Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

The Electronic Structure of $Ge_9[Si(SiMe_3)_3]_3^-$: A Superantiatom Complex

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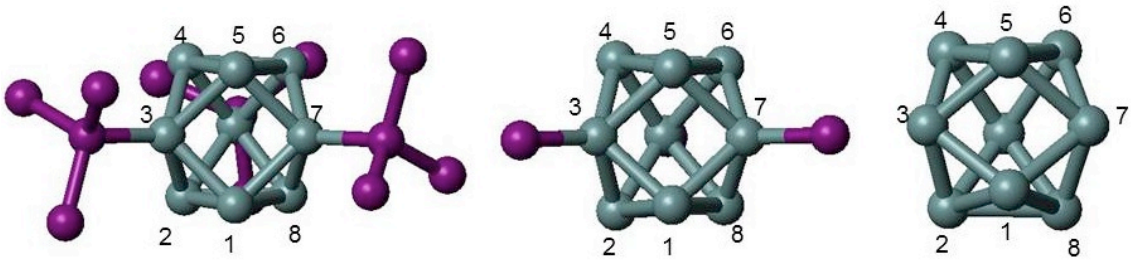

Figure S1. Molecular structures (bottom view) of $Ge_9[Si(SiMe_3)_3]_3^-$, $Ge_9(SiH_3)_3^-$ and $Ge_9H_3^-$ with labels corresponding to Table S1. The grey and purple ball represent the germanium and silicon atoms respectively; carbon and hydrogen atoms are omitted for clarity.

Table S1: Bond lengths (Angstroms) and dihedral angles for $Ge_9[Si(SiMe_3)_3]_3^-$, $Ge_9(SiH_3)_3^-$ and $Ge_9H_3^-$.

	$Ge_9[Si(SiMe_3)_3]_3^-$	$Ge_9(SiH_3)_3^-$	$Ge_9H_3^-$
Ge1-Ge2	2.72	2.68	2.76
Ge1-Ge3	2.58	2.58	2.58
Ge1-Ge8	2.68	2.70	2.78
Ge1-Ge7	2.58	2.57	2.57
Ge2-Ge3	2.58	2.58	2.54
Ge2-Ge8	2.70	2.77	2.66
Ge2-Ge4	3.38	3.48	3.75
Ge3-Ge4	2.58	2.58	2.55
Ge3-Ge5	2.58	2.57	2.58
Ge3-Ge7	3.62	3.43	3.79
Ge4-Ge5	2.71	2.69	2.76
Ge4-Ge6	2.71	2.76	2.66
Ge5-Ge6	2.67	2.71	2.77
Ge5-Ge7	2.59	2.57	2.57
Ge6-Ge7	2.59	2.58	2.55
Ge6-Ge8	3.55	3.39	3.68
Ge7-Ge8	2.59	2.58	2.55

Ge1-Ge3-Ge2	63.76	61.79	65.22
Ge2-Ge1-Ge8	59.98	58.60	57.29
Ge2-Ge3-Ge4	82.00	84.70	94.84
Ge3-Ge1-Ge7	89.10	83.70	94.89
Ge8-Ge7-Ge6	86.69	82.13	92.75

Table S2. Number of delocalized electrons (n_e) and calculated[#] HOMO-LUMO gaps (Gap) and Electron Affinities (EA) superatoms, superatom complexes and the superantiatom complex $Ge_9[Si(SiMe_3)_3]_3^-$. The energies are in eV.

	n_e	Gap	EA
$Ge_9[Si(SiMe_3)_3]_3^-$	40	2.17	n/a
$Ge_9[Si(SiMe_3)_3]_3$	39	0.36	2.9
Al_{13}^-	40	1.95	n/a
Al_{13}	39	0.58	3.4
$Au_{102}(SC_7O_2H_5)_{44}$	58	0.48	*
$Ga_{23}[N(SiMe_3)_2]_{11}$	58	1.34	2.5
$Al_{50}Cp^*_{12}$	138	0.94	1.7

*The electron affinity has not been determined.
[#]The HOMO-LUMO gaps and electron affinities were calculated using GPAW (see computational details in the main text for more information). The computational details for Al, Au, S, and Ga can be found in references 14 and 15 from the main text.

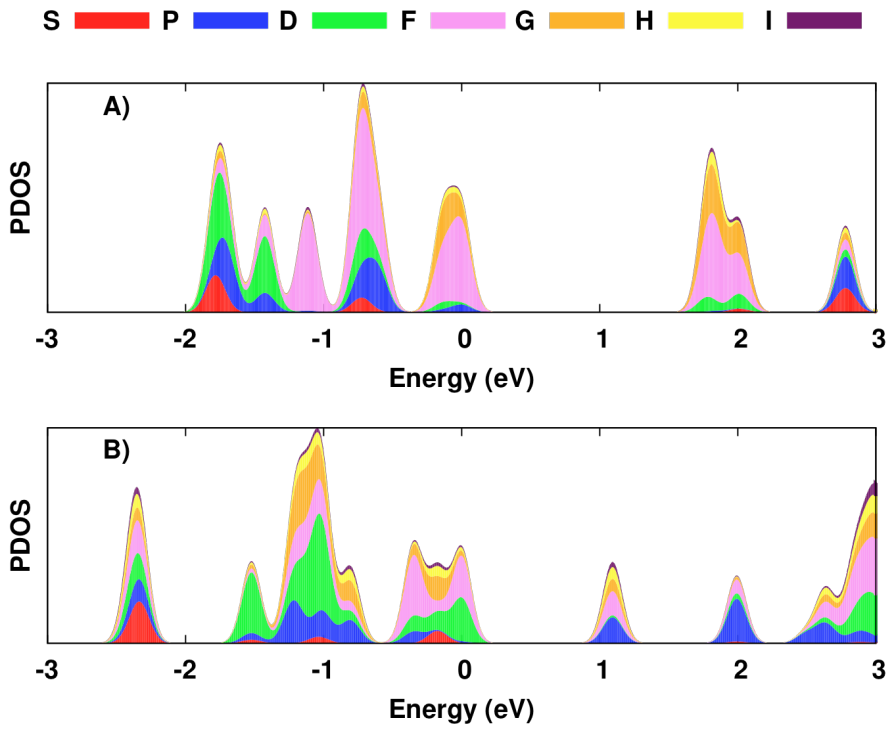

Figure S2. The angular-momentum-projected electron density of states (PDOS) between -3 to 3 eV for Ge_9 (Panel A) and $Ge_9[Si(SiMe_3)_3]_1^-$ (Panel B). For more information refer to Figure 2 in the main text.