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A density functional theory study of five-, six- and seven-atom germanium clusters: distortions from ideal bipyramidal deltahedra in hypoelectronic structures

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Density functional theory (DFT) at the hybrid B3LYP level has been applied to the germanium clusters Ge_n^z ($n = 5, 6, 7; z = -2, 0, +2$) starting from a variety of initial configurations. Double zeta quality LANL2DZ basis functions extended by adding one set of polarization (*d*) and one set of diffuse (*p*) functions were used. Bipyramidal global minima were found for Ge_5^{2-} and Ge_7^{2-}. These bipyramids were computed to become oblate (*i.e.*, compressed along a major axis) without reduction in symmetry upon loss of two electrons to form the corresponding neutral species. For the six-vertex Ge_6^{2-}/Ge_6 system our computations indicate that the oblate tetragonal bipyramid structure previously found for the 12-skeletal electron In_6^{6-} undergoes further distortion to give a less symmetrical C_s structure best regarded as an edge-capped trigonal bipyramid. Further removal of electrons from the neutral Ge_n clusters to give the dications Ge_n^{2+} having $2n - 2$ skeletal electrons was found to lead to more complicated structural changes. Thus for Ge_5^{2+} the lowest energy structure is a completely unsymmetrical (C_1) array of three fused triangles whereas for Ge_6^{2+} the edge-capped trigonal bipyramid found for Ge_6 undergoes further distortion to give a somewhat more symmetrical looking structure best regarded as an edge-bicapped butterfly. Only for the lowest energy computed structure of Ge_7^{2+} does the oblate pentagonal bipyramid found for Ge_7 remain recognizable although it undergoes further distortion to an unsymmetrical prolate (elongated) bipyramid related to the prolate trigonal antiprisms previously computed for In_6^{4-} and Tl_6^{4-}.

1. Introduction

Previous papers from our group[1,2] discuss our results from density functional theory (DFT) computations on six-vertex polyhedral clusters of the Group 13 elements boron, indium and thallium. These computations were motivated by the experimental observations that Tl_6^{8-} has a regular octahedral structure[3] whereas Tl_6^{6-} has a compressed (oblate) tetragonal bipyramidal structure.[4,5]

A general difficulty in performing these computations was found to be the relatively high negative charges on the cluster anions of interest, namely Ic_6^{z-} ($z = 4, 6, 8$; Ic = B, In, Tl). Thus attempts to optimize structures led in some cases to convergence to the individual atoms beyond bonding distances, presumably because of the high negative charges. In order to avoid this difficulty we have begun some analogous DFT computations on clusters isoelectronic to these Group 13 clusters of interest but with lower charges. We now report our initial work on such less highly charged clusters using the Group 14 metal germanium. Thus the six-vertex clusters Ge_6^{2-}, Ge_6, and Ge_6^{2+} are isoelectronic with the clusters Ic_6^{8-}, Ic_6^{6-}, and Ic_6^{4-}, respectively, discussed in our previous papers.[1,2] This paper also reports our DFT computations on the five- and seven-vertex bipyramidal clusters Ge_5^{2-} and Ge_7^{2-} as well as the corresponding hypoelectronic clusters Ge_5, Ge_5^{2+}, Ge_7, and Ge_7^{2+}.

2. Computational methods

Geometry optimizations were carried out at the hybrid DFT B3LYP level[6] with the LANL2DZ double zeta quality basis functions[7] extended by adding one set of polarization (*d*) and one set of diffuse (*p*) functions[8] by using the Gaussian 94 package of programs.[9] The following initial geometries were chosen for each type of cluster:

Ge_5^z: Trigonal bipyramid, square pyramid, and planar pentagon;

Ge_6^z: Regular octahedron, pentagonal pyramid, capped trigonal bipyramid, bicapped tetragonal pyramid, trigonal prism, and planar hexagon;

Ge_7^z: Pentagonal bipyramid, hexagonal pyramid, capped octahedron, bicapped trigonal bipyramid, and capped trigonal prism.

The geometries were optimized without symmetry restrictions and finally converged to the shapes described in Tables 1–3 and depicted in Figs. 1–3. Vibrational analysis shows that all structures included in these tables are genuine minima at the B3LYP/LANL2DZdp level without any imaginary frequencies.

Graphical work-up of the Gaussian 94 output was performed using the Windows versions of MOLEKEL[10] and Re_View.[11]

3. Results and discussion

3.1 The five-vertex clusters

The optimized structures for the minima of Ge_5^z clusters are depicted in Fig. 1 and their relative energies are depicted in Table 1. For the dianion Ge_5^{2-} with the $12 = 2n + 2$ skeletal electrons suggested by Wade's rules[12] the trigonal bipyramid is found to be the only minimum. The computed Ge–Ge edge lengths for Ge_5^{2-} (Table 2) are ~0.1 Å longer than those found by X-ray diffraction studies[13] on the salt $(2,2,2\text{-crypt-}K^+)_2$-$Ge_5^{2-}$·THF. However, the computed eq–eq/eq–ax length ratio of 1.09 for Ge_5^{2-} is within 0.01 of the 1.08 ratio found experimentally in $(2,2,2\text{-crypt-}K^+)_2Ge_5^{2-}$·THF. Similar eq–eq/eq–ax length ratios of 1.08 are found experimentally for the isoelectronic heavier Group 14 metal clusters[14] Sn_5^{2-} and Pb_5^{2-} and an only slightly greater eq–eq/eq–ax length ratio of 1.10 is

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Table 1 Minima of the five-vertex germanium clusters Ge_5^z found in this work

Formula	Structure and symmetry	Total energies/a.u.	Relative energies/kcal mol^{-1}	Distances/Å
Ge_5^{2-}	Trigonal bipyramid (D_{3h})	−18.9269203	0.0	Ge1–Ge4 = Ge1–Ge5 = Ge2–Ge4 = Ge2–Ge5 = Ge3–Ge4 = Ge3–Ge5 = 2.577; Ge1–Ge2 = Ge1–Ge3 = Ge2–Ge3 = 2.818; Ge4 ··· Ge5 = 3.997
Ge_5	Oblate trigonal bipyramid (D_{3h})	−18.9069742	0.0	Ge1–Ge4 = Ge1–Ge5 = Ge2–Ge4 = Ge2–Ge5 = Ge3–Ge4 = Ge3–Ge5 = 2.491 Å; Ge1 ··· Ge2 = Ge2 ··· Ge3 = Ge1 ··· Ge3 = 3.351; Ge4–Ge5 = 3.141
Ge_5	Three fused triangles (C_{2v})	−18.8624184	28.0	Ge2–Ge4 = Ge1–Ge5 = 2.409; Ge3–Ge4 = Ge3–Ge5 = 2.592; Ge1–Ge2 = Ge2–Ge3 = Ge3–Ge1 = 2.466
Ge_5^{2+}	Three fused triangles (C_1)	−18.1992774	0.0	Ge1–Ge2 = 2.475; Ge1–Ge3 = 2.779; Ge1–Ge5 = 2.921; Ge2–Ge3 = 2.482; Ge2–Ge4 = 2.570; Ge3–Ge4 = 2.736; Ge3–Ge5 = 2.496

Table 2 Minima of the six-vertex germanium Clusters Ge_6^z found in this work

Formula	Structure and symmetry	Total energies/a.u.	Relative energies/kcal mol^{-1}	Distances/Å
Ge_6^{2-}	Regular octahedron (O_h)	−22.7325347	0.0	All octahedral edges = 2.687; Ge1 ··· Ge3 = Ge2 ··· Ge4 = Ge5 ··· Ge6 = 3.800
Ge_6^{2-}	Bicapped tetrahedron (C_{2v})	−22.7154148	10.7	Ge1–Ge2 = 2.574; Ge1–Ge3 = Ge1–Ge4 = Ge2–Ge3 = Ge2–Ge4 = 2.920; Ge1–Ge5 = Ge2–Ge6 = 2.614; Ge3–Ge5 = Ge3–Ge6 = Ge4–Ge5 = Ge4–Ge6 = 2.583; Ge3–Ge4 = 2.708
Ge_6^{2-}	Four fused triangles (D_{3h})	−22.7117565	13.0	Ge1–Ge2 = Ge2–Ge6 = Ge6–Ge5 = Ge5–Ge4 = Ge4–Ge3 = Ge3–Ge1 = 2.437; Ge2–Ge3 = Ge3–Ge5 = Ge5–Ge2 = 2.906
Ge_6	Edge-capped trigonal bipyramid (~C_{2v})	−22.7184755	0.0	Ge2–Ge5 = Ge4–Ge5 = 2.575; Ge2–Ge6 = Ge4–Ge6 = 2.585; Ge3–Ge5 = 2.813; Ge3–Ge6 = 2.779; Ge2–Ge4 = 2.970; Ge2–Ge3 = Ge3–Ge4 = 2.617; Ge1–Ge2 = Ge1–Ge4 = 2.530; Ge1 ··· Ge5 = 3.164; Ge1 ··· Ge6 = 3.117
Ge_6^{2+}	Edge-bicapped butterfly (~C_{2v})	−22.0299653	0.0	Ge2–Ge6 = Ge4–Ge6 = 2.512; Ge2–Ge5 = Ge4–Ge5 = 2.514; Ge2–Ge3 = 2.615; Ge3–Ge4 = 2.618; Ge1–Ge5 = 2.616; Ge1–Ge6 = 2.617; Ge1 ··· Ge2 = 3.224; Ge1 ··· Ge4 = 3.229; Ge2 ··· Ge4 = 3.392; Ge3 ··· Ge5 = 3.226; Ge3. . .Ge6 = 3.227; Ge5. . .Ge6 = 3.391
Ge_6^{2+}	Pentagonal pyramid (C_{5h})	−22.0052746	15.5	Ge1–Ge2 = Ge2–Ge3 = Ge3–Ge4 = Ge4–Ge5 = Ge5–Ge1 = 2.877; Ge1–Ge6 = Ge2–Ge6 = Ge3–Ge6 = Ge4–Ge6 = Ge5–Ge6 = 2.576

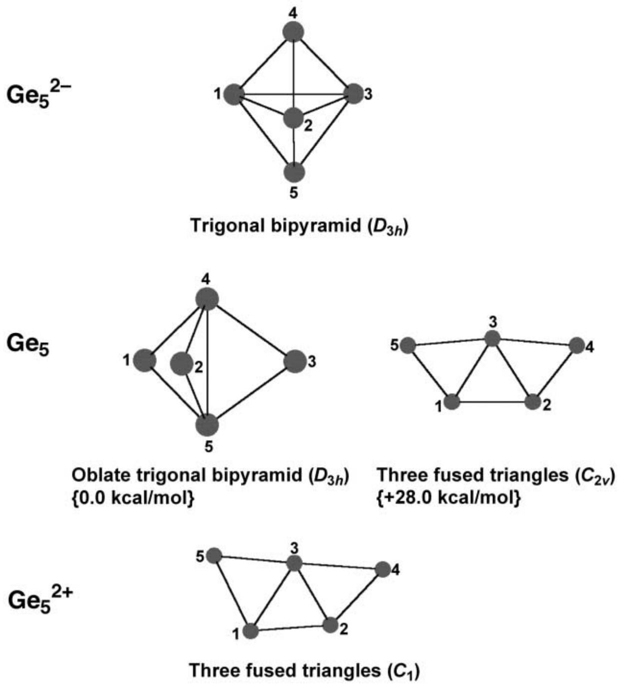

Fig. 1 Optimized structures for Ge_5^z ($z = -2, 0, +2$). In Figs. 1, 2, and 3, the relative energies are indicated in kcal mol^{-1} for two or more structures of the same stoichiometries.

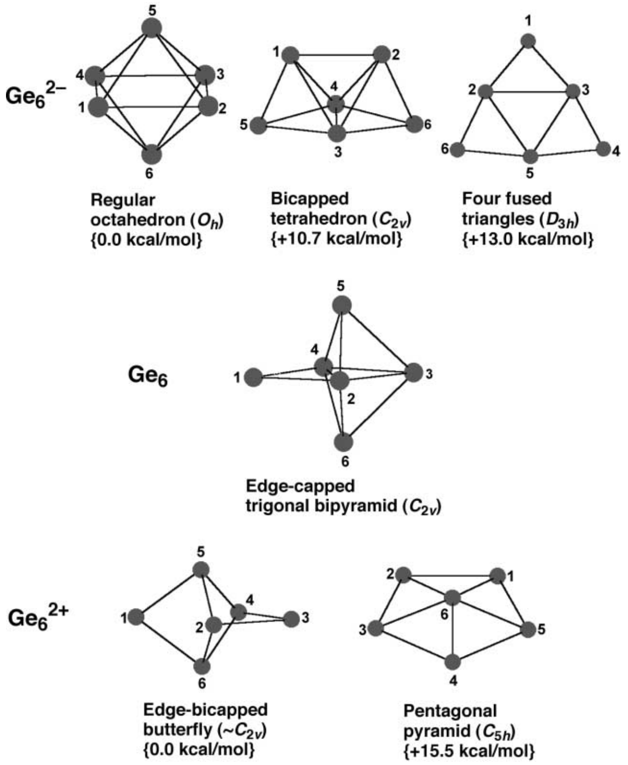

Fig. 2 Optimized structures for Ge_6^z ($z = -2, 0, +2$).

found for the isoelectronic Group 15 metal cluster[15] Bi_5^{3+} (Table 4). However, for the isoelectronic Tl_5^{7-} cluster in various environments, the corresponding eq–eq/eq–ax length ratio is appreciably less (1.02 to 1.05).[16,17] This may relate to the relatively high charge on the thallium clusters requiring a large number of counterions for charge balance. The packing of these counterions in the crystal lattice could cause some

Table 3 Minima of the seven-vertex germanium clusters Ge_7^z found in this work

Formula	Structure and symmetry	Total energies/a.u.	Relative energies/kcal mol^{-1}	Distances/Å
Ge_7^{2-}	Pentagonal bipyramid (D_{5h})	−26.5401831	0.0	Ge1–Ge2 = Ge2–Ge3 = Ge3–Ge4 = Ge4–Ge5 = Ge5–Ge1 = 2.578; Ge1–Ge6 = Ge2–Ge6 = Ge3–Ge6 = Ge4–Ge6 = Ge5–Ge6 = Ge1–Ge7 = Ge2–Ge7 = Ge3–Ge7 = Ge4–Ge7 = Ge5–Ge7 = 2.829; Ge6 ··· Ge7 = 3.575
Ge_7^{2-}	Edge-capped pentagonal pyramid (C_s)	−26.5072155	20.7	Ge1–Ge2 = 2.481; Ge1–Ge6 = 2.480; Ge2–Ge3 = 2.497; Ge2–Ge6 = 2.639; Ge2–Ge7 = 2.731; Ge3–Ge4 = 2.524; Ge3–Ge7 = 2.894; Ge4–Ge5 = 2.525; Ge4–Ge7 = 2.812; Ge5–Ge6 = 2.496; Ge5–Ge7 = 2.895; Ge6–Ge7 = 2.733
Ge_7	Oblate pentagonal bipyramid (D_{5h})	−26.5289294	0.0	Ge4–Ge6 = 2.825; all other Ge–Ge edges = 2.689
Ge_7	Tricapped tetrahedron (C_{3v})	−26.5009687	17.5	Ge1–Ge3 = Ge1–Ge5 = Ge3–Ge5 = 2.987; Ge1–Ge7 = Ge3–Ge7 = Ge5–Ge7 = 2.789; Ge2–Ge1 = Ge2–Ge3 = Ge4–Ge3 = Ge4–Ge5 = Ge6–Ge5 = Ge6–Ge1 = 2.447; Ge7–Ge2 = Ge7–Ge4 = Ge7–Ge6 = 3.158
Ge_7	Irregular pentagonal bipyramid (C_{2v})	−26.4808769	30.1	Ge1–Ge2 = Ge4–Ge5 = 2.535; Ge2–Ge3 = Ge3–Ge4 = 2.448; Ge3–Ge6 = Ge3–Ge7 = 2.703; Ge1–Ge5 = 2.824; Ge1–Ge6 = Ge1–Ge7 = 2.724; Ge5–Ge6 = Ge5–Ge7 = 2.725; Ge2 ··· Ge6 = Ge2 ··· Ge7 = Ge4 ··· Ge6 = Ge4 ··· Ge7 = Ge3 ··· Ge5 = Ge3 ··· Ge4 = 3.330; Ge6 ··· Ge7 = 3.998
Ge_7	Face-capped octahedron (C_{3v})	−26.4786795	31.5	Ge1–Ge4 = Ge1–Ge5 = Ge2–Ge3 = Ge2–Ge5 = Ge3–Ge6 = Ge4–Ge6 = 2.669; Ge3–Ge4 = Ge3–Ge5 = Ge4–Ge5 = 2.732; Ge3–Ge7 = Ge4–Ge7 = Ge5–Ge7 = 2.617; Ge1–Ge2 = Ge1–Ge6 = Ge2–Ge6 = 2.811
Ge_7^{2+}	Oblate irregular pentagonal bipyramid (C_{2v})	−25.8421861	0.0	Ge1–Ge6 = Ge1–Ge7 = Ge5–Ge6 = Ge5–Ge7 = 2.636; Ge1–Ge2 = Ge4–Ge5 = 2.681; Ge6–Ge7 = 3.089; Ge3–Ge6 = Ge3–Ge7 = 2.628; Ge2–Ge6 = Ge2–Ge7 = Ge4–Ge6 = Ge4–Ge7 = 3.114; Ge2–Ge3 = Ge3–Ge4 = 2.481; Ge1 ··· Ge5 = 3.434
Ge_7^{2+}	Warped/distorted hexagonal wheel (D_{3h})	−25.8380470	2.6	Ge7–Ge1 = Ge7–Ge3 = Ge7–Ge5 = 2.596; Ge7–Ge2 = Ge7–Ge4 = Ge7–Ge6 = 2.742; Ge1–Ge2 = Ge2–Ge3 = Ge3–Ge4 = Ge4–Ge5 = Ge5–Ge6 = Ge6–Ge1 = 2.623

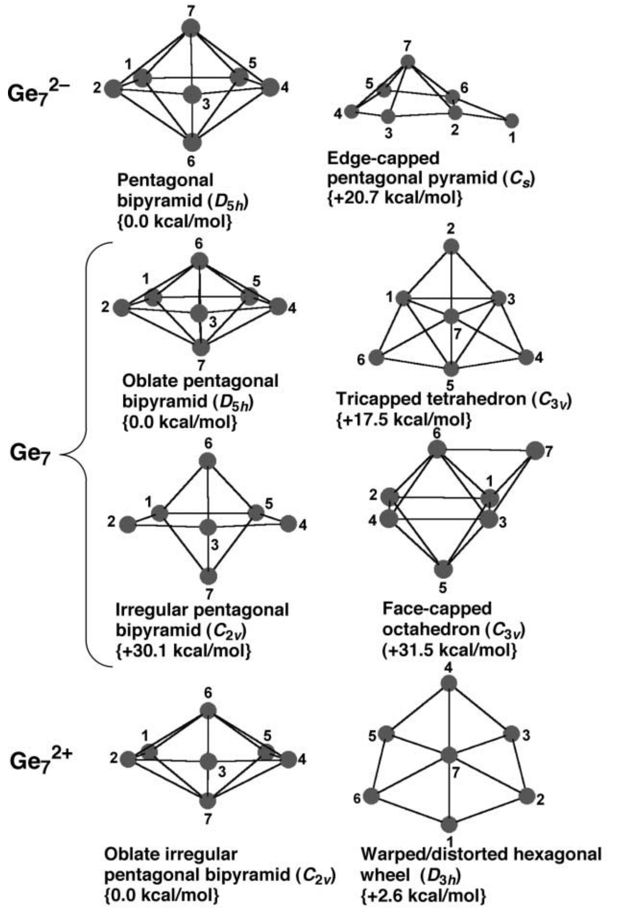

Fig. 3 Optimized structures for Ge_7^z ($z = -2, 0, +2$).

distortion of the trigonal bipyramidal structure leading to a significant change in the eq–eq/eq–ax length ratio.

Removing two electrons from Ge_5^{2-} gives the hypoelectronic neutral Ge_5 cluster, which was also recently studied computationally by Archibong and St-Amant.[18] Our results agree with their results that the lowest energy optimized structure is the oblate trigonal bipyramid, which is compressed along the three-fold axis. This compression leads to a higher eq–eq/eq–ax length ratio (1.34–1.35) for Ge_5 than that found for the dianion Ge_5^{2-}. In addition, this compression makes the ax–ax distance in Ge_5 (3.14 Å) less than the eq–eq distance of 3.32–3.35 Å. A similar compression of a regular octahedron in the $2n + 2$ skeletal electron Tl_6^{8-} to give an oblate tetragonal bipyramid in the $2n$ skeletal electron Tl_6^{6-} has been observed both computationally[1,2] and experimentally.[3,4,5]

Fig. 4 and Table 5 compare the bonding molecular orbitals (MOs) for the trigonal bipyramidal (D_{3h}) structure of Ge_5^{2-} and Ge_5. Using the terminology of tensor surface harmonic (TSH) theory[19,20,21,22] the four lowest lying MOs may be assigned to the single "in phase" S orbital (a_1'; designated in Fig. 4 as S^+) with no nodes and the three uninodal P orbitals ($a_2'' + e'$). The next six MOs are the five binodal D orbitals ($a_1' + e' + e''$) and the single "out of phase" S orbital (a_1'; designated here as S^-). This leaves the highest occupied molecular orbital (HOMO) for the dianion Ge_5^{2-}, namely the a_2'' orbital, which has the appearance of an $F(z^3)$ orbital. When the axial vertices of Ge_5^{2-} are compressed to within bonding distance in going from the ordinary trigonal bipyramid of Ge_5^{2-} to the oblate trigonal bipyramid of Ge_5, this $F(z^3)$ orbital, which has a node along the C_3 axis between the two axial vertices, becomes more strongly σ-antibonding thereby accounting for the two less skeletal electrons in an oblate trigonal bipyramidal structure. This pattern of molecular orbital energy changes in going from a $2n + 2$ skeletal electron deltahedral cluster to the corresponding $2n$ skeletal electron cluster was previously observed in our computations[1,2] on the six-vertex Group 13 clusters Ic_6^{8-} and Ic_6^{6-} (Ic = B, In, Tl).

Our computations on neutral Ge_5 led also to a higher energy (+28.0 kcal) local minimum for an open structure of C_{2v} symmetry consisting of three fused triangles looking like a squashed pentagon (Fig. 1). Archibong and St-Amant[18] found

Table 4 Dimensions of trigonal bipyramidal clusters

Dimensions/Å (average when non-equivalent)					
Cluster	eq–eq	eq–ax	ax···ax	eq–eq/eq–ax	Ref.
Ge_5^{2-}	2.818	2.577	3.997	1.09	This work
Ge_5^{2-}	2.68 ± 0.02	2.49 ± 0.03	3.90 ± 0.02	1.08	13
Sn_5^{2-}	3.238	3.002	4.70	1.08	14
Pb_5^{2-}	3.095	2.877	4.49	1.08	14
Bi_5^{3+}	3.326	3.013	4.646	1.10	15
Tl_5^{7-}	3.280	3.214		1.02	16
Tl_5^{7-}	3.32	3.15 ± 0.01		1.05	17
Ge_5	3.351	2.491	3.141	1.35	This work
Ge_5	3.320	2.476	3.135	1.34	18

Table 5 Molecular orbital energies and symmetry labels for the lowest energy isomers of Ge_n^{z-} ($n = 5, 6, 7$; $z = -2, 0$)[a]

No.	Ge_5^{2-} (D_{3h})	Ge_5 (D_{3h})	Ge_6^{2-} (O_h)	Ge_6 (C_s)	Ge_7^{2-} (D_{5h})	Ge_7 (D_{5h})
1	$-0.2949\ a_1'$	$-0.6110\ a_1'$	$-0.3245\ a_{1g}$	$-0.6376\ a'$	$-0.3295\ a_1'$	$-0.6478\ a_1'$
2	$-0.1658\ a_2''$	$-0.4583\ a_2''$	$-0.1823\ t_{1u}$	$-0.4925\ a'$	$-0.2224\ e_1'$	$-0.5207\ e_1'$
3	$-0.1184\ e'$	$-0.4580\ e'$	$-0.1822\ t_{1u}$	$-0.4887\ a'$	$-0.2224\ e_1'$	$-0.5207\ e_1'$
4	$-0.1184\ e'$	$-0.4580\ e'$	$-0.1822\ t_{1u}$	$-0.4616\ a''$	$-0.1814\ a_2''$	$-0.4572\ a_2''$
5	$-0.0382\ a_1'$	$-0.3241\ a_1'$	$-0.0673\ e_g$	$-0.3870\ a'$	$-0.0986\ a_1'$	$-0.3909\ e_2'$
6	$0.0569\ a_1'$	$-0.2509\ a_1'$	$-0.0672\ e_g$	$-0.3474\ a'$	$-0.0951\ e_2'$	$-0.3909\ e_2'$
7	$0.0750\ e''$	$-0.2387\ e''$	$0.0263\ a_{1g}$	$-0.2568\ a'$	$-0.0951\ e_2'$	$-0.3821\ a_1'$
8	$0.0750\ e''$	$-0.2387\ e''$	$0.0403\ t_{2g}$	$-0.2532\ a''$	$0.0183\ a_1'$	$-0.2576\ e_1''$
9	$0.0961\ e'$	$-0.2225\ e'$	$0.0404\ t_{2g}$	$-0.2496\ a''$	$0.0257\ e_1''$	$-0.2576\ e_1''$
10	$0.0961\ e'$	$\underline{-0.2225\ e'}$	$0.0404\ t_{2g}$	$-0.2411\ a'$	$0.0257\ e_1''$	$-0.2553\ a_1'$
11	$\underline{0.0979\ a_2''}$	$-0.1112\ a_2''$	$0.0922\ t_{1u}$	$-0.2209\ a'$	$0.0612\ e_2'$	$-0.2328\ e_2''$
12	$0.1954\ e'$		$0.0923\ t_{1u}$	$\underline{-0.2190\ a'}$	$0.0612\ e_2'$	$-0.2328\ e_2''$
13	$0.1954\ e'$		$\underline{0.0923\ t_{1u}}$	$-0.1090\ a''$	$0.0685\ e_2''$	$-0.2246\ e_2'$
14			$0.1905\ t_{1u}$		$0.0685\ e_2''$	$\underline{-0.2246\ e_2'}$
15			$0.1905\ t_{1u}$		$\underline{0.0950\ a_2''}$	$-0.1184\ a_2''$
16			$0.1905\ t_{1u}$		$0.1769\ a_2''$	

[a] The HOMO is underlined in each column; MOs below the underline are unoccupied MOs starting with the LUMO.

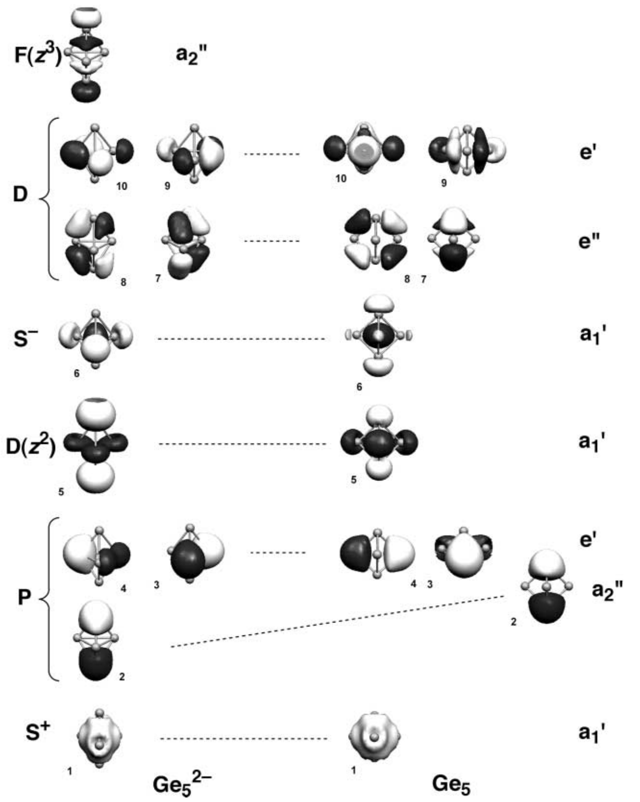

Fig. 4 A comparison of the bonding MOs for trigonal bipyramidal Ge_5^{2-} and Ge_5.

a related "trapezoid" structure +37.0 kcal above their trigonal bipyramid minimum. For the dication Ge_5^{2+} the only true minimum that we found has a similar but completely unsymmetrical (C_1) structure consisting of three fused triangles looking like a trapezoid. The seven edge lengths of our three-triangle (squashed pentagon) structure for Ge_5 all fall in the range 2.40–2.60 Å. However, three of the corresponding edges in Ge_5^{2+} are appreciably longer (2.921, 2.779, and 2.736 Å) possibly owing to the presence of two fewer bonding electrons in Ge_5^{2+} relative to Ge_5. In any case our calculations suggest that a minimum of 10 skeletal electrons (= $2n$ for n = 5) are required for a Ge_5^z cluster to assume a closed polyhedral structure rather than an open structure consisting of fused triangles.

3.2 The six-vertex clusters

The optimized structures for the minima of Ge_6^z clusters are depicted in Fig. 2 and their relative energies are depicted in Table 2. For the dianion Ge_6^{2-} with the 14 = $2n$ + 2 skeletal electrons suggested by Wade's rules,[12] the regular octahedron is found to be the global minimum in accord with expectations and previous DFT computations[1,2] on the isoelectronic Group 13 metal clusters Ic_6^{8-} (Ic = B, In, Tl). The computed edge lengths in octahedral Ge_6^{2-} are 2.687 Å as compared with 2.541 Å found experimentally by X-ray diffraction[23] for the hexakis-(pentacarbonylchromium) complex $[Ge_6\{Cr(CO)_5\}_6]^{2-}$. Higher in energy by 10.7 kcal mol⁻¹ is the bicapped tetrahedron, which in isolable species [*e.g.*, the osmium carbonyl[24] $Os_6(CO)_{18}$] has 12 apparent skeletal electrons rather than the 14 skeletal electrons in Ge_6^{2-}. However, the C_{2v} symmetry of a bicapped tetrahedron leads only to non-degenerate molecular orbitals, which could imply some flexibility in the skeletal electron count. A planar structure consisting of a symmetrical D_{3h} configuration of four triangles is the highest energy local minimum (+13.0 kcal mol⁻¹) found for Ge_6^{2-}.

Removal of two skeletal electrons from Ge_6^{2-} leads to the neutral species Ge_6, which is isoelectronic with the Group 13 clusters Ic_6^{6-} (Ic = B, In, Tl), previously[1,2] computed to have

Table 6 Dimensions of pentagonal bipyramidal clusters

	Dimensions/Å (average when non-equivalent)				
Cluster	eq–eq	eq–ax	ax···ax	eq–eq/eq–ax	Ref.
Ge_7^{2-}	2.578	2.829	3.575	0.91	This work
$B_7Br_7^{2-}$	1.62	1.80		0.90	30
Ge_7	2.69	2.69	2.82	1.00	This work
Tl_7^{7-}	3.29	3.27	3.39	1.01	31
$Au_7(PPh_3)_7^+$	2.95	2.82	2.58	1.05	32

oblate (squashed) D_{4h} bicapped tetragonal pyramidal structures. A related structure was initially computed for Ge_6. However, this structure was found to undergo further distortion to a C_{2v} structure, which can be interpreted as a trigonal bipyramid with the sixth vertex capping one of the equatorial edges (Fig. 2). A trigonal bipyramid requires $12 = 2n + 2$ skeletal electrons as noted above in the discussion of Ge_5^{2-}. If the capping germanium vertex in the edge-capped trigonal bipyramidal Ge_6 donates the same two electrons as the other germanium vertices, then Ge_6 has the required 12 skeletal electrons for its trigonal bipyramidal core.

Removal of two additional skeletal electrons from Ge_6 leads to the dication Ge_6^{2+}. The lowest energy computed structure for Ge_6^{2+} can be derived by further distortion of the edge-capped trigonal bipyramid of Ge_6 to a related figure, likewise of C_{2v} symmetry, conveniently described as an edge-bicapped butterfly (Fig. 2). A higher energy local minimum (+15.5 kcal mol^{-1}) for Ge_6^{2+} is the pentagonal pyramid.

3.3 The seven-vertex clusters

Among the five topologically distinct seven-vertex deltahedra[25,26] three have distinctive symmetries (Fig. 3). Thus, the pentagonal bipyramid has five-fold symmetry (D_{5h}) and the capped octahedron and tricapped tetrahedron have three-fold symmetry (C_{3v}). However, only the pentagonal bipyramid has no degree three vertices and thus can be a possible deltahedron for a three-dimensional aromatic system.[27,28] In this connection the lowest energy minimum for the 16 skeletal electron (= $2n + 2$ for $n = 7$) Ge_7^{2-} is a pentagonal bipyramid (Table 3) in accord with Wade's rules.[12] Higher in energy than the pentagonal bipyramid for Ge_7^{2-} by 20.7 kcal mol^{-1} is a C_s edge-capped pentagonal pyramid. The pentagonal pyramid is a *nido* six-vertex structure found in B_6H_{10} and expected by Wade's rules[12] to have $2n + 4 = 16$ skeletal electrons for $n = 6$. If the seventh capping germanium vertex contributes the same two skeletal electrons as the six germanium vertices of the pentagonal pyramid, then Ge_7^{2-} has exactly these required 16 skeletal electrons.

No bare metal seven-atom clusters with 16 skeletal electrons isoelectronic with Ge_7^{2-} have been characterized experimentally. Even the structure of the corresponding unsubstituted pentagonal bipyramidal deltahedral borane $B_7H_7^{2-}$ has not been determined crystallographically, presumably owing to its hydrolytic instability compared with the other deltahedral boranes.[29] However, the perbrominated seven-vertex deltahedral borane $B_7Br_7^{2-}$ has been shown by X-ray diffraction[30] to have the expected pentagonal bipyramidal structure with an eq–eq/eq–ax ratio of 0.90 very close to the 0.91 computed for Ge_7^{2-} (Table 6).

Removal of two electrons from Ge_7^{2-} gives the neutral Ge_7 species, which is computed to have an oblate (squashed) pentagonal bipyramidal structure as the lowest energy minimum (Fig. 3). The oblate nature of this structure for Ge_7 is indicated by an eq–eq/eq–ax ratio of 1.00 (*i.e.*, coincidentally equal eq–eq and eq–ax distances) as compared with an eq–eq/eq–ax ratio of 0.91 for the dianion Ge_7^{2-} (Table 6).

No examples of seven-atom germanium clusters have yet been synthesized. However, the Tl_7^{7-} anion isoelectronic with Ge_7 is found in the intermetallic $Na_{12}K_{38}Tl_{48}Au_2$. Determination of the structure of this Tl_7^{7-} anion by X-ray diffraction[31] indicates an eq–eq/eq–ax ratio of 1.01 very close to the computed value of 1.00 for Ge_7. Another example of an oblate pentagonal bipyramid occurs in the gold cluster $Au_7(PPh_3)_7^+$, which has an even more oblate Au_7 pentagonal bipyramid with an experimentally determined eq–eq/eq–ax ratio of 1.05.[32]

Fig. 5 and Table 5 compare the bonding MOs for the pentagonal bipyramidal (D_{5h}) structures of Ge_7^{2-} and Ge_7. As for the corresponding five-vertex clusters Ge_5^{2-} and Ge_5, the four lowest lying MOs in both Ge_7^{2-} and Ge_7 may be assigned to the single "in phase" S^+ orbital (a_1') with no nodes and the three uninodal P orbitals (e_1' and a_2''). The next six MOs are the five binodal D orbitals ($a_1' + e_1'' + e_2'$) and the single "out of phase" S^- orbital (a_1'). Above this group of ten lowest lying bonding MOs ($S^+ + S^- + P + D$) lie five trinodal F orbitals ($a_2'' + e_2' + e_2''$). For the dianion Ge_7^{2-} these F orbitals are all bonding MOs leading to a total of 15 bonding MOs requiring 30 electrons corresponding to seven lone pairs and eight skeletal bonding pairs (16 skeletal electrons). The highest lying of these five F orbitals, namely the HOMO in Ge_7^{2-}, is the F(z^3) orbital of similar symmetry as the F(z^3) HOMO in Ge_5^{2-}. When the axial vertices of Ge_7^{2-} are compressed to within bonding distance in going from the ordinary pentagonal bipyramid of Ge_7^{2-} to the oblate pentagonal bipyramid of Ge_7, this F(z^3)

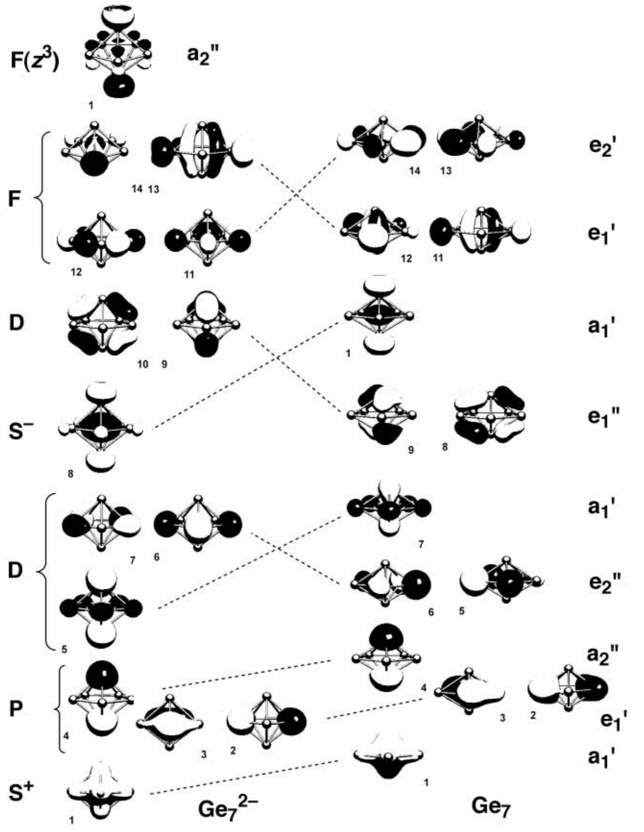

Fig. 5 A comparison of the bonding MOs for pentagonal bipyramidal Ge_7^{2-} and Ge_7.

orbital becomes more strongly σ-antibonding thereby accounting for the two less skeletal electrons in an oblate pentagonal bipyramidal structure. The bonding MO patterns in the five- and seven-vertex bipyramidal clusters, namely Ge_5^{2-}/Ge_5 and Ge_7^{2-}/Ge_7, respectively, are thus completely analogous except for four more F bonding orbitals in the seven-vertex clusters corresponding to the two "extra" vertices and the eight additional total electrons.

Three higher-energy local minima were found for Ge_7 in the following sequence of increasing energies (Table 3 and Fig. 3):

(1) The tricapped tetrahedron (+17.5 kcal mol^{-1}): This is one of the five topologically distinct seven-vertex deltahedra. Note that the six edges to the unique degree 6 vertex alternate in length between 2.79 and 3.16 Å.

(2) An irregular pentagonal bipyramid (+30.1 kcal mol^{-1}): This is a higher energy variation of the oblate pentagonal bipyramid where the squashing does not occur along the five-fold axis but along an axis perpendicular to the five-fold axis. This destroys the five-fold symmetry of the pentagonal bipyramid thus reducing the overall symmetry from D_{5h} to its subgroup C_{2v}.

(3) A face-capped octahedron (+31.5 kcal mol^{-1}): This deltahedron is found in the metal carbonyl clusters $Os_7(CO)_{21}$ (ref. 33) and $Rh_7(CO)_{16}^{3-}$ (ref. 34), both of which have 14 apparent skeletal electrons like Ge_7.

Loss of two further electrons from Ge_7 gives the dication Ge_7^{2+}. The lowest energy structure is an oblate irregular pentagonal bipyramid obtained by squashing the irregular pentagonal bipyramid obtained for Ge_7 along the five-fold axis. Such a deltahedron squashed along two of the three axes is equivalent to a prolate deltahedron elongated along the third axis. Such prolate deltahedra (elongated D_{3d} trigonal antiprisms) were computed to be the lowest energy minima for the Group 13 clusters In_6^{4-} and Tl_6^{4-},[1,2] which, like Ge_7^{2+}, are $2n - 2$ skeletal electron structures.

The dication Ge_7^{2+} was also found to have a second local minimum at only slightly higher energy (+2.6 kcal mol^{-1}) corresponding to a D_{3h} structure that can be described as a warped hexagonal wheel. The edges forming the rim of the hexagon are the same length (2.623 Å) whereas the six spokes of the wheel alternate in length between 2.596 and 2.742 Å.

4. Summary

The computations on the germanium clusters Ge_n^{z-} (n = 5, 6, 7; z = −2, 0) show that the axial compression of bipyramidal deltahedra in going from the $2n + 2$ skeletal electrons of Wade's rules[12] in Ge_n^{2-} to $2n$ skeletal electrons in Ge_n occurs not only in octahedra but also in trigonal and pentagonal bipyramids. In the latter cases the axial compression to give oblate bipyramids does not represent a reduction in symmetry in contrast to the previously discussed octahedral Group 13 clusters[1,2] in which axial compression reduces the symmetry from O_h to D_{4h}. For the six-vertex Ge_6^{2-}/Ge_6 system our computations indicate that the oblate tetragonal bipyramid structure previously found[1,2] for the 12-skeletal electron In_6^{6-} undergoes further distortion to give a C_s structure best regarded as an edge-capped trigonal bipyramid.

Further removal of electrons from the neutral Ge_n clusters to give the dications Ge_n^{2+} having $2n - 2$ skeletal electrons leads to more complicated structural changes. Thus for Ge_5^{2+} the lowest energy structure is an unsymmetrical array of three fused triangles whereas for Ge_6^{2+} the edge-capped trigonal bipyramid found for Ge_6 undergoes further distortion to give a somewhat more symmetrical looking structure best regarded as an edge-bicapped butterfly. Only for Ge_7^{2+} does the oblate pentagonal bipyramid found for Ge_7 undergo further distortion to an unsymmetrical prolate (elongated) bipyramid related to the prolate trigonal antiprisms previously[1,2] computed for In_6^{4-} and Tl_6^{4-}.

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