Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

SUPPORTING INFORMATION

Tri-metallic deltahedral Zintl ions: A theoretical survey of the series $[Sn_{9-m-n}Ge_mBi_n]^{(4-n)-}$ for n = 1 – 4 and m = 0 – (9-n). Prediction and rationalization of their possible structures.

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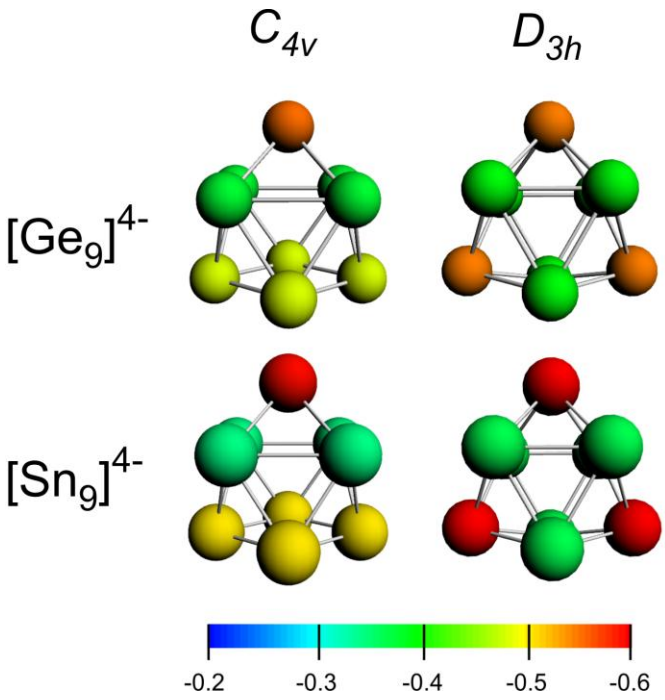

Figure S1. Natural Charge distribution in both $[Ge_9]^{4-}$ and $[Sn_9]^{4-}$ displaying C_{4v} and D_{3h} structures.

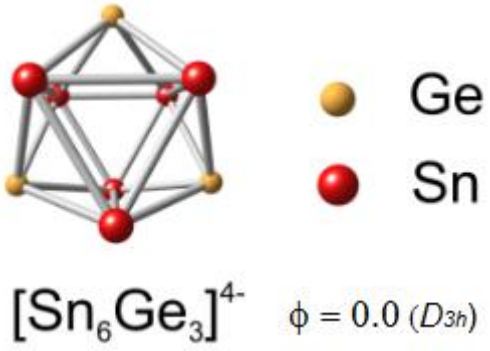

Figure S2. Global minimum structure for $[Sn_6Ge_3]^{4-}$.

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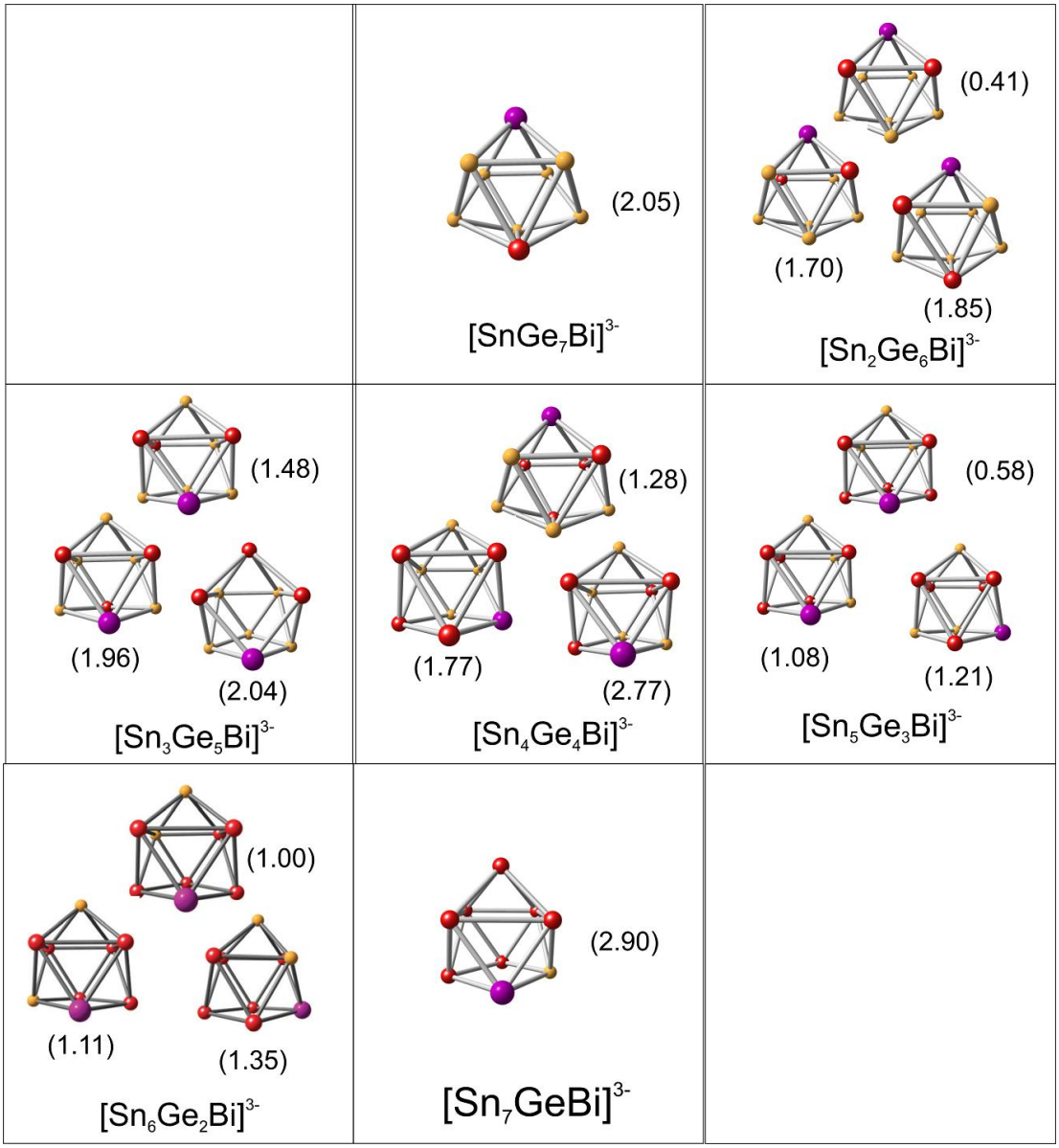

Figure S3. Low-energy isomers of the series $[Sn_{8-m}Ge_mBi_1]^{3-}$ for m = 0 - 8. The difference in energy (kcal/mol) from the global minimum is given in parenthesis.

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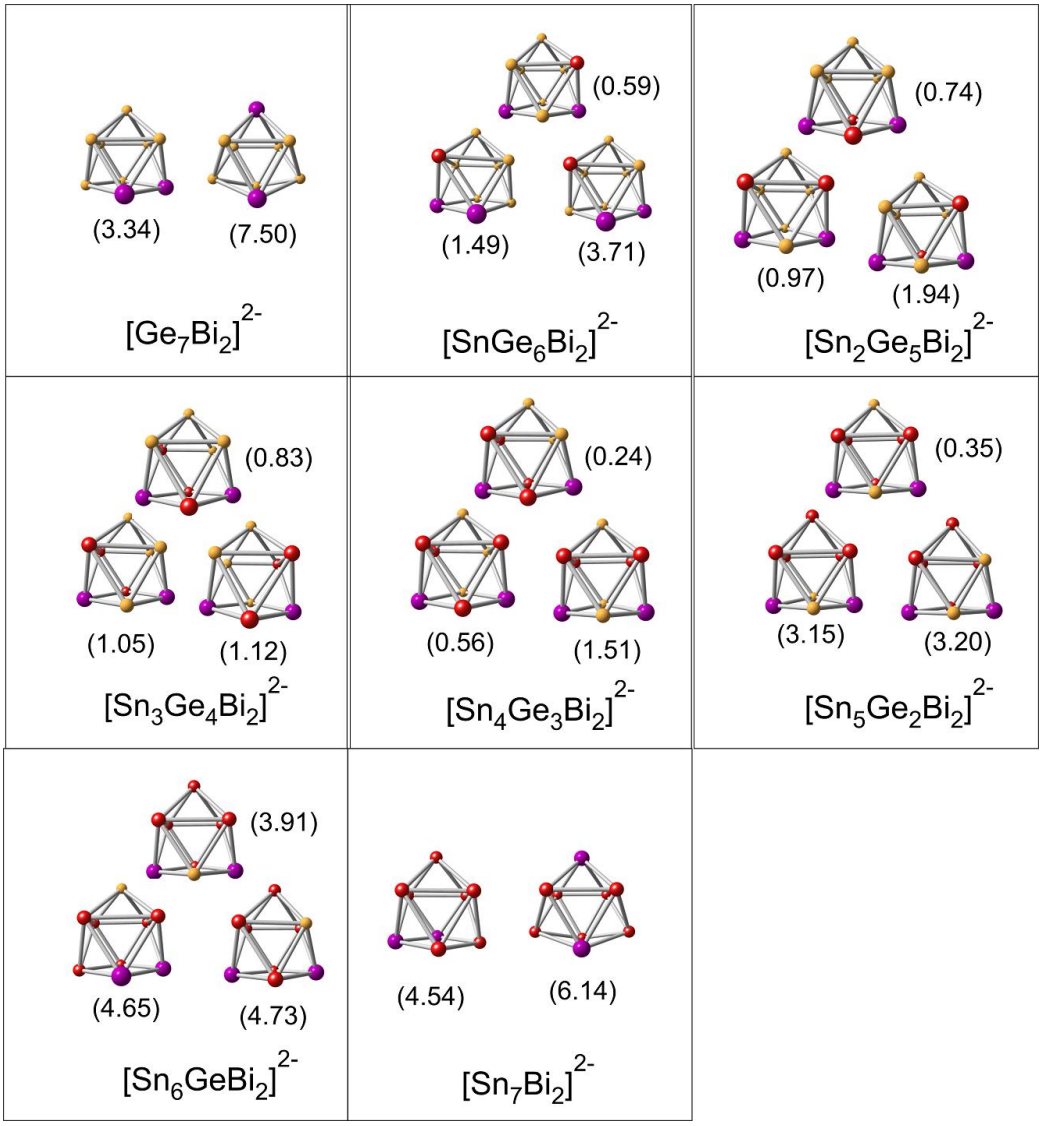

Figure S4. Low-energy isomers of the series $[Sn_{7-m}Ge_mBi_2]^{2-}$ for m = 0 - 7. The difference in energy (kcal/mol) from the global minimum is given in parenthesis.

SUPPORTING INFORMATION

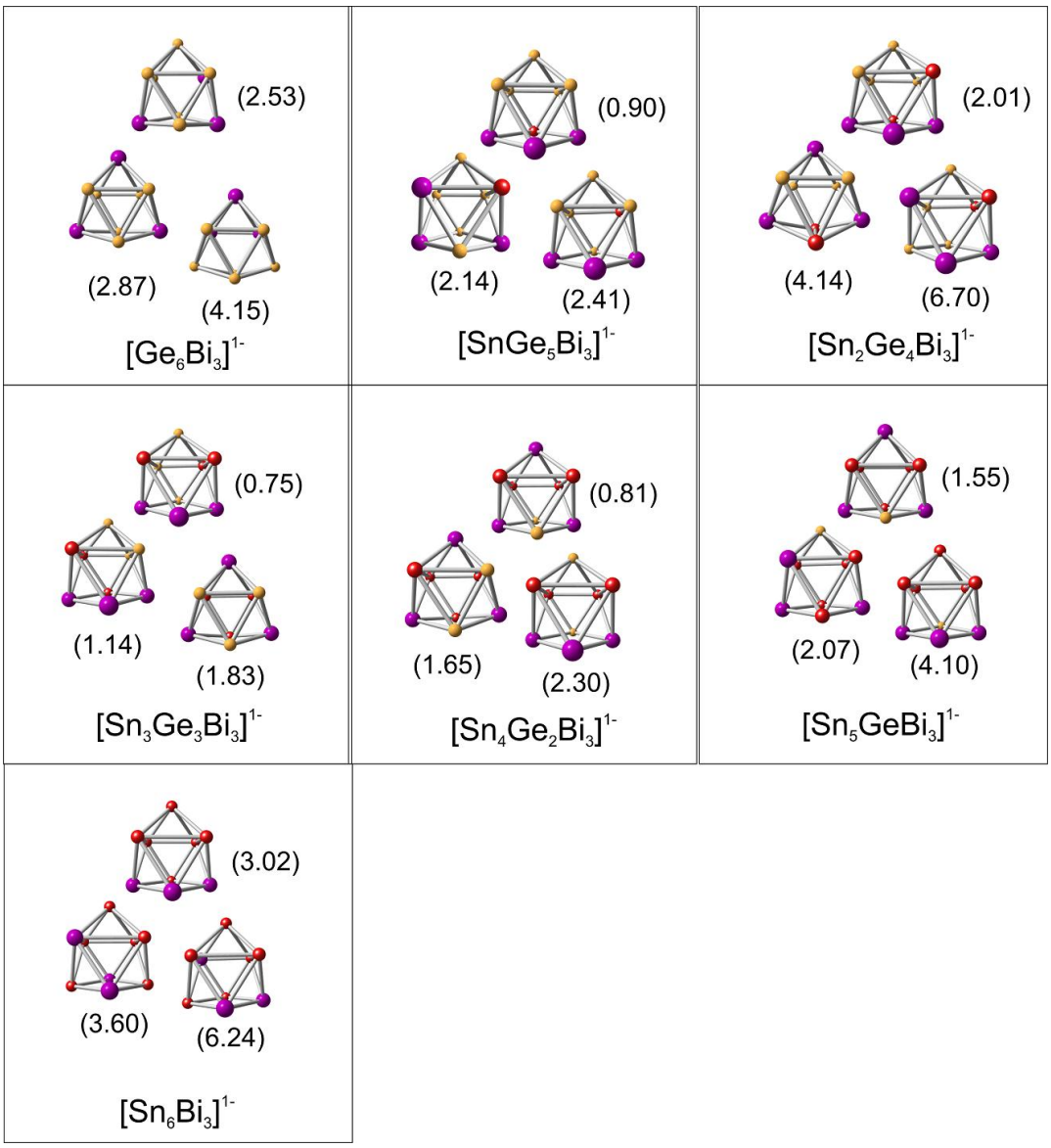

Figure S5. Low-energy isomers of the series $[Sn_{6-m}Ge_mBi_3]^{1-}$ for m = 0 - 6. The difference in energy (kcal/mol) from the global minimum is given in parenthesis.

SUPPORTING INFORMATION

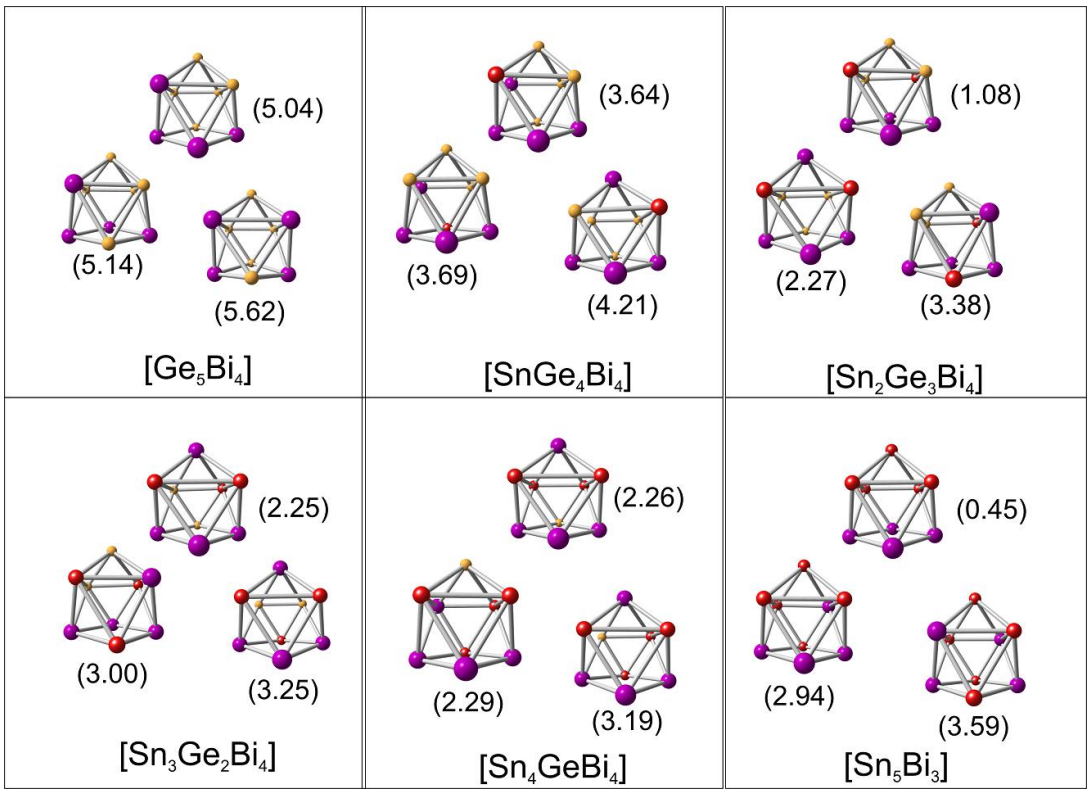

Figure S6. Low-energy isomers of the series $[Sn_{5-m}Ge_mBi_4]$ for m = 0 - 5. The difference in energy (kcal/mol) from the global minimum is given in parenthesis.

SUPPORTING INFORMATION

Table S1. Total bonding energies (TBE) for the global minima of the Sn-Ge-Bi trimetallic deltahedral Zintl ions with various stoichiometries.

Composition	TBE (eV)[a]
$[Ge_8Bi]^{3-}$	-24.5671
$[SnGe_7Bi]^{3-}$	-24.0916
$[Sn_2Ge_6Bi]^{3-}$	-23.6624
$[Sn_3Ge_5Bi]^{3-}$	-23.1884
$[Sn_4Ge_4Bi]^{3-}$	-22.7652
$[Sn_5Ge_3Bi]^{3-}$	-22.2569
$[Sn_6Ge_2Bi]^{3-}$	-21.8156
$[Sn_7GeBi]^{3-}$	-21.3653
$[Sn_8Bi]^{3-}$	-20.8604
$[Ge_7Bi_2]^{2-}$	-27.9900
$[SnGe_6Bi_2]^{2-}$	-27.4557
$[Sn_2Ge_5Bi_2]^{2-}$	-26.9466
$[Sn_3Ge_4Bi_2]^{2-}$	-26.4894
$[Sn_4Ge_3Bi_2]^{2-}$	-25.9587
$[Sn_5Ge_2Bi_2]^{2-}$	-25.4537
$[Sn_6Ge_1Bi_2]^{2-}$	-25.0252
$[Sn_7Bi_2]^{2-}$	-24.4361
$[Ge_6Bi_3]^{-}$	-27.8418
$[SnGe_5Bi_3]^{-}$	-27.3292
$[Sn_2Ge_4Bi_3]^{-}$	-26.8592
$[Sn_3Ge_3Bi_3]^{-}$	-26.2902
$[Sn_4Ge_2Bi_3]^{-}$	-25.5336
$[Sn_5GeBi_3]^{-}$	-25.2701
$[Sn_6Bi_3]^{-}$	-24.7807
$[Ge_5Bi_4]$	-23.9934
$[SnGe_4Bi_4]$	-23.7368
$[Sn_2Ge_3Bi_4]$	-23.0077
$[Sn_3Ge_2Bi_4]$	-22.5404
$[Sn_4GeBi_4]$	-22.0813
$[Sn_5Bi_4]$	-21.4782

[a]Corrected values according to V. Branchadell, M. Sodupe, *Chem.Phys.Lett.* **1997**, 265, 481. These values indicate that the inclusion of Sn nuclei decrease the bonding energy in each series.

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Table S2. Results from the *Continuos-Shape-Measure* (CShM) calculations. Each number represents the deviation of a given nine-atom deltahedral Zintl ion from a perfect *msa* or *ttp* polyhedron. Smaller deviation (denoted in bold) indicates better fit with the corresponding shape. Deviations of around 0.5 and 1.5 indicate intermediate situation.

Composition	CShM *msa*	CShM *ttp*	ϕ	Symmetry
$[Ge_8Bi]^{3-}$	1.192	**0.832**	0.10	~D_{3h}
$[SnGe_7Bi]^{3-}$	**0.704**	1.030	1.00	C_{4v}
$[Sn_2Ge_6Bi]^{3-}$	**0.478**	1.455	0.50	~C_{2v}
$[Sn_3Ge_5Bi]^{3-}$	1.205	**0.870**	0.05	D_{3h}
$[Sn_4Ge_4Bi]^{3-}$	1.306	**0.904**	0.06	D_{3h}
$[Sn_5Ge_3Bi]^{3-}$	1.089	**0.706**	0.01	D_{3h}
$[Sn_6Ge_2Bi]^{3-}$	0.840	**0.594**	0.06	D_{3h}
$[Sn_7GeBi]^{3-}$	**0.332**	0.902	0.97	C_{4v}
$[Sn_8Bi]^{3-}$	0.924	**0.581**	0.23	~D_{3h}
$[Ge_7Bi_2]^{2-}$	**0.564**	1.597	0.40	~C_{2v}
$[SnGe_6Bi_2]^{2-}$	**0.618**	1.627	0.71	~C_{2v}
$[Sn_2Ge_5Bi_2]^{2-}$	**0.458**	1.409	0.89	~C_{4v}
$[Sn_3Ge_4Bi_2]^{2-}$	**0.458**	1.409	0.49	~C_{2v}
$[Sn_4Ge_3Bi_2]^{2-}$	**0.569**	1.388	1.00	C_{4v}
$[Sn_5Ge_2Bi_2]^{2-}$	**0.394**	1.281	0.96	C_{4v}
$[Sn_6Ge_1Bi_2]^{2-}$	**0.234**	1.148	0.98	C_{4v}
$[Sn_7Bi_2]^{2-}$	**0.247**	1.042	0.99	C_{4v}
$[Ge_6Bi_3]^{-}$	**0.722**	1.691	0.96	C_{4v}
$[SnGe_5Bi_3]^{-}$	**0.677**	1.674	0.47	~C_{2v}
$[Sn_2Ge_4Bi_3]^{-}$	**0.626**	1.677	0.59	~C_{2v}
$[Sn_3Ge_3Bi_3]^{-}$	**0.640**	1.657	0.68	~C_{2v}
$[Sn_4Ge_2Bi_3]^{-}$	**0.219**	0.657	0.81	~C_{4v}
$[Sn_5GeBi_3]^{-}$	**0.312**	0.422	0.96	C_{4v}
$[Sn_6Bi_3]^{-}$	1.062	**0.064**	0.00	D_{3h}
$[Ge_5Bi_4]$	**0.691**	1.799	0.93	C_{4v}
$[SnGe_4Bi_4]$	**0.700**	1.808	0.96	C_{4v}
$[Sn_2Ge_3Bi_4]$	**0.516**	1.656	0.49	~C_{2v}
$[Sn_3Ge_2Bi_4]$	**0.382**	1.554	0.97	C_{4v}
$[Sn_4GeBi_4]$	**0.247**	1.435	1.00	C_{4v}
$[Sn_5Bi_4]$	**0.174**	0.830	0.58	~C_{2v}