

RESEARCH ARTICLE



# On predicting bonding patterns of small clusters of alkaline-earth (Be, Mg) and triel (B, Al) fluorides: a balance between atomic size and electron-deficient character

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## ABSTRACT

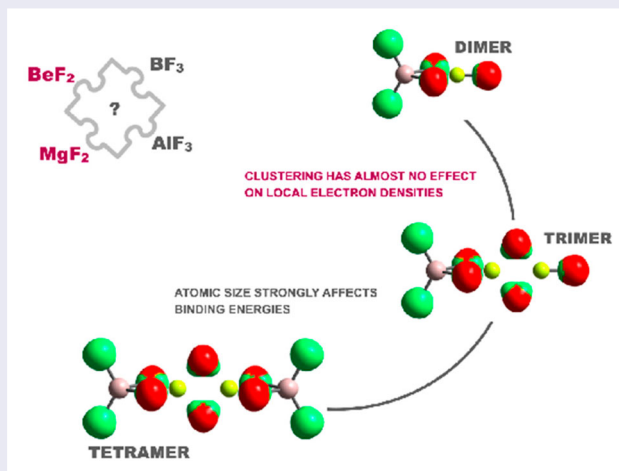
The structures, bonding and stability of  $(MF_2)_m:(M'F_3)_n$  ( $M = \text{Be, Mg}; M' = \text{B, Al}; m = 0,1,2; n = 0,1,2$ ) clusters were obtained at the B3LYP/aug-cc-pVTZ level of theory. To understand trends across this set of closely related atoms, an analysis of the results obtained using atoms in molecules (AIM), electron localisation function (ELF) and electron density shift (EDS) approaches, permits to identify subtle dissimilarities when the first-row elements, Be and B, are replaced by the second-row counterparts, Mg and Al. For dimers this replacement involves an increase in the bonding enthalpies as a direct consequence of a much larger ionic character of the derivatives including second-row elements. For trimers and tetramers, rather stable structures involving penta-coordinated aluminium atoms are formed, which are not found for the B-containing analogues. In all clusters investigated the electronic environment around each monomer does not change significantly neither with nature of the monomers interacting with it or with the size of the cluster, though some small cooperative effects are observed when analyzing the binding enthalpies. The important consequence is that the stability of larger clusters can be easily predicted through a statistical treatment of the values obtained for the smaller ones.

## ARTICLE HISTORY

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## Introduction

Computation and theoretical chemistry play a key role in the understanding of chemical bonding and structure since the middle of the last century. One of the milestones in this process clearly was the publication

of the theoretical study of methylene in 1960 by Foster and Boys, [1] who using a Configuration Interaction (CI) procedure concluded that the ground state of methylene was a <sup>3</sup>B<sub>1</sub> state, in which the H–C–H angle was 129°. At that time no experimental information on

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$\text{CH}_2$  was available to compare with. Just one year later, Herzberg, through the analysis of the electronic spectrum of methylene concluded that in its triplet ground state this molecule was linear [2]. One year later this conclusion would be ratified by Jordan and Longuet-Higgins [3] by using a semi-empirical quantitative theory. It was necessary to wait almost a decade to have new theoretical predictions, this time based on *ab initio* valence bond theory, [4] indicating that methylene was bent in its ground triplet state with a bond angle of  $138^\circ$ . A year later in 1970, Bender and Schaefer [5] through the use of CI calculations including a total of  $408\ ^3\text{B}_1$  configurations, concluded again that in its ground state  $\text{CH}_2$  was bent with a bond angle of  $131.5^\circ$ . Little later, electron paramagnetic resonance (EPR) studies confirmed  $136^\circ$  as the most probable value for the bond angle of methylene [6]. Another very interesting case was that of diborane. The first serious attempt to elucidate its electronic structure was reported by Mulliken in 1935, but his work predicted that  $\text{B}_2\text{H}_6$  should probably, but not certainly, be paramagnetic [7]. Almost ten years later, Longuet-Higgins and Bell [8] suggested that diborane contained  $\text{B}\cdots\text{H}\cdots\text{B}$  hydrogen-bridge linkages and that this description was supported by experimental data from electron diffraction, Raman and infrared spectroscopy. However, they assumed this structure to be the result of the resonance between structures containing only normal electron-pair bonds. In 1954 Ebergardt et al. introduced the concept of localised three-centre bonds to describe the bonding of boron hydrides [9]. The three-centre bond theory would be extended by Hoffman and Lipscomb to describe a large series of boron hydrides [10].

Nowadays, the contribution of computation and theoretical chemistry to the development of modern chemistry is clearly out of question, and after the pioneering works mentioned above many researchers all around the world had been working in developing new formalisms to make theoretical chemistry a very reliable tool either to explain or even to predict molecular properties. This is the case of the researcher to whom this special issue is dedicated. P. Gill has made very significant contributions, too many to be summarised here, but among them we can singularise as representative examples the intracule function for the two electron density, [11] the quadrature grid for DFT, [12] the BFW density functional for transition metal clusters, [13] or the density functional triple jumping, [14] among many others.

One of the advantages of theoretical calculations is that they provide a safe way to predict the properties of substances whose experimental study is very dangerous due to their high toxicity. This is the case, for instance, of beryllium and its derivatives, [15] with the obvious consequence that the experimental information

on Be-containing compounds is rather scarce. Be and the elements of its group in the periodic table together with boron and the elements of its group are electron-deficient systems [16]. The obvious consequence is that they are intrinsically good Lewis acids and yield rather stable complexes when interacting with different Lewis bases. This is behind the high stability and enhanced acidity of phosphine-boranes [17] and aminoboranes [18]. The high Lewis acidity of Be derivatives is manifested in the formation of the so called beryllium bonds, [19] when they interact with Lewis bases, changing common hydrocarbons into strong acids in the gas-phase, [20] or inducing the spontaneous formation of ion-pairs, [21] or the formation of anion sponges [22].

An interesting and closely related question is what the behaviour of these electron-deficient systems would be when they interact each other. In the gas phase, beryllium fluoride and boron fluoride may form  $\text{Be}\cdots\text{F}\cdots\text{Be}$  and  $\text{B}\cdots\text{F}\cdots\text{B}$  bridges, but mixing both compounds in small clusters lead to the question of what bonding patterns should be expected, as both atoms can reach tetra-coordination. We published recently a first attempt to answer this question by analyzing the structure and stability of clusters containing Be and B fluorides [23]. The conclusion was that the differences between Be and B are already evident when looking at the possible dimers. Whereas the  $(\text{BeX}_2)_2$  homodimers are very stable, the  $(\text{BX}_3)_2$  homodimers are not and, in most cases, they are not formed, and the  $\text{BeX}_2\text{:BX}_3$  heterodimers are systematically less stable than Be-homodimers. Similarly for the trimers the  $(\text{BeX}_2)_2(\text{BX}_3)$  arrangement is more stable than the  $\text{BX}_3\text{-BeX}_2\text{-BX}_3$  one, whereas no stable  $\text{BeX}_2(\text{BX}_3)_2$  trimers can be found. Consistently, for  $(\text{BeX}_2)_2(\text{BX}_3)_2$  tetramers, the  $(\text{BeX}_2)_2$  subunit is systematically at the centre of the cluster.

The aim of this paper is to analyze what is the behaviour of mixed clusters when we include in the set the elements of the second row, i.e. Mg and Al, and in particular when the mixed clusters envisaged include compounds of these two groups when they are of a different row, that is, what are the characteristics not only of Be-B or Mg-Al clusters but also of Be-Al and B-Mg clusters. For this purpose, we have chosen the fluorine derivatives,  $\text{BeF}$ ,  $\text{MgF}_2$ ,  $\text{BF}_3$ ,  $\text{AlF}_3$ , and we include mixed dimers, trimers and tetramers.

## Computational details

We have adopted the same computational model used in our previous investigation of Be-B clusters [23] which is based on B3LYP/aug-cc-pVTZ calculations, which implies the use of a rather flexible triple-zeta basis set with an adequate number of diffuse functions.



This formalism was found to reproduce the energetic trends obtained at the more expensive CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level of theory.

The electron density redistribution that takes place when these mixed clusters are formed was analyzed by means of the Quantum Theory of Atoms in Molecules (QTAIM) [24]. This topological method permits to localise critical points of the molecular electron density,  $\rho(\mathbf{r})$ , in particular the so-called bond critical points (BCPs), associated to the bonding interaction between two atoms of the system, or the so-called ring critical points that appear when a cyclic structure is formed. On top of that, the changes in electron density in the BCP associated with a chemical bond are a good way to detect the strengthening or weakening of the bond when its environment changes.

A complementary formalism is the electron localisation function (ELF) [25]. The ELF allows finding highly localised electrons in regions of the molecular space, these regions being characterised by a low value of the excess local kinetic energy. These regions, called basins and whose population can be quantified, permit therefore to identify atom cores and electron pairs. Monosynaptic basins are associated to a single atom, being either from the core or electron lone-pairs. The disynaptic (or polysynaptic) basins are associated to two or more atoms of the system and they correspond to bonding pairs. In our ELF plots we have used an isovalue (0.80) that favours a good visualisation of the different basins. Note however, that the isovalue used only affects the shape of the basins but not their populations. Finally, a clear and direct picture of the electron density shift (EDS) that takes place from the Lewis base to the Lewis acid when the cluster is formed can be obtained from the EDS method [26]. This method evaluates and plot the difference between the electron density of the complex and the electron density of each of the isolated monomers that formed the complex, when maintaining the geometry they have in the complex. In this way is very easy to identify which areas of the electron donor are preferentially depopulated and which areas of the Lewis acid are preferentially populated.

## Results and discussion

### Dimers: the basic patterns

Let us start our discussion with the analysis of the dimers investigated. In Figure 1 we present, associated to their optimised structures, the binding enthalpy as the enthalpy necessary to dissociate the cluster into the corresponding monomers in their equilibrium conformation.

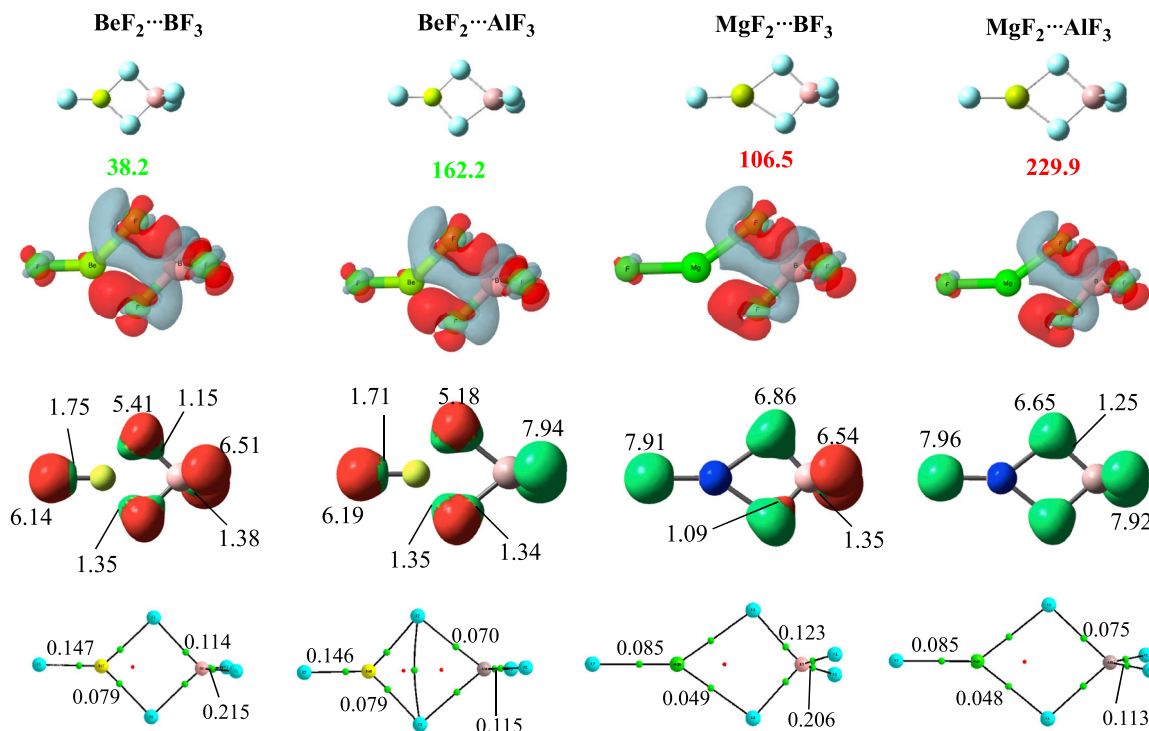
The first conspicuous fact, as already found in ref [23], for the case the  $\text{BeF}_2$ - $\text{BF}_3$  dimer, is that the  $\text{BeF}_2$

( $\text{MgF}_2$ ) monomers, which are linear molecules, become bent within the cluster because they accommodate into the empty  $p$  orbitals of the Be (Mg) atom a significant electron density coming from the lone pairs of one of the fluorine atoms of the  $\text{BF}_3$  ( $\text{AlF}_3$ ) monomers. This is nicely visualised in the EDS plots (see second row of Figure 1) where the red lobes denote the areas in which the electron density is accumulated, whereas grey ones correspond to areas where the electron density is depleted. This electron density transfer results in a hybridisation change at the Be (Mg) atom from the initial  $sp$  arrangement into a  $sp^2$ -like one. Concomitantly, the EDS plots also show a similar electron density transfer from one of the F atoms of the  $\text{BeF}_2$  moiety into the empty  $p$  orbital of the B (Al) atom of the  $\text{BF}_3$  ( $\text{AlF}_3$ ) unit, that changes the initial planar tricoordinated arrangement ( $sp^2$  hybridisation) into a tetrahedral distribution and  $sp^3$  hybridisation. The obvious consequence of the significant distortion of both monomers within the cluster is that the cluster dissociation energy into the monomers, with the geometry they have in the cluster (diabatic process), is from 1.5 to 6.7 times larger than the adiabatic one (see Table S1 of the Supporting Information).

The second important fact is the huge increase in the binding enthalpies when  $\text{BF}_3$  is replaced by  $\text{AlF}_3$  or when  $\text{BeF}_2$  is replaced by  $\text{MgF}_2$ . To well understand these significant energetic stabilisations, it is convenient to look to the ELF plots for each of the dimers, that are shown in the third line of Figure 1. The first evident change on going from the  $\text{BeF}_2$ - $\text{BF}_3$  dimer to the  $\text{BeF}_2$ - $\text{AlF}_3$  analogues is the change in the nature of the interatomic interactions. For the  $\text{BeF}_2$ - $\text{BF}_3$  cluster the bonding between both Be and B with the F atoms is typically of a covalent polar linkage. For the Be-F linkages there is a disynaptic basin with populations 1.35 and 1.75 e, and monosynaptic basins with populations 5.4 and 6.1 e, corresponding to the fluorine lone pairs. The same description is observed for the B-F interactions, with disynaptic basins (populations 1.15 and 1.38) and monosynaptic ones (populations 6.5 and 5.4 e). When  $\text{BF}_3$  is replaced by  $\text{AlF}_3$  as shown in the ELF plot, the Al-F become ionic, with disynaptic basins on the F atoms attached to Al with a population close to 8 e. A similar change is observed, if we compared now the ELF plot of the  $\text{BeF}_2$ - $\text{BF}_3$  dimer with that of the  $\text{MgF}_2$ - $\text{BF}_3$  one. For the former, as just mentioned in the previous paragraph, the Be-F bonding exhibits disynaptic Be-F basins, whereas for the  $\text{MgF}_2$  containing analogue the Mg-F bonding is ionic, with disynaptic basins on the F atoms with populations close to 8 e.

It is important to emphasise that the ionic-covalent character is not related strictly with the valence populations but with the distribution of the electron density according to the ELF picture. For instance, if we compare





**Figure 1.**  $\text{MF}_2\cdots\text{M}'\text{F}_3$  ( $\text{M} = \text{Be, Mg}$ ;  $\text{M}' = \text{B, Al}$ ) dimers. First row contains the optimised structure and the corresponding binding enthalpy ( $\text{kJ}\cdot\text{mol}^{-1}$ ). Green (light-grey) and red (dark-grey) values ( $\text{kJ}\cdot\text{mol}^{-1}$ ) correspond to Be- and Mg-containing clusters, respectively. Second row shows the EDS plots. Red (dark-grey) and grey (light-grey) lobes correspond to areas in which the electron density is accumulated and depleted, respectively. Third row presents the ELF plots with an isovalue of 0.80. The population of each basin is indicated in electrons. Monosynaptic basins are shown in red (dark-grey) and disynaptic in green (light-grey). Fourth line shows the molecular graphs including the electron densities (a.u.) at the corresponding BCPs (green dots).

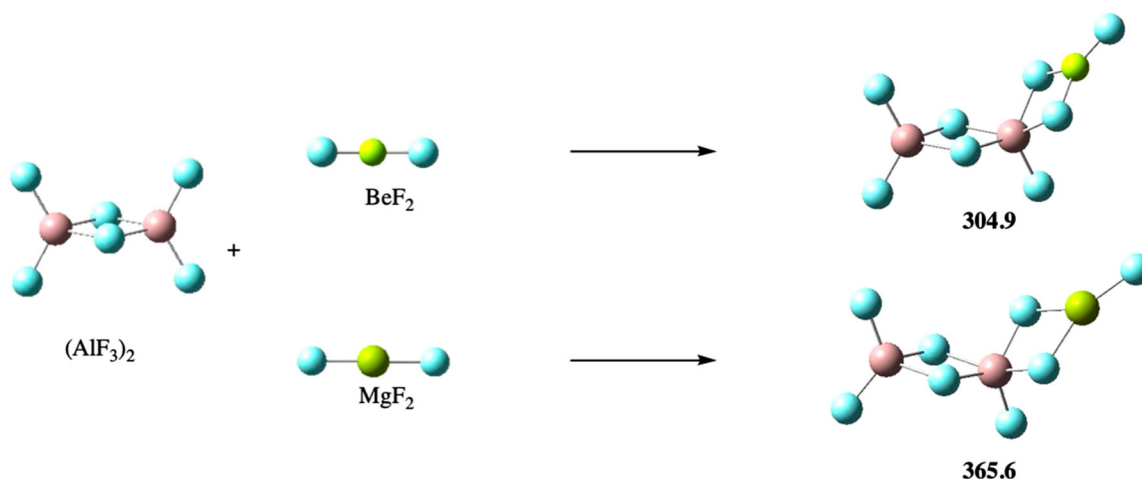
$\text{BeF}_2\cdots\text{BF}_3$  with  $\text{MgF}_2\cdots\text{BF}_3$  in Figure 1, and we look only at the two F atoms attached only to Be and Mg, we realise that the total valence populations around them are  $6.14 + 1.75 = 7.89\text{ e}^-$  for the F attached to Be and  $7.91\text{ e}^-$  for the F attached to Mg, which are practically equal. However, the shape and synapticity of the two F basins, which are shown in the picture, are different, as it is the volume (not shown in the figure) of the two F basins ( $162.64\text{ u}^3$  for the F attached to Be and  $191.98\text{ u}^3$  for the F attached to Mg). Moreover, the location of the centre of the F basins (see Figure S1 of the Supporting Information) is also pretty different.

Going now to the  $\text{MgF}_2\cdots\text{AlF}_3$  analogues, both Mg-F and Al-F are essentially ionic. Another important feature revealed by the ELF is that on going from the  $\text{BeF}_2\cdots\text{BF}_3$  to the  $\text{BeF}_2\cdots\text{AlF}_3$  complex the populations of the disynaptic basins in which Be participates remain practically constant. Similarly, on going from the  $\text{BeF}_2\cdots\text{AlF}_3$  to the  $\text{MgF}_2\cdots\text{AlF}_3$  the populations of the basins in which Al participates remain practically unchanged. Hence in general the electron density distribution around a certain monomer is not much affected by the nature of the other monomer with which it interacts.

This description is coherent with the one obtained with the AIM approach which show again that the electron density at the BCPs of the bonds in which the Be or the Mg atom participates is essentially the same in complexes with  $\text{BF}_3$  or  $\text{AlF}_3$ . Coherently, the electron density at the BCPs of the bonds in which B or Al atoms participate is essentially the same in complexes with  $\text{BeF}_2$  or  $\text{MgF}_2$ . Also, the increase of the ionic character of the interactions when Be is replaced by Mg or B is replaced by Al, is reflected in a decrease of the electron density at the Mg-F or Al-F BCPs with respect to the Be-F or B-F analogues.

The fact that the Mg-F and Al-F bonds are ionic is at the origin of the huge increase in the binding energies observed when Be is replaced by Mg or B is replaced by Al. Indeed, if in the  $\text{BeF}_2\cdots\text{BF}_3$  cluster  $\text{BF}_3$  is replaced by  $\text{AlF}_3$ , there is a huge increase in the binding enthalpy that can be easily understood if one takes into account that the natural atomic charge which at the B atom is +1.2, at the Al atom is +2.2. Also, whereas the natural charge of the F atoms attached to the B atom are  $-0.5$  and  $-0.6$ , when attached to Al become  $-0.8$  and  $-0.75$ . Hence, since in the  $\text{AlF}_3$  containing cluster





**Figure 2.** The interaction of  $\text{BeF}_2$  or  $\text{MgF}_2$  with  $(\text{AlF}_3)_2$  dimer leads to a cluster in which one of the Al atoms is penta-coordinated. Their dissociation enthalpies into the three monomers are given in  $\text{kJ}\cdot\text{mol}^{-1}$ .

the ionic interactions dominate and the net charges are much larger than for the  $\text{BF}_3$ -containing analogue, the calculated binding enthalpy is also much larger (162 vs  $38 \text{ kJ}\cdot\text{mol}^{-1}$ ). A similar but less pronounced phenomenon occurs when  $\text{BeF}_2$  is replaced by  $\text{MgF}_2$  (230 vs  $106 \text{ kJ}\cdot\text{mol}^{-1}$ ), because the net natural charge at the Mg atom (+1.9) is larger than at the Be atom (+1.7) and the net charges at the F atoms are pretty similar ( $-0.9$  if bound to Mg and  $-0.8$  if bound to Be). Essentially, Be and Mg are more alike than B and Al, and therefore although still the  $\text{MgF}_2$ -containing clusters exhibit a larger binding enthalpy than the  $\text{BeF}_2$ -containing analogues ( $106$  vs.  $38 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $230$  vs  $162 \text{ kJ}\cdot\text{mol}^{-1}$ ), the difference is smaller.

### Trimers: appearance of highly coordinated structures

Two different series of trimers can be envisaged, the ones that involved two  $\text{BeF}_2$  (or two  $\text{MgF}_2$ ) units interacting with one molecule of  $\text{BF}_3$  (or  $\text{AlF}_3$ ) or those in which the duplicated units are  $\text{BF}_3$  (or  $\text{AlF}_3$ ) interacting with a monomer of  $\text{BeF}_2$  (or  $\text{MgF}_2$ ). Within each of these series there are two possible arrangements:  $\text{M}'\text{M}'\text{M}$  or  $\text{M}'\text{MM}'$ . For the particular case in which  $\text{M}' = \text{BF}_3$  and  $\text{M} = \text{BeF}_2$  it was found that the  $\text{M}'\text{M}'\text{M}$  cluster is not prone to be formed [23], because the formation of  $(\text{BF}_3)_2$  dimers is practically endothermic [27]. The situation changes dramatically when  $\text{BF}_3$  is replaced by  $\text{AlF}_3$ , due to the ionic nature of the latter. Indeed, unlike in  $(\text{BF}_3)_2$ , the formation of the  $(\text{AlF}_3)_2$  dimer is exothermic by  $185.2 \text{ kJ}\cdot\text{mol}^{-1}$ . The obvious consequence is that whereas the  $\text{BF}_3\text{-BF}_3\text{-BeF}_2$  clusters are not prone to be formed, [23] the  $(\text{AlF}_3)_2\text{BeF}_2$  and  $(\text{AlF}_3)_2\text{MgF}_2$  are predicted to be very stable with binding energies of 304.9 and

$365.6 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively; but with one remarkable peculiarity. When attaching  $\text{BeF}_2$  or  $\text{MgF}_2$  to the  $(\text{AlF}_3)_2$  dimer, a spontaneous migration of one F atom towards the Al centre takes place leading to a penta-coordinated Al centre (see Figure 2).

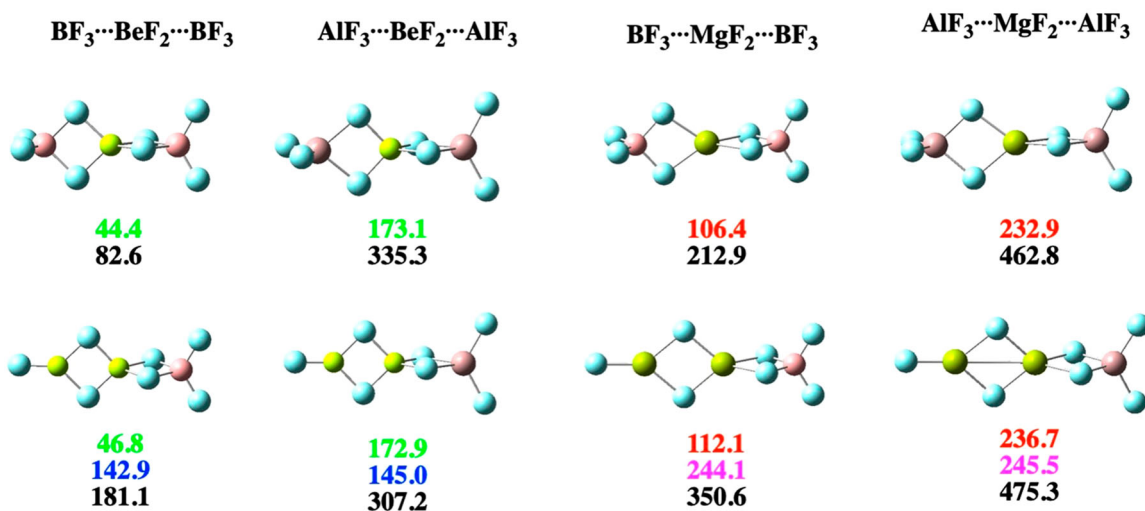
Perhaps the novelty is that although the existence of Al penta-coordinated atoms is well known in zeolites, catalysis and solid-state chemistry, [28] in our case we are dealing with rather small clusters in the gas-phase. Furthermore, an inspection of the corresponding molecular graphs (see Figure S2 of the Supporting Information) shows that the new Al-F bond formed in this transfer is the strongest one since that fluorine atom is the only of five around Al not shared with any other atom. We can already say that a similar scenario will be observed when dealing with tetramers, where, as shown in the second row of Figure S2 of the Supporting Information, also structures with penta-coordinated aluminium atoms are local minima of the potential energy surface.

Nevertheless, the  $\text{M}'\text{M}'\text{M}$  ( $\text{M}' = \text{Al}$ ,  $\text{M} = \text{Be}$ ,  $\text{Mg}$ ) clusters in Figure 2 are less stable than the  $\text{M}'\text{MM}'$  isomers ( $304.9$  vs.  $335.3$  and  $365.6$  vs.  $462.8 \text{ kJ}\cdot\text{mol}^{-1}$ , see first line of Figure 3), because as in the case of boron [23] the interactions  $\text{Al}\cdots\text{Be}$  or  $\text{Al}\cdots\text{Mg}$  through fluorine bridges are more stabilising than the  $\text{Al}\cdots\text{Al}$  ones.

Due again to the larger ionicity of  $\text{MgF}_2$  the binding energy for  $(\text{MgF}_2)_2$  ( $238.6 \text{ kJ}\cdot\text{mol}^{-1}$ ) is  $104.3 \text{ kJ}\cdot\text{mol}^{-1}$  larger than that of  $(\text{BeF}_2)_2$  [23]. This is also reflected in a larger stability of the trimers involving Mg-dimers ( $350.6$  and  $475.3 \text{ kJ}\cdot\text{mol}^{-1}$ ) with respect to those involving Be-dimers ( $181.1$  and  $307.2 \text{ kJ}\cdot\text{mol}^{-1}$ ), as illustrated in the second row of Figure 3.

The formation of these  $\text{M}'\text{MM}'$  and  $\text{MMM}'$  clusters involves some interesting cooperativity effects. This is evident if one compares the dissociation energies to yield





**Figure 3.** Structure and energetics of M'MM' (first row) and MMM' (second row) trimers. The dissociation enthalpies (in  $\text{kJ}\cdot\text{mol}^{-1}$ ) are listed below each structure as follows: bottom values correspond to dissociation of the trimer into the three monomers, upper values correspond to the breaking of  $\text{BeF}_2$  interactions either with  $\text{BF}_3$  or  $\text{AlF}_3$ , or to the breaking of  $\text{MgF}_2$  interactions either with  $\text{BF}_3$  or  $\text{AlF}_3$ . Middle values represent the breaking of  $\text{BeF}_2\text{--BeF}_2$  or  $\text{MgF}_2\text{--MgF}_2$  interactions.

$\text{BF}_3$  (or  $\text{AlF}_3$ ) monomers (green and red values) with those found for the dimers in Figure 1 (44.4 and 46.8 vs. 38.2; 173.1 and 172.9 vs.  $162.2\text{ kJ}\cdot\text{mol}^{-1}$ , as suitable examples). The variations are, however, not significantly large, reflecting that, as mentioned above, the electron density distribution around a certain monomer is not much affected by the interaction with other monomers within the cluster. This is once more very well reflected in the corresponding molecular graphs shown in Figure S3 of the Supporting Information, which show that the electron densities at the BCPs for a given monomer do not change significantly when going from the dimers to the trimers. This is consistent with the scenario in terms of the ELF and the EDS plots (see Figure S4 of the Supporting Information) which shows that the nature of the ELF basins and their populations for these trimers are very similar to those for the dimers in Figure 1, whereas the EDS areas, in which the electron density is accumulated or depleted, are almost identical to the ones shown for the dimers in Figure 1. The same feature explains that for MMM' trimers (second row in Figure 3) the breaking of the MM interaction ( $M = \text{Be}, \text{Mg}$ ) does not change significantly when  $\text{BF}_3$  ( $142.9$  and  $244.1\text{ kJ}\cdot\text{mol}^{-1}$ ) is replaced by  $\text{AlF}_3$  ( $145.0$  and  $245.5\text{ kJ}\cdot\text{mol}^{-1}$ ), confirming that the electron density distribution of the MM dimer is not much altered when the dimer is involved in an MMM' trimer. Again consistently, the corresponding molecular graphs for these trimers indicate that the electron densities at the MM dimers remain practically unaltered when the dimer interacts with  $\text{BF}_3$  or  $\text{AlF}_3$  (see the last two rows in Figure S3 of the Supporting Information).

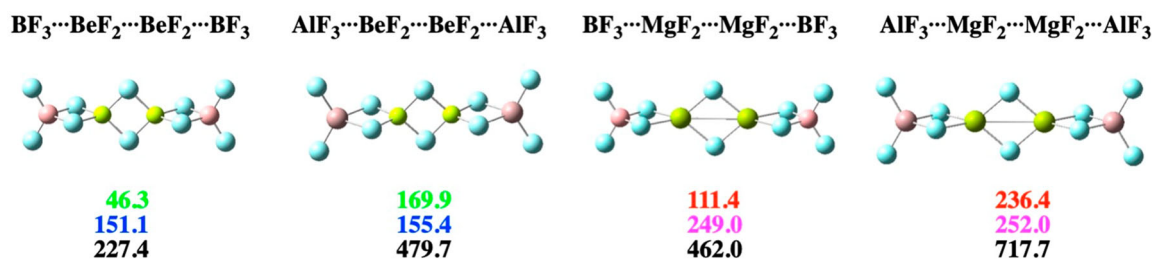
Of course, the topology of the corresponding potential energy surfaces is very rich, and there are other structural arrangements, as shown in Figures S5 and S6 of the Supporting Information, but all of them less stable than the ones discussed above.

#### **Tetramers: confirming the trends and predicting new values**

In this section we have restricted our analysis to cluster containing two alkaline-earth fluorides and two triel fluorides. Just as a consequence of the fact that the  $(\text{M}'\text{F}_3)_2$  ( $M' = \text{B}, \text{Al}$ ) dimers are much less stable than the  $(\text{MF}_2)_2$  ( $M = \text{Be}, \text{Mg}$ ) ones, the more stable tetramers correspond always the sequence M'MMM' which are presented in Figure 4, though as shown in Figure S7 of the Supporting Information many other less stable local minima can be found in the corresponding potential energy surface. It is interesting to note that the most stable mixed tetramers exhibit only tetracoordinated electron-deficient atoms in a linear fashion, resembling that of one of the well-known polymorphs of  $\text{BeCl}_2$  in the solid phase [29]. Interestingly,  $\text{BeF}_2$  in the solid phase, although still tetracoordinated, is an alpha quartz polymer [30].

As it was found for the different trimers, also for tetramers very small cooperative effects appear, which confirms that the local electron density distribution is rather independent of the number of monomers participating in the interaction. Indeed, if we take the dissociation enthalpies for the trimers into the three monomers (black numbers in Figure 3) and we add to them the corresponding green (or red) values that correspond to the





**Figure 4.** Structure and energetics of M'MMM' tetramers. Dissociation enthalpies (in  $\text{kJ}\cdot\text{mol}^{-1}$ ). Same convention of colours as in Figure 3.

interaction to be added to form the tetramer, the values obtained are 227.9, 480.1, 462.7 and  $712.0 \text{ kJ}\cdot\text{mol}^{-1}$ , which are in a very good agreement with the values shown in Figure 4.

This is a clear indication that very likely there is a general correlation accounting for the trends in the binding enthalpies of all the dimers, trimers and tetramers included in our survey. Hence, we have carried out a statistical analysis of our results in terms of the six interactions (B/Be, B/Mg, Al/Be, Al/Mg, Be/Be, Mg/Mg) and the four M-F (M = Be, B, Mg, Al) bonds, whose basic lines are described in the Supporting Information. As a result of this statistical analysis the following two multiple regressions are fulfilled:

$$\begin{aligned}
 E = & (143 \pm 2)\text{Be-Be} + (246 \pm 2)\text{Mg-Mg} \\
 & + (167 \pm 1)\text{Al-Be} + (41 \pm 1)\text{B-Be} \\
 & + (107 \pm 1)\text{B-Mg} + (232 \pm 1)\text{Al-Mg}, n = 16, \\
 R^2 = & 0.99996
 \end{aligned} \quad (1)$$

and

$$\begin{aligned}
 E = & -(23 \pm 2)\text{B-F} + (102 \pm 2)\text{Al-F} + (68 \pm 1)\text{Be-F} \\
 & + (126 \pm 1)\text{Mg-F}, n = 16, R^2 = 0.9998
 \end{aligned} \quad (2)$$

Eq. 1 corresponds to the interaction between atoms of groups 2 and 13 through the fluorine atoms, where it is possible to separate these coefficients into individual atomic contributions, as shown in the Supporting Information, and Eq. 2 is the heat of bond heterolytic formation. This model is a tool to predict, with small error, the binding energies of mixed clusters with more than two different metals not considered in the set of compounds.

### Concluding remarks

Chemists nowadays are aware that the first row of the periodic table, from Li to F, is somehow a singularity and therefore nobody is surprised, for instance, by the

significant differences between the chemistry of silicon with respect to the chemistry of carbon. This paper illustrates that when looking at the interactions between electron-deficient systems from groups 2 and 13 of the periodic table, subtle dissimilarities also appear when Be and B are replaced by the second-row counterparts, Mg and Al. The first evidence appears already when looking at the dimers, whose binding enthalpies when the first-row derivatives ( $\text{BeF}_2$  or  $\text{BF}_3$ ) are replaced by the second-row counterparts ( $\text{MgF}_2$  and  $\text{AlF}_3$ ) become from two to four times larger. This is a direct consequence of the much larger ionic character of the derivatives involving elements of the second row. Another interesting difference when looking at larger clusters (trimers and tetramers) is the formation of rather stable structures involving penta-coordinated aluminium atoms, which are not stable if Al is replaced by B. Another common characteristic of these aggregates is that the local electron density distribution is rather independent of the number of monomers participating in the interaction. In other words, the electronic environment around a  $\text{BeF}_2$  monomer is rather similar if it interacts with a  $\text{BF}_3$  or an  $\text{AlF}_3$  monomer and is not either significantly altered when moving to a trimer or a tetramer, though some small cooperative effects are observed. Consequently, the stability of larger clusters can be easily predicted from the values obtained for smaller ones, and a statistical treatment of the results obtained for dimers, trimers and tetramers permits to predict, with small error, the binding energies of mixed clusters not included in our survey.

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