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Selected $AB_4^{2-/-}$ ($A = C, Si, Ge$; $B = Al, Ga, In$) ions: a battle between covalency and aromaticity, and prediction of square planar Si in $SiIn_4^{2-/-+}$

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Abstract

$CAI_4^{2-/-}$ (D_{4h} , $^1A_{1g}$) is a cluster ion that has been established to be planar, aromatic, and contain a tetracoordinate planar C atom. Valence isoelectronic substitution of C with Si and Ge in this cluster leads to a radical change of structure toward distorted pentagonal species. We find that this structural change goes together with the cluster acquiring partial covalency of bonding between Si/Ge and Al_4 , facilitated by hybridization of the atomic orbitals (AOs). Counter intuitively, for the $AAI_4^{2-/-}$ ($A = C, Si, Ge$) clusters, hybridization in the dopant atom is strengthened from C, to Si, and to Ge, even though typically AOs are more likely to hybridize if they are closer in energy (*i.e.* in earlier elements in the Periodic Table). The trend is explained by the better overlap of the hybrids of the heavier dopants with the orbitals of Al_4 . From the thus understood trend, it is inferred that covalency in such clusters can be switched off, by varying the relative sizes of the AOs of the main element and the dopant. Using this mechanism, we then successfully killed covalency in Si, and predicted a new aromatic cluster ion containing a tetracoordinate square planar Si, $SiIn_4^{2-/-}$.

Introduction

Nano- and sub-nano-clusters gain popularity in various fields of science and technology. At the same time, clusters formed by just a few atoms in a way represent one of the last frontiers of inorganic chemistry, because our intuition about their shapes and properties is very limited. So the applied cluster science remains largely empirical. The traditional tool for rationalization and design of molecular structures and properties in chemistry is the theory of chemical bonding, *i.e.* a set of simple qualitative concepts such as (anti)aromaticity, covalency, hyperconjugation, *etc.* When it comes to clusters, we have, thus far, a very limited number of such qualitative chemical bonding concepts, or tools that would enable our intuition about what shapes and properties a cluster of a given composition might have.

[†]Electronic supplementary information (ESI) available: All low-energy isomers of discussed clusters identified in GEGA and MC searches, and calculated molecular properties of the global minima and most competitive isomers. See DOI: 10.1039/c2cp41821e

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Indeed, development of a theory of chemical bonding for clusters has really begun only during the last decade or two. Among the recently discovered chemical bonding phenomena in clusters are multiple aromaticity and antiaromaticity, delocalized bonding concepts found to be characteristic of even all-metal systems.^{1–4} Partial covalent bonding achieved through the hybridization of atomic orbitals (AOs) was then also realized to occur in clusters,^{5,6} and was further suggested to compete with delocalized bonding in governing some cluster shapes. Both aromaticity and covalency exhibit a greater diversity than in organic chemistry, where they were first discovered, due to a wider variety of types of AOs engaged in the bonding of clusters. The fundamental aspect of the present work is probing the extent to which our knowledge about aromaticity and covalency, accumulated over a number of example systems, could be used to rationally manipulate cluster structures, *i.e.* truly design them.

We report on the Al_4 , Ga_4 , and In_4 cluster anions doped with a single atom of C, Si, or Ge. The $\text{CAL}_4^{2-/-}$, SiAl_4^- , and GeAl_4^- series of ions has been studied previously, and the global minimum structures of these species are known.^{7,8} The structures are dramatically different along the series. The CAL_4^{2-} ion, alone and in the form of a Li salt, has been characterized both theoretically and experimentally.⁷ This cluster adopts an unusual square planar structure, with C residing in the centre of the Al_4 square, whereas intuitively tetracoordinated C should be tetrahedral. Planar carbon chemistry is undergoing its boom, and has been extensively reviewed over the past few years, starting from seminal works by Schleyer and co-workers.^{9–25} This planar square shape was explained on the basis of the nature of the HOMO in the doubly-charged cluster, which corresponds to the 4-center bond in the Al_4 cycle. The corresponding neutral cluster, CAL_4 , is tetrahedral. In contrast, SiAl_4^- and GeAl_4^- clusters are instead distorted pentagons with C_{2v} symmetry. A related cluster, $\text{CB}_4^{2-/-}$, has also been studied, and its structure is analogous to that of SiAl_4^- and GeAl_4^- .²⁶ It was then proclaimed that the square planar geometry was not adopted by the SiAl_4^- and GeAl_4^- clusters because Si and Ge are too big to fit in the Al_4 cycle. However, we would like to raise a controversy, by pointing out that the studied dopant atoms become more metallic and approach Al in electronegativity, from C, to Si, to Ge. The character of the chemical bonding between the Al_4 part of the cluster and the dopant is expected to change as one moves along the series. Therefore, attributing the observed structural effect just to the size of the dopant atom might be misleading.

In the present study, we first confirm and analyze this structural trend in the original AAl_4 -series ($\text{A} = \text{C}, \text{Si}, \text{Ge}$). We show that as the dopant atom gets heavier, the chemical bonding in the clusters acquires more and more covalent character as aromatic character diminishes. After explicating these chemical bonding trends, we use the gained understanding in a rational search for tetracoordinated square planar Si, by analogy with tetracoordinated planar C. The study is done by means of electronic structure theory calculations and our in-house stochastic algorithms for the unbiased search for global minima.

Theoretical methods

An automated extensive search for the global minima was performed for all discussed clusters. Two different methods were used for this purpose: *ab initio* Gradient Embedded Genetic Algorithm (GEGA),^{27–29} and coarse-grained Metropolis Monte Carlo (MC),³⁰ both operating at the B3LYP^{31–33}/3-21G^{34,35} level of theory. The choice for this initial theoretical level is a compromise between accuracy and speed. From our experience, at least for clusters composed of main group elements, the small basis set may lead to some geometric contraction of structures, but does not qualitatively change their geometries or energy ordering.

GEGA was previously shown to perform exceptionally well for finding the global minima of clusters, as was confirmed in numerous joint theoretical and experimental spectroscopic studies. Details of the algorithm can be found elsewhere.^{27–29} Briefly, it operates on the population of local minima for a given cluster composition, found *via* geometry optimization and vibrational frequency analysis. Species in the population are set to exchange their structural information (geometric halves), subject to fit-dependent probability. The fit is defined by the total energy of the species. For every iteration, a small portion of the population also undergoes mutations *via* random displacements of atoms. All structures produced *via* breeding or mutations are again optimized to the nearest local minima. Simulations proceed to convergence in terms of the leading lowest energy structure found thus far. Separate GEGA searches were performed for singlets and triplets of the doubly-charged ions in this study. For every cluster composition, and every multiplicity, three independent runs of the GEGA search were performed. The population size was 30, and the convergence was considered sufficient when the current most stable structure was the same for 20 consecutive iterations.

Our additional MC simulations were organized as follows. An initial configuration for each cluster was assumed for the start; the geometry was generated randomly, and the interatomic distances were kept within the Lennard-Jones (LJ) radii. Two types of moves were done on this initial structure: atom switches and atom displacements. The energy of every newly generated structure was roughly evaluated based on the LJ potential. Moves were accepted according to standard Metropolis acceptance criteria.²⁰ After 20 000 events, the coarse-grained representation was forgone, and the currently leading structure was optimized to the nearest stationary point, which could be a minimum or a saddle point, at the B3LYP/3-21G level. The MC course-grained pre-filtering and leading structure optimization was continued for hundreds of tries for each cluster composition. This method allowed for a very fast and aggressive sampling of the potential energy surfaces (PESs), with less “learned-on-the-fly” information about the system, as opposed to the operating principle of GEGA. The combination of MC followed by B3LYP/3-21G calculations, and *ab initio* GEGA permitted us to identify myriads of isomers. Some of the isomers were found only by MC, and missed by GEGA.

The lowest energy isomers found to be within 10 kcal mol^{−1} from the global minima were retained for further consideration. The number of thus considered isomers of each cluster was anywhere from 3 to 10. Since our study focuses on singly- and doubly-charged ions, care had to be exercised in their theoretical characterization.³⁶ Their geometries and harmonic vibrational frequencies were refined at the B3LYP/6-311+G*, MP2^{37–39}/6-311+G*, and CCSD(T)^{40–43}/6-311+G* levels of theory. Single point energy calculations were also done at the CCSD(T)/6-311+G(2df)//CCSD(T)/6-311+G* level. For In, the CEP-121g+spd^{44,45} basis set was used in structure refinement. The analysis of the chemical bonding was done with the Natural Population Analysis (NPA)^{46–50} at the B3LYP/6-311+G* level (CEP-121g+spd for In), and MO analysis at the HF/6-311+G* level. In addition, single point energy calculations using CASSCF(*n,m*)^{51–57}/6-311+G* (*n* = 4–6, *m* = 4–6) (CEP-121g+spd for In) were carried out for the B3LYP geometries, in order to check the validity of the single determinant methods. It was confirmed that all considered species have unequivocally single configuration wave functions, and hence, the single reference methods should be reliable. *Gaussian 09*⁵⁸ was used for all calculations.

Results and discussion

1. CAI₄^{2−/−}, SiAl₄^{2−/−}, and GeAl₄^{2−/−} cluster ions

Structure—Using our automated search engines, we first repeated the search for the global minima of the CAI₄^{2−}, SiAl₄^{2−}, and GeAl₄^{2−} species. In the past, these global minima

were identified by hand, and so we performed an automated unbiased search, to confirm the earlier findings. Fig. 1 shows the global minima, whereas all found low energy isomers are presented in the ESI[†] (Fig. S1–S3). The calculated molecular parameters of the low energy isomers are also given in the ESI.[†] We then also calculated singly charged ions, starting from the geometries of the isomers of the doubly charged ones. This was done with the purpose of saving time, since the independent exhaustive searches for the global minima of the open-shell ions would take much longer time. From our previous experience with studies of clusters, this approximation is good. Singly and doubly charged ions adopt similar structures, and the global minima remain of the same type.

In agreement with earlier data, the global minimum of the $\text{CAI}_4^{2-/}$ clusters is square species with a tetracoordinated planar C in the middle (Fig. 1). The valence-isoelectronic substitution of C with Si and Ge leads to the change in structure from square (D_{4h}), to distorted pentagonal (C_{2v}). Typically, in chemistry, we believe that isoelectronic substitution in molecules and materials can be done without a significant change in structure. In clusters, this is not always the case, as was once pointed out in the example of doped alkali metal clusters.⁶ Evidently, it is not the case here either. Again, previously reported results are fully reproduced.

An additional observation can be made that not even high energy square isomers exist for $\text{SiAl}_4^{2-/}$ and $\text{GeAl}_4^{2-/}$. Such species are third order saddle points on the corresponding PESs. The square pyramidal species with the Si/Ge atom above the Al_4 plane are second order saddle points with a degenerate imaginary frequency leading to the global minimum C_{2v} isomers.

Chemical bonding—Let us elaborate on this structural trend, from the perspective of the chemical bonding in the studied clusters. We then will use the acquired understanding in cluster design. Fig. 2 shows the valence MOs of the representative presented cluster ions, the square and the distorted pentagon. Parameters characterizing bonding, atomic charges and MO compositions are presented in Table 1.

$\text{CAI}_4^{2-/}$ is a triply aromatic cluster, as has been explicated before, and confirmed here.⁷ Briefly, the HOMO-4 is a fully delocalized, completely-bonding π -MO. No other π -MOs are populated. The 2 electrons residing on the HOMO-4 make the cluster obey the $(4n+2)$ Hückel rule for aromatic compounds ($n=0$), and render the cluster π -aromatic. Next, in the degenerate HOMO-2, and HOMO-3, the Al atoms contribute their unhybridized 3p-AOs, lying in the cluster plane, and pointing inward. C contributes slightly, with its s- or p-AOs, depending on the symmetry of the MO. These MOs are of a radial σ -type. The HOMO-3 is a completely bonding fully delocalized MO of this kind, and the HOMO-2 is a nonbonding pair of MOs. The last remaining MO is antibonding, and it is higher in energy and not populated in these clusters. Therefore, this subset of MOs in the cluster represents a delocalized radial σ -bonding. Containing a total of 6 electrons, the subset makes the cluster obey the $(4n+2)$ rule for the second time, with $n=1$. Thus, the cluster is σ -aromatic. The HOMO is another orbital of σ -type, peripheral. It is formed by the p-AOs on Al atoms that still lie in plane, but are perpendicular to those forming the HOMO-2 and HOMO-3. The HOMO is also completely bonding, fully delocalized, and populated by 2 electrons makes the cluster possess the second type of σ -aromaticity, and the 4-center bond in Al_4 . In the singly-charged ion, it contains 1 electron, but the bonding picture remains the same. Thus, triple-aromaticity is confirmed. The remaining MOs in the clusters, the HOMO-1, HOMO-5, and HOMO-6, are linear combinations of the four 3s-AOs on the Al atoms in the cycle.

[†]Electronic supplementary information (ESI) available: All low-energy isomers of discussed clusters identified in GEGA and MC searches, and calculated molecular properties of the global minima and most competitive isomers. See DOI: 10.1039/c2cp41821e

These MOs, being fully populated, can be thought of as 3s-lone pairs on the atoms of Al, and mixing with the p-AOs on Al is insignificant. C contributes 2p-AOs to the HOMO-5 degenerate pair, and 2s-AO to the HOMO-6, as allowed by symmetry.

At this point, we would like to make an important observation. In the $\text{CAI}_4^{2-/}$ ions, no s-p hybridization of AOs can be found. Every MO has contributions from the AOs of C and Al exclusively of one type (s- or p-), or the other, but not mixed. It is well-known that C is typically very prone to 2s-2p hybridization. However, in this case, it is not adopted. Apparently, due to the poorer overlap between the AOs of C and the larger AOs of Al, the bonding in the system does not gain much from AO-hybridization, which is typically employed to enhance an AO-overlap. Instead, the cluster is stabilized through the triple aromaticity of the Al_4 unit. As another manifestation of the lack of covalency in the bonding of this cluster, the charge on C in the singly-charged cluster is -2.810 |e|. Hence, C binds to the rest of the cluster primarily ionically. This is also in accord with the relative electronegativities of Al (1.5) and C (2.5). In the next two clusters, we will observe how this triple aromaticity is conquered through covalent interactions of AO-hybrids.

In Fig. 2B, we show the MOs typical for all the studied distorted pentagonal clusters, $\text{SiAl}_4^{2-/}$ and $\text{GeAl}_4^{2-/}$. We will discuss the case of $\text{SiAl}_4^{2-/}$, as representative; $\text{GeAl}_4^{2-/}$ and all other clusters of this kind are bound in a similar fashion. In $\text{SiAl}_4^{2-/}$, the 3s-3p-AO separation in the constituent elements is no longer preserved, and these AOs mix whenever the symmetry of the MO permits. Firstly, the HOMO-3 is the only π -MO, making the cluster π -aromatic, in the same way as $\text{CAI}_4^{2-/}$ is π -aromatic. The HOMO-4, HOMO-6, HOMO-7, and HOMO-8 are deep MOs formed mostly by the 3s AOs on the Al atoms, with a subtle mixing of 3p. Si contributes to these MOs with its p- and s-AOs, depending on the orbital symmetry. There are 4 remaining MOs: the HOMO, HOMO-1, HOMO-2, and HOMO-5; the Al atoms contribute their 3p-AOs lying in cluster plane and slightly mixed with the 3s-AOs. Additionally, unlike in the square cluster, these MOs form a single, inseparable class of σ -MOs, so that it is no longer possible to distinguish radial and peripheral σ -MOs. The contribution of Si to these MOs is also different. As quantified in Table 1, there is a strong 3s-3p_z hybridization of the AOs on Si, in the HOMO and HOMO-2. This 3s-3p_z mixing is even apparent from the look of these orbitals (Fig. 2B). In both MOs, the hybridization enhances the overlap of the AOs on Si with the lobe of the MO beneath it provided by the Al rim of the cluster. Hybridization leading to stronger overlap and enhanced bonding is a signature of covalency. Si and Al are more inclined to bind covalently than do C and Al, because Si and Al are closer in orbital size and electronegativity than C and Al. This is additionally illustrated by the charge on the Si atom in the cluster, -1.363 , which is significantly smaller than that in $\text{CAI}_4^{2-/}$ (Table 1).

The chemical bonding picture in the $\text{GeAl}_4^{2-/}$ clusters is quite analogous to that in $\text{SiAl}_4^{2-/}$. The MOs look and are composed in a like manner (Table 1). In this case, the size and electronegativities of Ge and Al are also similar, and so, as with Si, Ge contributes sp_z AO hybrids to the HOMO and HOMO-2. However, now, both the overall contributions of Ge to the full electron density of the MOs are greater, and the mixing of s-AOs into the hybrids is stronger than in the case of $\text{SiAl}_4^{2-/}$ (see Table 1). Hence, the cluster is even more covalent. Since the electronegativities of Si and Ge are the same, this effect is rooted in the better complementary size between the AOs of Al and Ge, as compared to those of Al and Si.

From the above analysis, it is apparent that the covalency facilitated by the sp-AO hybridization in the dopant element increases along the series, $\text{CAI}_4^{2-/}$, $\text{SiAl}_4^{2-/}$, and $\text{GeAl}_4^{2-/}$. This is paradoxical, since typically, greater hybridization is expected between AOs that are similar in energy. The smallest valence s-p energy splitting among C, Si, and

Ge is in C. In heavier elements, the larger nuclear charge favours AOs of lower angular momenta, thus increasing the splitting. Therefore, an uninformed guess would probably be that C would undergo greater hybridization among the three elements, all else being equal. Yet, the reverse is found. In the studied case, the degree of hybridization in the dopant element is a function of the quality of the overlap with the rest of electron density in the cluster.

2. Prediction of tetracoordinated square planar Si

Again, what allows for the appearance of tetracoordinated planar C in $\text{CAI}_4^{2-/-}$ is the discouraged covalency, due to the mismatch in the sizes of the AOs of the dopant and the rest of the cluster. Therefore, the question is can we now analogously discourage covalency in Si and design a cluster with tetracoordinated square planar Si? In order to obtain such a cluster, one would need to choose the main element in the cluster that would have p-AOs that are yet bigger than those of Al, and overlap more poorly with the AOs of Si.

Al could be replaced with Ga or In, provided the structure of the cluster does not change to something completely different in these cases. We performed the global minimum searches for $\text{SiGa}_4^{2-/-}$. The global minima are still similar to those of $\text{SiAl}_4^{2-/-}$ and $\text{GeAl}_4^{2-/-}$. It is a C_{2v} distorted pentagonal structure (Fig. 3A). However, unlike $\text{SiAl}_4^{2-/-}$ and $\text{GeAl}_4^{2-/-}$, the doubly-charged anion of SiGa_4^{2-} does have a higher in energy square isomer, with Si being slightly pushed out of the cluster plane (structure **II**, Fig. 3A). This isomer does not exist for the singly-charged anion, however. Calculated molecular parameters of the low-energy isomers are presented in the ESI.†

The conclusion so far is that replacing Al with Ga does not give the desired result of square planar Si.

We then replaced Al with In. In this case, it worked. The global minimum of $\text{SiIn}_4^{2-/-}$ indeed appears to have a tetracoordinated Si located in the centre of the In_4 square (analogous to that of $\text{CAI}_4^{2-/-}$) (Fig. 3B). At our lowest level of theory, B3LYP/3-21G, which was used to search for the global minima, the structure of the doubly-charged anion is planar (D_{4h} , $^1A_{1g}$), species **I** in Fig. 3B. This planar species is basically isoenergetic with the second square isomer, which is pyramidal with shorter In–In distances, and Si residing slightly above the cluster plane (C_{4v} , 1A_1 species **II**, Fig. 3B). When the larger basis set, cep-121g+spd, was used in calculations, only the square pyramidal isomer(**II**) was confirmed. Structure **II** is the global minimum of the doubly-charged anion also at the MP2/CEP-121g+spd level of theory. Calculated molecular properties of this species, as well as other competitive isomers are presented in the ESI.† Other low-energy isomers of $\text{SiIn}_4^{2-/-}$ are the quasi-planar structure **III** (Fig. 3B), which is at least 8 kcal mol^{−1} higher in energy. The order of the isomers is the same, and their relative energies are very close for the doubly- and singly-charged anions (Fig. 3B).

The chemical bonding in the square $\text{SiIn}_4^{2-/-}$ species is very similar to that in $\text{CAI}_4^{2-/-}$. The NPA B3LYP/CEP-121g+spd charge on Si in the singly-charged anion is −1.753, indicating a more ionic bonding, although not as pronounced as in CAI_4^- . The MOs of the square planar isomer (Fig. 4) are very similar to those of $\text{CAI}_4^{2-/-}$. The only exception is that due to the symmetry of the cluster being reduced from D_{4h} to C_{4v} , the completely bonding σ -MO, formed by the p-AOs pointing into the cycle, and the π -MO, formed by the p_z -AOs on the atoms, have the same symmetry and mix. The resulting HOMO-2 and HOMO-4 cannot be called distinct σ - or π -, even though they are still completely bonding, fully delocalized, and possess the highest symmetry within the C_{4v} point group. This σ - π mixing thus does not significantly alter the overall bonding picture. The HOMO-1 is a degenerate pair analogous to the HOMO-2 in $\text{CAI}_4^{2-/-}$. The HOMO is also analogous to

that in $\text{CAI}_4^{2-/-}$. Thus, $\text{SiIn}_4^{2-/-}$ anions are also triply aromatic. Importantly, the In_4^{2-} anion and its alkali metal salts have been studied experimentally and theoretically.⁵⁹ The anion was found to be square planar and described as aromatic.

Concerning covalency, there is a slight symmetry-allowed mixing of the 3s and 3p_z-AOs on Si in all MOs of a_1 symmetry, in the $\text{SiIn}_4^{2-/-}$ clusters. This distinguishes the bonding in this cluster from that in $\text{CAI}_4^{2-/-}$. However, no pronounced hybridization leading to distortion of the cluster symmetry and directional covalent binding between Si and In₄, as in $\text{SiAl}_4^{2-/-}$, $\text{GeAl}_4^{2-/-}$, and $\text{SiGa}_4^{2-/-}$, can be found. We therefore successfully switched off covalency and altered the structure of the cluster, by choosing an appropriate combination of the dopant (Si) and the main element (In).

It is also remarkable that the distorted pentagonal structure analogous to those of the global minima of $\text{SiAl}_4^{2-/-}$, $\text{GeAl}_4^{2-/-}$, and $\text{SiGa}_4^{2-/-}$ does not exist for the $\text{SiIn}_4^{2-/-}$ ions. This is because being in the “central” position in the distorted pentagon requires the dopant atom to undergo the most significant AO-hybridization. For example, in isomer **III** of $\text{SiIn}_4^{2-/-}$, Si does not experience such pressure to hybridize. This effect was noticed previously for clusters of LiK_4^- , as opposed to LiNa_4^- .⁶

Compounds containing square planar Si are relatively rare.^{60–67} Some of the reported molecules contain Si in this coordination due to the presence of bulky ligands that impose strain in the Si atom thus enforcing planarity.⁶⁰ In contrast, in the found global minimum structure of $\text{SiIn}_4^{2-/-}$, planarity is a purely electronic effect. Electronically driven planar Si exists only in a few other clusters found so far. For example, Si-doped metal hydrides such as SiAg_5H_5 , $\text{SiPd}_5\text{H}_5^-$, and SiCu_6H_6 were found. In these species, Si resides in the centre of the cyclic metal hydride, and is planar or quasi-planar.^{61,62} Si bound to clusters of Au of certain sizes also exhibits planarity.⁶³ The newly found cluster, $\text{SiIn}_4^{2-/-}$ is therefore a member of a scarcely populated family, and it is important that it was found *via* rational design driven by chemical bonding and electronic structure insight.

Conclusions

We report on the structures and chemical bonding in the $\text{AB}_4^{2-/-}$ ($\text{A} = \text{C}, \text{Si}, \text{Ge}$; $\text{B} = \text{Al}, \text{Ga}, \text{In}$) series of cluster ions. We first explicated the observed structural differences in the $\text{AAI}_4^{2-/-}$ clusters. Depending on the dopant element, the structure of the cluster can be square planar ($\text{A} = \text{C}$), or distorted pentagonal ($\text{A} = \text{Si}, \text{Ge}$). We explained this trend on the basis of two opposing effects: those of aromaticity and covalency in the studied species. $\text{CAI}_4^{2-/-}$ is aromatic, whereas $\text{SiAl}_4^{2-/-}$ and $\text{GeAl}_4^{2-/-}$ are covalent species. This effect is rooted in different degrees of s–p AO hybridization in the atom of the dopant, in response to binding to Al. Better overlap between s and p AOs on Si and Ge with the MOs formed by the Al_4 cluster subunit leads to AO mixing in the dopants, and stronger and more directional bonding. Orbital size mismatch makes such a mixing unfavourable for C. Thus, seemingly counterintuitively, along the series C, Si, Ge, AO-hybridization in C is the weakest, and strongest in Ge.

Once the mechanism for switching covalency off and driving the cluster toward square geometries was understood, we went on a hunt for a square planar Si atom. We found that an isoelectronic substitution of In for Al leads to successful dismissal of covalency in the bonding of $\text{SiIn}_4^{2-/-}$ cluster ions. Thus, $\text{SiIn}_4^{2-/-}$ was predicted and then confirmed to have a quasi-planar structure with Si residing in the centre of the In₄ square. The bonding in this species is analogous to that in $\text{CAI}_4^{2-/-}$: it is a triply-aromatic cluster.

It is also remarkable that $\text{SiAl}_4^{2-/-}$ and $\text{GeAl}_4^{2-/-}$ do not have square (planar or pyramidal) isomers at all, and $\text{SiGa}_4^{2-/-}$ has one, but it is high in energy. Covalency in these clusters is a strong driving force in defining cluster structures, and it is not easily abolished.

In this work, we again show that aromaticity and covalency are opposing effects in terms of determining cluster structures. Furthermore, we now demonstrate how they can be used as two “knobs” of cluster design.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1.
The global minima of the $\text{CAl}_4^{2-/-}$, $\text{SiAl}_4^{2-/-}$, and $\text{GeAl}_4^{2-/-}$ clusters.

Fig. 2. Valence MOs of (A) CAL_4^- , a square aromatic cluster with a tetracoordinated planar dopant C, and (B) SiAl_4^- , as a representative of a covalent, distorted pentagonal cluster; analogous MOs are found in SiAl_4^{2-} , $\text{GeAl}_4^{2-/}$, and $\text{SiGa}_4^{2-/}$.

Fig. 3. The global minima and low-energy isomers of the (A) $\text{SiGa}_4^{2-/-}$, and (B) $\text{SiIn}_4^{2-/-}$ clusters. Relative energies and structural parameters shown are calculated at the MP2 level. For some of these clusters, singly-charged ions are not minima, in which case their spectroscopic states are not shown in the figure. Relative energies are shown within groups of clusters of the same composition and charge.

Fig. 4.
The valence MOs of the global minimum of the SiIn_4^{2-} cluster.

Table 1

NPA//B3LYP/6-311+G* charges on the Si/Ge dopant atoms, and contributions of Si/Ge AOs to the valence MOs in which AO-hybridization occurs (HF/6-311+G*)

	SiAl₄⁻ (C_{2v}, ²A₁)	GeAl₄⁻ (C_{2v}, ²A₁)
Q(C/Si/Ge)	-1.4 e	-1.3 e
HOMO	-0.02(3s) - 0.04(4s) + 0.08(5s) + 0.08(7p _z) - 0.05(8p _z) - 0.09(9p _z) + 0.10(10p _z) + 0.27(11p _z) + 0.25(12p _z) (5% s + 95% p)	+0.01(3s) + 0.02(4s) - 0.03(5s) - 0.05(6s) + 0.12(7s) + 0.01(8s) + 0.12(9s) - 0.03(9p _z) + 0.01(10p _z) + 0.05(11p _z) - 0.12(12p _z) - 0.04(13p _z) + 0.14(14p _z) + 0.23(15p _z) + 0.31(16p _z) (13% s + 87% p)
HOMO-2	+0.01(3s) + 0.01(4s) - 0.02(5s) - 0.01(7p _z) + 0.03(8p _z) + 0.05(9p _z) - 0.06(10p _z) - 0.17(11p _z) - 0.13(12p _z) (0.1% s + 99.9% p)	+0.01(5s) + 0.01(6s) - 0.03(7s) - 0.01(8s) - 0.06(9s) - 0.03(11p _z) + 0.07(12p _z) + 0.02(13p _z) - 0.08(14p _z) - 0.15(15p _z) - 0.13(16p _z) (8% s + 92% p)