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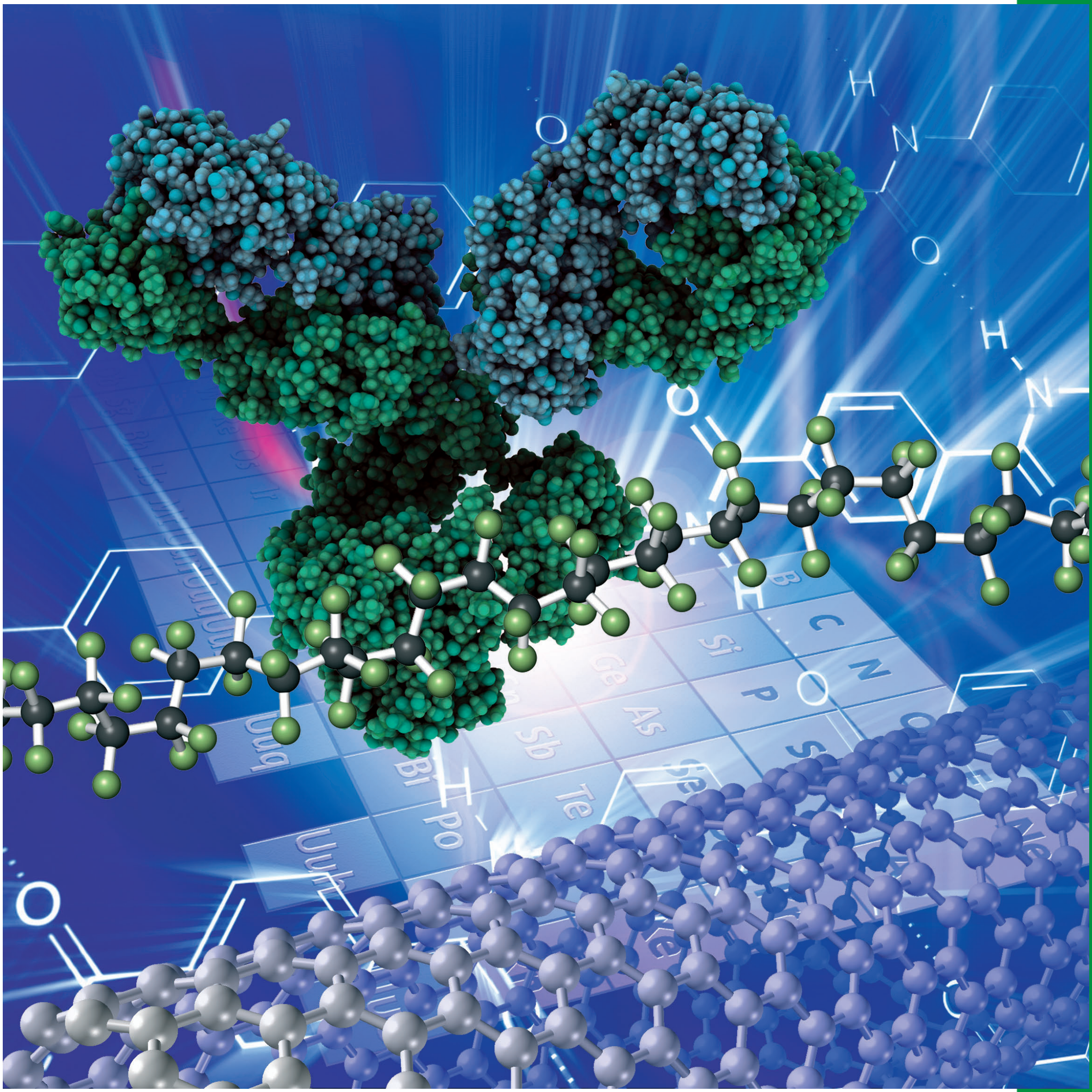

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DFT Study on the Structures and Stability of Be_nSn_n ($n = 1$ – 5) and $Be_{2n}Sn_n$ ($n = 1$ – 4) Clusters.

Silvina E. Fioressi,[a] Pablo Duchowicz,[b] and Daniel E. Bacelo*[a]

The equilibrium geometries and stabilities of bimetallic Be_nSn_n ($n = 1$ – 5) and $Be_{2n}Sn_n$ ($n = 1$ – 4) clusters were investigated through DFT calculations. Cluster geometries were optimized using DFT Monte Carlo simulated annealing and the energies ordered via single-point Quadratic Configuration Interaction (Q-QCISD(T)) calculations evaluated at the optimized B3LYP geometries. Tridimensional highly symmetric structures were generally found as the most stable ones. They have much more in common with the beryllium silicides and germanides than with the carbides. In the larger clusters, a trend to form beryllium sub-structures capped by tin atoms was observed. The bonding between Be and Sn is largely covalent in character, which suggests that there exist the possibility of obtaining larger structures with novel properties and potential for the development of new materials.

Introduction

Clusters of tetravalent elements C, Si, Ge and Sn are of interest as possible sources of materials with new electronic and structural properties.[1,2] The growing interest in the design of new nanomaterials drives the need to understand the growth behavior, chemical bonds and geometries of clusters in this group. A number of experimental and theoretical studies have been published for neutral and charged clusters.[3–6] Among the elements of its group, tin presents the unique feature that exhibits both, covalent and metallic character in bulk phase.[7] Pure tin clusters containing up to 68 atoms have been characterized.[8] Sn_2 and Sn_3 ground states are triplet, with bond lengths of 2.757 and 2.841 Å, respectively. Sn_4 cluster is a distorted rhombus with Sn–Sn distances slightly larger than Sn_3, Sn_5 is a trigonal bipyramid, and Sn_6 is a distorted octahedron, all three of singlet symmetry. In general, these small tin clusters adopt the same geometries than the corresponding Si and Ge clusters and can be compared to those of the corresponding boron hydrides B_nH_n.[9] However, it has been found that the structures and stabilities of doped clusters may be different and dependent on the nature of the dopant and the host. Several studies on tin clusters doped with metallic and nonmetallic atoms have been published.[10–14]

Beryllium finds fewer uses than tin, partly due to its toxicity.[15,16] However, owing to its unmatched physical and chemical properties, beryllium is used to create alloys that are light and rigid with applications in space research,[17] optical devices,[18] computer components,[19] hydrogen storage,[20] and fusion reactors.[21] The structures, electron affinities, and ionization energies of pure beryllium clusters have been studied at different levels of theory.[22–25] Beryllium atom is pseudo-closed-shell, so the diatomic potential well is quite shallow and sensitive to both static and dynamic correlation effects. The *2s–2p* energy gap in Be is small, so a significant *2 s* and *2p* orbital mixing can be produced that induces hybridization and favors the formation of covalent bonds. In light of this interpretation the better electron donors in the group IVA should be examined as potential constituents of stable tridimensional clusters. Tin is a metallic element, with lower electronegativity than the previous elements in its group, therefore there exist the possibility of forming covalent bonds with beryllium.

The present study is grounded in previous examinations of clusters of beryllium with other elements of group IVA (Si, C, and Ge)[26–29] and driven by the need to understand stability, bonding and structure in Be–Sn clusters per sé and in comparison to the corresponding silicides, carbides, and germanides. The combination of beryllium and tin is relatively scarce in chemistry. The two coexist in some rare minerals and alloys.[30–32] However, both elements have received significant attention in the last years and are being intensively used in the development of novel materials and devices with application in electronics, optoelectronics, photocatalysis, and batteries. Ternary chalcopyrites containing Be and Sn have been proposed as potential materials for nonlinear optics and opto-electronics, but in these structures both elements are not bonded directly to each other.[33] A recent DFT study on the electronic properties of doped stanene, found that beryllium atoms induce the formation of dumbbell sub-structures on stanene surfaces, modifying the charge concentration of the surface and consequently its electronic and magnetic characteristics.[34] The theoretical study of clusters and nanostructures are nowadays

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.201802832 a powerful tool in the development of new materials. Many examples of successful experimental validations of theoretical predictions[35–37] encourage the exploration of new compounds with unique electronic, magnetic and optical characteristics.

We focus our present study on examining small low-energy clusters formed by beryllium and tin combined in equal proportions (Be_nSn_n) or containing twice beryllium than tin atoms ($Be_{2n}Sn_n$). To the best of our knowledge, there are not studies on these particular structures. Moreover, this expansion of our aforementioned examinations of beryllium clusters[26–29] may identify trends in cluster progression, bonding and stability of the clusters formed by elements of the carbon group with beryllium.

Results and discussion

In this section, the structures and stabilities of Be_nSn_n clusters with n ranging from 1 to 5 and $Be_{2n}Sn_n$ clusters with $n = 1 - 4$ are discussed ordered by n, the number of tin atoms. The structures of the lowest-energy isomers and a few low-lying isomers for each cluster size are shown in Figures 1–6, and the corresponding Tables 1–7 list the calculated B3LYP and QCISD (T) energies of clusters and selected interatomic distances. The three rightmost columns of the Tables show, respectively, cluster atomization energies, atomization energies divided by number of atoms less one, and the QCISD(T) energy of each structure relative to the most stable. In each Figure tin atoms are depicted as larger and darker in color, berylliums smaller and lighter.

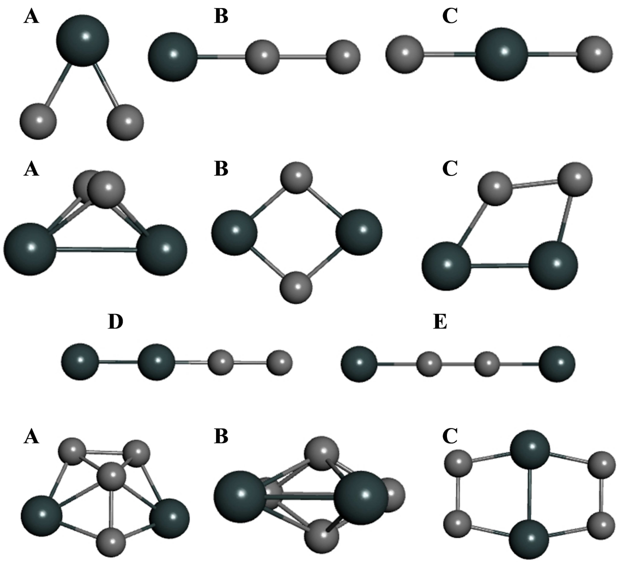

Figure 1. B3LYP optimized structures of Be_2Sn, Be_2Sn_2 and Be_4Sn_2. Tin atoms are larger and in darker color; beryllium atoms are smaller and lighter.

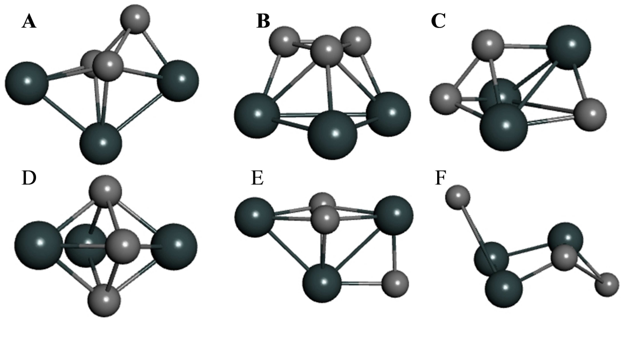

Figure 2. Optimized structures of low-energy Be_3Sn_3 clusters.

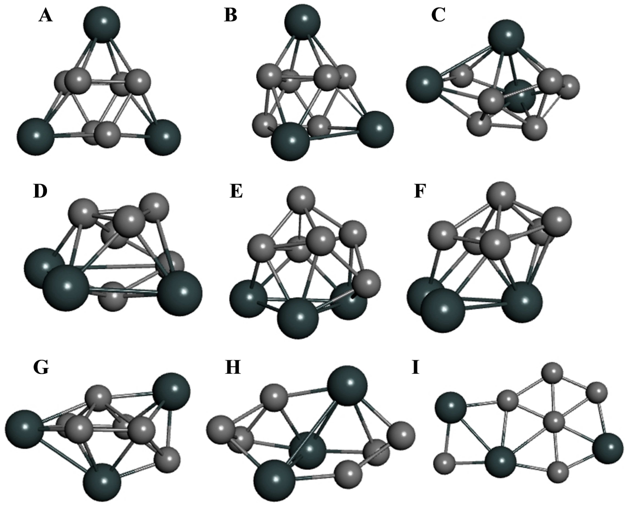

Figure 3. Optimized structures of low-energy Be_6Sn_3 clusters.

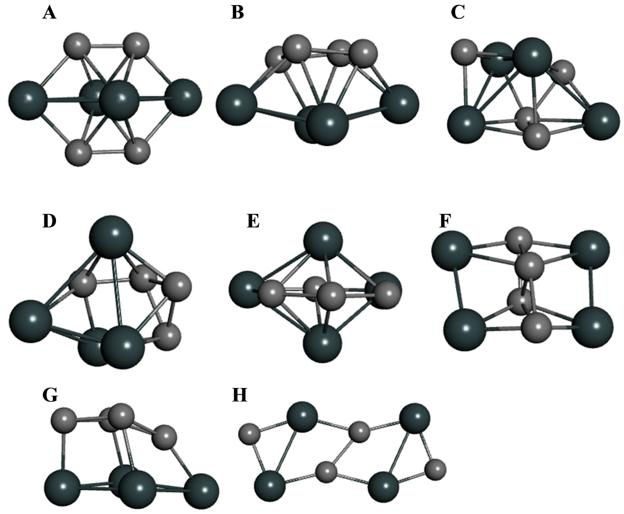

Figure 4. Optimized structures of low-energy Be_4Sn_4 clusters.

BeSn and Be_2Sn. The ground state of BeSn is a triplet at the QCISD(T) level with bond length of 2.37 Å (see Table 1). A singlet lies 0.72 eV (16.67 kcal/mol) above the ground state and a quintet somewhat higher. The ground states of BeC, BeSi, and BeGe are also $^3\Sigma^-$ with bond lengths of 1.67,[29] 2.12,[26] and 2.14 Å[28] respectively, thus BeSn follows the trend of increasing bond length in the group.

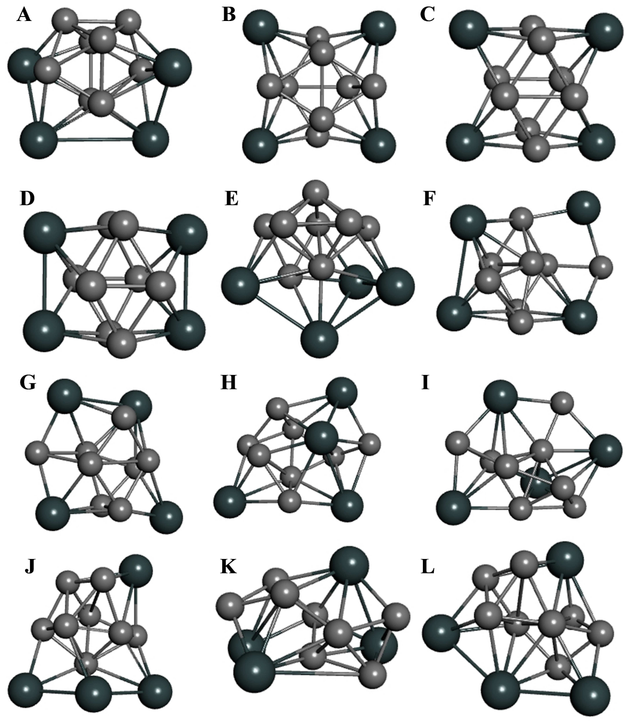

Figure 5. Optimized structures of low-energy Be_8Sn_4 clusters.

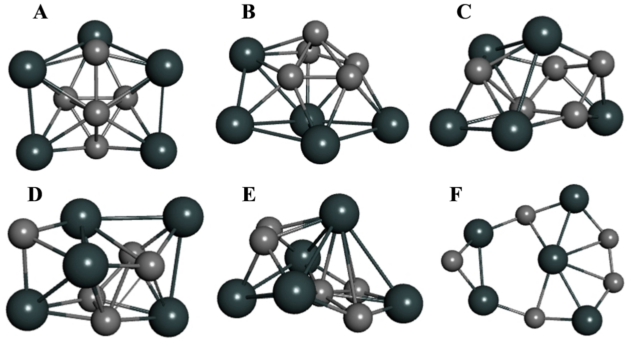

Figure 6. Optimized structures of low-energy Be_5Sn_5 clusters.

A nearly equilateral triangle is the ground state of Be_2Sn (Figure 1), with the Be–Be distances slightly shorter than the Be–Sn. The singlet and triplet states of structure A are very close in energy, less than 0.05 eV apart. Two linear structures are found at higher energy (Figure 1), very similar to those found in Be_2C and Be_2Ge but with progressively larger heteroatomic bonds; the lowest energy state for isomer B is a triplet and for isomer C is a quintuplet, the same states found for Be_2Ge linear isomers. Some charge transfer is seen in Be_2Sn as well as in BeSn; less than one-quarter of an electron is transferred from Be to the Sn atoms. The magnitude of charge transferred is smaller to that seen in Be_2Si and in Be_2Ge, although in the later it is in opposite direction.

Be_2Sn_2. The global minimum energy structure is a non-planar isomer (Figure 1, isomer A) with singlet multiplicity. It resembles a distorted tetrahedron with the tin atoms 3.34 Å apart and a noticeable short Be–Be bond (1.91 Å), even shorter than that of tetrahedral Be_4 (2.03 Å).[22] These short Be–Be distances have also been found in the germanide and silicide analogues, although they do not correspond to the minimal energy structures. For Be_2C_2, however, no stable three-dimensional structures were found. A triplet lies less than 7 kcal/mol above the ground state, with similar geometry than isomer A, though with elongated Be–Be bond and shortened Be–Sn distances. There is not significant charge transfer between beryllium and tin in these clusters, evidencing the covalent character of the bonds. About 4 kcal/mol above the global minimum is structure B, a rhombus of alternating Be and Sn of D_{2h} symmetry in singlet state. This isomer is similar to the most stable isomers of Be_2Si_2 and Be_2Ge_2. In Be_2C_2 the most stable cluster resembles isomer C in Figure 1, probably stabilized by the presence of a C–C triple bond. Relatively higher in energy are two linear structures D and E. Linear structures were not explored for Be_2Si_2, but were found in Be_2C_2 and Be_2Ge_2, and they are also high-lying isomers.

Be_4Sn_2. Only three structures of Be_4Sn_2 were identified, being an almost-regular pentagonal pyramid with C_s symmetry the low-lying isomer (Figure 1). The ground state has singlet multiplicity, whereas the corresponding triplet is almost 12 kcal/mol above the singlet (Table 2), exhibiting a structure slightly more compact. This beryllium- capped pentagonal isomer is also the low-energy form of Be_6,[22] Be_4Si_2,[26] and Be_4Ge_2.[28] Only 1.79 kcal/mol above the global minimum is the singlet of structure B, a square bipyramid with berylliums at the apices and a Sn–Sn separation of 3.05 Å. Much higher in energy is the planar structure C, also a singlet forming a bent irregular hexagon with D_{2h} symmetry.

Be_3Sn_3 and Be_6Sn_3. Six isomers of Be_3Sn_3 were optimized, the two most stable are separated by less than 3 kcal/mol. The global minimum isomer A (Figure 2) is a bicapped tetrahedron with the three Sn atoms bonded at 2.91 Å (Table 3), a distance comparable to that of the pure tin trimer (2.841 Å).[5] The beryllium atoms are forming an equilateral triangle with sides of 2.03 Å length, showing a strong Be–Be bond with distances even shorter than the Be_3 cluster. Isomer B is also a compact structure, a distorted trigonal prism formed by two triangles, one of berylliums and other of tins, very similar to the second most stable isomer of Be_3Si_3[26] and a higher energy isomer of Be_3Ge_3.[28] Isomers C and D are very close in energy, both in singlet state. Structure C is a bicapped tetrahedron, with the beryllium and tin atoms more evenly distributed than in the isomer A. Structure D is an octahedron of C_{2v} symmetry, with three atoms of each type forming triangles that intersect at right angles. The structure closely resembles the global minima of Be_3Si_3[26] and Be_3Ge_3[28] and is also observed among the isomers of Be_3C_3.[29] Isomer F is the only structure of Be_3Sn_3 that does not show a cage-like structure. It is a bent hexagon that resembles the "chair" conformation of cyclohexane. This geometry was not observed in the carbide, silicide, and germanide analogues.

Among the nine structures of Be_6Sn_3 found (Figure 3), the global minimum is a trigonal prism of berylliums tricapped

Table 1. Energies and minimum distances of BeSn, Be$_2$Sn and Be$_2$Sn$_2$ clusters. Column contents are described in the text.

Specie	State	B3-LYP[a]	QCISD(T)[a]	d(Sn–Sn)	d(Sn–Be)	d(Be–Be)	E_{At}[b]	$E_{At}/(N\text{-}1)$[b]	ΔE_{Rel}[b]
BeSn									
	$^{3}\Sigma^{-}$	-18.0309707	-17.9389907		2.366		42.87	42.87	0.00
	$^{1}\Sigma^{+}$	-18.0043479	-17.9124249		2.367		26.20	26.20	16.67
	$^{5}\Sigma^{-}$	-17.9850143	-17.896939		2.134		16.48	16.48	26.39
Be$_2$Sn									
A	$^{1}A_1$	-32.7516555	-32.6032729		2.295	2.150	74.41	37.20	0.00
A	$^{3}B_1$	-32.7585589	-32.6016571		2.423	2.058	73.39	36.70	1.01
B	$^{3}\Sigma^{+}$	-32.7324572	-32.5739612		2.340	2.126	56.01	28.01	18.39
B	$^{5}\Sigma^{+}$	-32.7200482	-32.5649825		2.368	2.095	50.38	25.19	24.03
B	$^{1}\Sigma^{+}$	-32.7121092	-32.5579403		2.355	2.089	45.96	22.98	28.45
C	$^{5}\Sigma_u^{+}$	-32.7145135	-32.5540212		2.361	4.722	43.50	21.75	30.91
C	$^{3}\Sigma_g$	-32.6952760	-32.5337204		2.242	4.484	30.76	15.38	43.64
C	$^{1}\Sigma_g$	-32.6510474	-32.5004198		2.118	4.224	9.87	4.93	64.54
Be$_2$Sn$_2$									
A	$^{1}A'$	-36.1923102	-36.0113371	3.3406	2.452	1.913	169.41	56.47	0.00
B	^{1}A	-36.1862899	-36.0044679	3.501	2.337	3.097	165.10	55.03	4.31
A	$^{3}A'$	-36.1844575	-36.0003418	3.590	2.393	2.145	162.51	54.17	6.90
C	^{1}A	-36.1692561	-35.9843588	2.795	2.332	2.089	152.49	50.83	16.93
C	^{3}A	-36.1699920	-35.9829708	2.891	2.385	1.991	151.61	50.54	17.80
C	^{5}A	-36.1403162	-35.9502206	3.153	2.481	2.080	131.06	43.69	38.35
D	$^{1}\Sigma^{+}$	-36.1199489	-35.9327163	2.618	2.227	2.048	120.08	40.03	49.34
B	$^{5}A'$	-36.1571675	-35.9325454	4.508	2.501	2.169	119.97	39.99	49.44
E	$^{1}\Sigma^{+}$	-36.1052530	-35.9068858	7.013	2.479	2.055	103.87	34.62	65.54
D	$^{3}\Sigma^{+}$	-36.1348509	-35.8959576	2.657	2.379	2.127	97.01	32.34	72.40
E	$^{5}\Sigma$	-36.1231309	-35.8845508	6.949	2.428	2.092	89.85	29.95	79.56

[a]Energies in atomic units. [b]Energies in kcal/mol. Distances in angstroms

Table 2. Energies and minimum distances of Be$_4$Sn$_2$ clusters. Column contents are described in the text.

Specie	State	B3-LYP[a]	QCISD(T)[a]	d(Sn–Sn)	d(Sn–Be)	d(Be–Be)	E_{At}[b]	$E_{At}/(N\text{-}1)$[b]	ΔE_{Rel}[b]
A	$^{1}A'$	-65.6732777	-65.3729322	4.091	2.396	2.011	253.22	50.64	0.00
B	$^{1}A_1$	-65.6671415	-65.3700871	3.046	2.328	2.025	251.44	50.29	1.79
A	$^{3}A''$	-65.6563713	-65.3545064	3.607	2.352	2.001	241.66	48.33	11.56
B	$^{3}A_1$	-65.6420143	-65.3393000	4.249	2.451	2.059	232.12	46.42	21.10
A	$^{5}A'$	-65.6287182	-65.3268742	4.445	2.424	2.060	224.32	44.86	28.90
B	$^{5}B_1$	-65.6470861	-65.3227013	4.813	2.455	1.957	221.70	44.34	31.52
C	^{1}A	-65.6318175	-65.3211252	2.922	2.357	1.972	220.71	44.14	32.51
C	^{3}A	-65.6158754	-65.3128581	3.278	2.418	2.067	215.53	43.11	37.70
C	^{5}A	-65.6104954	-65.3014848	3.004	2.351	1.993	208.39	41.68	44.83

[a]Energies in atomic units. [b]Energies in kcal/mol. Distances in angstroms

Table 3. Energies and minimum distances of Be$_3$Sn$_3$ clusters. Column contents are described in the text.

Specie	State	B3-LYP[a]	QCISD(T)[a]	d(Sn–Sn)	d(Sn–Be)	d(Be–Be)	E_{At}[b]	$E_{At}/(N\text{-}1)$[b]	ΔE_{Rel}[b]
A	^{1}A	-54.3571727	-54.0910261	2.910	2.329	2.029	300.57	60.11	0.00
B	^{1}A	-54.3567555	-54.0862856	2.898	2.377	1.993	297.60	59.52	2.97
A	^{3}A	-54.3464504	-54.0787276	3.139	2.470	2.018	292.85	58.57	7.72
C	^{1}A	-54.3428104	-54.0766454	3.010	2.377	1.994	291.55	58.31	9.02
D	$^{1}A_1$	-54.3352273	-54.0762443	3.051	2.379	2.286	291.29	58.26	9.28
E	^{1}A	-54.3394002	-54.0744752	3.113	2.317	2.063	290.18	58.04	10.39
B	$^{3}A'$	-54.3460852	-54.0477529	2.955	2.447	2.007	273.42	54.68	27.15
C	^{5}A	-54.2875240	-54.0135278	3.058	2.458	2.006	251.94	50.39	48.63
F	^{1}A	-54.2520638	-53.9769801	2.848	2.356	4.026	229.00	45.80	68.59

[a]Energies in atomic units. [b]Energies in kcal/mol. Distances in angstroms

Table 4. Energies and minimum distances of Be_6Sn_3 clusters. Column contents are described in the text.

Specie	State	B3-LYP[a]	QCISD(T)[a]	d(Sn–Sn)	d(Sn–Be)	d(Be–Be)	E_{At}[b]	$E_{At}/(N-1)$[b]	ΔE_{Rel}[b]
A	$^1A'$	-98.6407652	-98.2114431	4.537	2.526	2.059	475.24	59.41	0.00
B	^1A	-98.6358218	-98.2057557	3.167	2.443	2.050	471.67	58.96	3.57
C	^1A	-98.6247354	-98.1948329	3.123	2.431	1.976	464.82	58.10	10.42
D	^1A	-98.6220161	-98.190516	3.230	2.448	2.006	462.11	57.76	13.13
E	^1A	-98.6183328	-98.1857861	3.051	2.404	1.970	459.14	57.39	16.10
F	^1A	-98.6121855	-98.1793146	3.047	2.428	1.982	455.08	56.89	20.16
D	^3A	-98.6121984	-98.1787223	3.022	2.463	2.005	454.71	56.84	20.53
C	^3A	-98.6063819	-98.1744303	3.218	2.418	2.018	452.02	56.50	23.23
E	^3A	-98.6100554	-98.1730996	3.164	2.456	2.028	451.18	56.40	24.06
B	^3A	-98.6122162	-98.1695574	3.039	2.429	1.985	448.96	56.12	26.28
G	^1A	-98.5928535	-98.1682119	3.162	2.325	2.017	448.11	56.01	27.13
F	^3A	-98.6031741	-98.165047	3.031	2.462	2.019	446.13	55.77	29.11
G	^3A	-98.5931901	-98.1569378	3.255	2.345	2.039	441.04	55.13	34.20
E	^5A	-98.5852453	-98.1467131	2.878	2.423	2.002	434.62	54.33	40.62
C	^5A	-98.5672567	-98.1345160	3.244	2.402	2.015	426.97	53.37	48.27
F	^5A	-98.5736844	-98.1343659	2.912	2.446	2.010	426.88	53.36	48.37
A	$^5A'$	-98.5730936	-98.1300358	4.382	2.515	2.070	424.16	53.02	51.08
H	^1A	-98.5581887	-98.1236778	3.201	2.332	1.927	420.17	52.52	55.07
I	^3A	-98.5710758	-98.1174488	4.224	2.354	2.037	416.26	52.03	58.98
B	^5A	-98.5701914	-98.0910719	3.115	2.388	2.020	399.71	49.96	75.53
I	^1A	-98.5373869	-98.0870109	2.995	2.301	2.014	397.16	49.65	78.08

[a]Energies in atomic units. [b]Energies in kcal/mol. Distances in angstroms

Table 5. Energies and minimum distances of Be_4Sn_4 clusters. Column contents are described in the text.

Specie	State	B3-LYP[a]	QCISD(T)[a]	d(Sn–Sn)	d(Sn–Be)	d(Be–Be)	E_{At}[b]	$E_{At}/(N-1)$[b]	ΔE_{Rel}[b]
A	^1A	-72.5501255	-72.2118704	3.120	2.412	2.018	457.55	65.36	0.00
B	^1A	-72.5559812	-72.2089915	3.027	2.503	1.960	455.74	65.11	1.81
C	^1A	-72.5470101	-72.2084696	3.256	2.403	2.090	455.42	65.06	2.13
D	^1A	-72.5478067	-72.2018211	2.874	2.409	1.991	451.24	64.46	6.31
B	^3B	-72.5461099	-72.1967494	3.037	2.423	2.061	448.06	64.01	9.49
C	^3A	-72.5310896	-72.1910114	3.256	2.436	2.172	444.46	63.49	13.09
E	^1A	-72.5301633	-72.1886628	3.033	2.391	1.967	442.99	63.28	14.56
F	^1A	-72.5351534	-72.1882671	2.799	2.347	2.027	442.74	63.25	14.81
E	^3A	-72.5283454	-72.1867287	3.172	2.419	2.049	441.77	63.11	15.78
D	^3A	-72.5287150	-72.1800202	2.992	2.380	2.041	437.56	62.51	19.99
G	^1A	-72.5290312	-72.176448	2.964	2.401	1.956	435.32	62.19	22.23
G	^3A	-72.5207369	-72.1654713	2.969	2.454	2.012	428.44	61.21	29.12
A	^3A	-72.5132178	-72.162605	3.218	2.342	2.009	426.64	60.95	30.91
C	^5A	-72.5022176	-72.1616061	3.216	2.369	2.176	426.01	60.86	31.54
E	^5A	-72.4976908	-72.1547996	3.255	2.381	2.104	421.74	60.25	35.81
F	^5A	-72.4990910	-72.1542533	3.125	2.413	2.057	421.40	60.20	36.16
A	^5A	-72.4936305	-72.1526621	3.140	2.448	2.152	420.40	60.06	37.15
D	^5A	-72.4974593	-72.1483678	2.982	2.405	2.008	417.70	59.67	39.85
B	^5B	-72.4921182	-72.1405524	3.082	2.473	2.006	412.80	58.97	44.75
H	^1A	-72.4905064	-72.1340936	3.148	2.285	2.157	408.75	58.39	48.81
G	^5A	-72.4860062	-72.1321615	2.988	2.398	2.030	407.53	58.22	50.02
F	^3A	-72.5087639	-72.1156352	2.817	2.414	2.011	397.16	56.74	60.39
H	^3A	-72.4602913	-72.0853775	3.056	2.320	2.127	378.18	54.03	79.38
H	^5A	-72.4276810	-72.0594000	2.944	2.413	2.180	361.87	51.70	95.68

[a]Energies in atomic units. [b]Energies in kcal/mol. Distances in angstroms

with tin atoms. Similar structures were found for the corresponding silicide, carbide and germanide, however only for Be_6Si_3 this is the global minimum. The face capped trigonal prism is also the most stable geometry in pure Be_9 clusters with slightly larger distances between the Be atoms, 2.088 Å as compared with 2.059 Å in Be_6Sn_3 (Table 4).[24] However, the presence of large tin atoms on the main edges of the structure makes the Be_6Sn_3 cluster more expanded and voluminous than the Be_9. Only 3.57 kcal/mol above the global minimum lies isomer B, a similar structure to isomer A, but less symmetric and more compact with a beryllium atom as a cap and one tin forming part of the trigonal prism. Structure C consists of a capped irregular square prism forming a “9-vertex *isocloso*” structure as it is named in polyhedral borane chemistry,[9] very similar to the lowest energy structure of Be_6C_3 and Be_6Ge_3. With exception of the higher energy structure I, which is a planar

Table 6. Energies and minimum distances of Be_8Sn_4 clusters. Column contents are described in the text.

Specie	State	B3-LYP[a]	QCISD(T)[a]	d(Sn–Sn)	d(Sn–Be)	d(Be–Be)	E_{At}[b]	$E_{At}/(N-1)$[b]	ΔE_{Rel}[b]
A	^1A	-131.5718454	-131.0073513	3.017	2.486	2.035	670.53	60.96	0.00
B	^1A	-131.5678584	-131.0066902	4.289	2.401	2.169	670.12	60.92	0.41
C	^1A	-131.5690707	-131.0064806	3.876	2.486	2.051	669.98	60.91	0.55
D	^1A	-131.5670076	-131.0050875	3.013	2.491	2.046	669.11	60.83	1.42
A	^3A	-131.5664827	-131.0034532	3.038	2.451	2.012	668.08	60.73	2.45
E	^1A	-131.5660297	-131.0034119	3.142	2.417	1.968	668.06	60.73	2.47
D	^3A	-131.5694574	-131.0019133	3.086	2.539	2.084	667.12	60.65	3.41
F	^1A	-131.5651439	-131.0003096	3.408	2.361	2.013	666.11	60.56	4.42
G	^1A	-131.5594558	-130.9990706	3.244	2.334	2.033	665.33	60.48	5.20
H	^1A	-131.5541675	-130.9924371	3.168	2.404	1.975	661.17	60.11	9.36
I	^1A	-131.5539279	-130.9903732	3.408	2.388	1.981	659.88	59.99	10.65
J	^1A	-131.5155604	-130.9900047	2.892	2.499	1.990	659.64	59.97	10.89
K	^1A	-131.5510829	-130.9899383	3.229	2.398	1.988	659.60	59.96	10.93
G	^3A	-131.5486962	-130.9883168	3.352	2.345	2.036	658.59	59.87	11.94
F	^3A	-131.5486962	-130.9882963	3.355	2.345	2.037	658.57	59.87	11.96
J	^3A	-131.5542355	-130.9861139	2.897	2.427	2.016	657.20	59.75	13.33
I	^3A	-131.5475144	-130.9823711	3.321	2.380	1.992	654.85	59.53	15.68
H	^3A	-131.5425592	-130.9779124	3.154	2.442	2.024	652.06	59.28	18.47
L	^1A	-131.5389283	-130.9765736	2.988	2.358	2.000	651.22	59.20	19.31
E	^3A	-131.5410148	-130.9694134	2.918	2.401	2.007	646.72	58.79	23.81
C	^5A	-131.5318939	-130.9693498	3.951	2.477	2.096	646.68	58.79	23.85
H	^5A	-131.5321040	-130.9667229	3.102	2.437	2.061	645.04	58.64	25.49
E	^5A	-131.5047665	-130.9328887	2.972	2.395	2.005	623.80	56.71	46.73
J	^5A	-131.5313943	-130.9036855	3.003	2.449	2.050	605.48	55.04	65.05
G	^5A	-131.5388056	-130.9034043	3.245	2.334	2.033	605.30	55.03	65.23
F	^5A	-131.5277914	-130.9002324	4.396	2.370	2.080	603.31	54.85	67.22

[a] Energies in atomic units. [b] Energies in kcal/mol. Distances in angstroms

Table 7. Energies and minimum distances of Be_5Sn_5 clusters. Column contents are described in the text.

Specie	State	B3-LYP[a]	QCISD(T)[a]	d(Sn–Sn)	d(Sn–Be)	d(Be–Be)	E_{At}[b]	$E_{At}/(N-1)$[b]	ΔE_{Rel}[b]
A	^1A	-90.7346202	-90.3162893	2.996	2.415	2.086	604.22	67.14	0.00
B	^1A	-90.7360822	-90.3095050	3.018	2.430	1.970	599.97	66.66	4.26
C	^1A	-90.7171649	-90.2983131	3.157	2.385	2.078	592.94	65.88	11.28
B	^3A	-90.7184574	-90.2883781	3.084	2.464	2.022	586.71	65.19	17.51
D	^1A	-90.7029553	-90.2872273	3.115	2.389	2.076	585.99	65.11	18.24
E	^1A	-90.7119511	-90.2845061	3.398	2.283	1.949	584.28	64.92	19.94
A	^5A	-90.6932467	-90.2706768	3.015	2.474	2.066	575.60	63.96	28.62
E	^3A	-90.6936185	-90.2666724	3.220	2.348	2.030	573.09	63.68	31.14
D	^5A	-90.6849399	-90.2605190	3.144	2.325	2.105	569.23	63.25	35.00
B	^5A	-90.6772155	-90.2457034	3.093	2.504	2.026	559.93	62.21	44.29
C	^5A	-90.6654364	-90.2450265	2.989	2.341	2.126	559.51	62.17	44.72
C	^3A	-90.7132529	-90.2401455	2.889	2.355	2.167	556.44	61.83	47.78
F	^1A	-90.5936771	-90.1425040	3.019	2.295	2.037	495.17	55.02	109.05
F	^5A	-90.5730309	-90.1144524	2.948	2.378	1.985	477.57	53.06	126.65
F	^3A	-90.5973956	-90.0993148	2.899	2.254	1.996	468.07	52.01	136.15

[a] Energies in atomic units. [b] Energies in kcal/mol. Distances in angstroms

triplet, all Be_6Sn_3 isomers found are singlet cage-like clusters slightly expanded compared to the Be_3Sn_3 structures mainly due to larger Be–Sn distances.

Be_4Sn_4 and Be_8Sn_4. Even when triplets and quintuplets were located at relatively low energy (about 30–40 kcal/mol from the global minimum), the lower energy states for every Be_4Sn_4 and Be_8Sn_4 structure found were singlet. Eight low-lying isomers were found for Be_4Sn_4 (Figure 4). Structures A, B and C have a ground ^1A state and are within 2.1 kcal/mol in energy. Isomer A is a symmetrical hexagonal bipyramid formed by a Sn square bridged top and bottom by two Be atoms. This structure is just like the Be_4Ge_4 global minimum but with larger interatomic distances, not only for the larger tin atoms but also for the Be–Be bonds (2.018 Å for Be_4Sn_4 as shown in Table 5, and 1.962 Å for Be_4Ge_4).[28] Neither Be_4Si_4 nor Be_4C_4 present structures with this highly symmetric geometry. Isomer B is bicapped trigonal prism that can be seen as a Be_4 on top of a Sn_4 unit. The Be–Be distances are shorter than in isomer A and in pure Be_4 and comparable with those of Be_8 (1.965 Å).[24] The Sn–Sn distances are also larger than those found in structure A and in pure Sn_4 and similar to the Sn_8 distances (3.059 Å).[5] Isomer C resembles a bisdisphenoid structure with the greatest

Be–Be and Sn–Sn distances of the three lowest energy structures. This geometry was also found among the Be_4Ge_4 and Be_4Si_4 isomers but it is absent among the carbides.

The three lower energy isomers of Be_8Sn_4 are within less than one kcal/mol (Table 6). The isomer A is a nearly-regular icosahedron with the tin atoms bonded to each other forming a chain. There are not analogues to this structure among the carbides, silicides and germanides. Isomer B can be described as a distorted tetragonal prism of berylliums face capped with tin atoms, forming a hollow structure with D_{2d} symmetry also found in Be_8Si_4.[26] The tin atoms in this structure are not bonded to each other and arranged forming a square of 4.289 Å sides. Very close in energy lies isomer C, also a face capped prism but with a more compact and symmetrical structure. The inner rhombic prism of berylliums in C is regular and the tin atoms are at the edges of a square of 3.876 Å sides. Isomer D lies only 1.42 kcal/mol above the global minimum. The structure is a nearly regular icosahedron with D_{2h} symmetry very similar to the global minimum of Be_4Ge_8 and Be_4Si_8 that also appears among the isomers of Be_8C_4 but at relatively high-energy. The rest of the structures found (isomers E to L) present not planar asymmetric geometries. Planar clusters are also not seen among the germanides, silicides or carbides. All Be_8Sn_4 isomers show a common feature: the beryllium atoms tend to bond each forming a beryllium substructure capped with the tin atoms.

Be_5Sn_5. Six stable isomers were found (Figure 6), the same number as were identified for Be_5Ge_5 and Be_5Si_5. As in the germanides, all the Be_5Sn_5 isomers are in the ^1A ground state (Table 7), and only the highest energy structure F is planar. In contrast, fifteen stable structures were identified for Be_5C_5 featuring extensive C–Be–C bridging. The low energy structure of Be_5Sn_5 can be seen as a trigonal bipyramid of berylliums capped by tin atoms bonded to each other forming a U shape. The inner bipyramid resembles the ground state of the Be_5 cluster with almost the same interatomic distances[22,23] and the Sn–Sn bonds are 2.996 Å long. This structure was not observed among the corresponding germanides, silicides, and carbides.

Cluster Energetics and Bonding. The atomization energies divided by $N_{atoms}- 1$ (where N_{atoms} is the total number of atoms forming the cluster) is a measure of the cluster stability as an atom is added. For each structure, the atomization energies are listed in tables 1–7 (second column from the right) and the stability trends for the clusters of beryllium with C, Si, Ge and Sn are shown in Figure 7. It is observed for all the cluster families studied that stability is greater for the 1:1 clusters than for the 2:1 counterparts with the same number of group IVA atoms. This observation may be explained from the fact that the elements of group IVA contribute twice the number of valence electrons to each cluster as does each Be. This allows the 1:1 clusters to potentially form more bonds per atom. For each type of cluster stability per atom increases with cluster size and this increase seems to diminish as the cluster grows. This behavior is to be expected as the difference between $E_{atomization}/ (N_{atoms} - 1)$ with increasing N should approach zero as cluster sizes approach the bulk solid. The clusters of beryllium with Si, Ge and Sn shows similar stability trends; the carbides on the other hand show a greater stability and a much marked difference between the 1:1 and 2:1 clusters. The ability of C to form multiple bonds with large covalent character and its greater tendency to form planar structures may be the reasons for these differences.

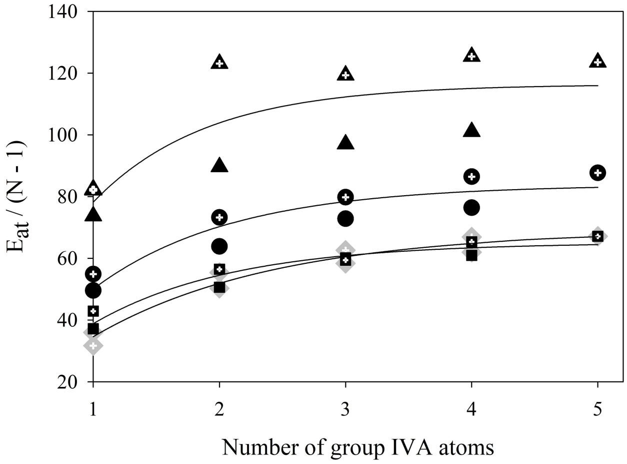

Figure 7. Stability trends for the clusters of beryllium with C (▲), Si (♦), Ge (●) and Sn (■). The crossed symbols represent the 1:1 clusters and the filled symbols the 2:1 counterparts with the same number of group IVA atoms.

Among Si, Ge and Sn, tin shows the larger covalent character of the bonds, either with atoms of its own as with berylliums. It is not surprising since tin exhibits the highest metallic character with an electronegativity value close to that of beryllium. Moreover, pure tin is stable as a covalent crystal (α-tin)[38] and organometallic molecules containing Sn–Sn triple bond and Li–Sn covalent bond has been reported in the literature.[39,40]

Conclusions

Small beryllium-tin clusters were examined in this study and tridimensional cage-like structures were generally found as the most stable ones. They have much more in common with the beryllium silicides and germanides than with the carbides, as expected considering the differences in size and electronegativity. In the smaller clusters (those formed by six atoms or less) the beryllium atoms show no preference to bond each other, whereas in the larger ones there is an evident trend to form beryllium sub-structures capped by tin atoms. The Be–Sn distances are relatively short, in the order of the sum of the covalent radii of both elements and not significant charge transfer is observed between Be and Sn, indicating that the bonds are largely covalent in character. The germanides and silicides generally display some significant transfer of electrons in the bonding with beryllium, whereas the carbides mostly show multiple bonding among C atoms and a greater tendency to form covalent planar structures.

The cluster stability measured as $E_{atomization}/ (N_{atoms} - 1)$, is greater for the clusters with the same number of berylliums and group IVA atoms than for those with a 2:1 ratio. This can be explained by taking into account that the group IVA atoms contribute with more valence electrons to each cluster than Be, therefore, clusters with lower proportion of Be atoms can form more bonds per atom. The atomization energies of carbides are significantly higher than those of the other elements, indicating great cluster stability based on the capability of carbon to form strong multiple bonds. In the other hand, the germanides are generally more stable than the silicides and stannides possible due to the ability of Ge to donate more charge to the Be atoms than does Si and Sn. The fact that Be–Sn clusters show a great covalent character is especially interesting because opens the possibility of expecting larger structures, such as those formed by carbon, with novel properties and potential for the development of new materials.

Supporting Information Summary

The computational details of this study are provided in the Supporting Information along with the corresponding references.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Beryllium · Clusters · Density functional calculations · Stannides · Tin

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