Li}_{12}\text{F}_{13}^{-}$ and $\text{M}^{+/2+}$ components.
- In each equilibrium structure of the complexes investigated the cation is hidden inside the $\text{Li}_{12}\text{F}_{13}^{-}$ molecular trap and thus cannot react with any species in the surrounding area. Therefore, the $\text{Li}_{12}\text{F}_{13}^{-}$ anion can be considered as a steric shielding agent with respect to selected metal ions.

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