Supporting Information

for

\[ (\eta^2-\text{Si/Ge}_4)\text{Zn}(\eta^2-\text{Si/Ge}_4) \] \(^6^−\) - Novel Zintl Clusters with Mixed Si/Ge Tetrahedra bridged by a Zn Atom

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Experimental Details:

All manipulations were carried out under argon atmosphere using standard Schlenk and glovebox techniques. \( \text{Ph}_2\text{Zn} \) (\( \text{Ph} = \text{phenyl}, 99\%\), ABCR) was used as received. [18]-crown-6 was sublimated under dynamic vacuum at 80 °C. [2.2.2]\text{crypt} was dried \textit{in vacuo}. Liquid ammonia was dried and stored over sodium metal. Si powder (99.9999\%, AlfaAesar) and Ge pieces (99.999\%, Chempur) were used as received, K was purified by liquatating.

X-ray powder diffraction: Phase analyses of \( \text{K}_{12}\text{Si}_{12}\text{Ge}_5 \) was performed using a Stoe STADI P diffractometer (Ge(111) monochromator; Cu\( \text{K}_{\alpha1} \) radiation) equipped with a linear position-sensitive detector. For sample preparation the products were finely ground in an agate mortar, mixed with diamond powder and filled into sealed glass capillaries. The samples were measured in Debye-Scherrer mode (\( 2\theta_{\text{max}} = 90^\circ \)). Data analysis was carried out using the Stoe WinXPOW software package.\(^1\)

Single-crystal structure determination: The thermally very unstable, air- and moisture-sensitive crystals of \( 1 \) and \( 2 \) were transferred from the reaction mixture into perfluoropolyalkyl ether oil at 213 K under a cold N\(_2\) stream. The single crystals were fixed on a glass capillary and positioned in a 120 K cold N\(_2\) stream using the crystal cap system. The data collection was performed at 120(2) K using an Oxford-Diffraction Xcalibur3 diffractometer (Mo\( \text{K}_{\alpha} \) radiation). Structures were solved by Direct Methods (SHELXS-97)\(^2\) and refined by full-matrix least-squares calculations.
against $F^2$ (SHELXL-97).\cite{1} CCDC-876865 and CCDC-876866 contain the supplementary crystallographic data for compounds 1 and 2. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

EDX analysis of the crystals of 1 and 2 was carried out on a JEOL-SEM 5900LV spectrometer equipped with an Oxford Instruments INCA energy dispersive X-ray microanalysis system.

The ternary Zintl phase $K_{12}Si_{17−x}Ge_x$ ($x = 5$) was synthesized from a mixture of 6.52 mmol alkali metal and the corresponding molar ratio of a ball milled Si/Ge alloy in sealed tantalum containers. This mixture was heated to 900 °C, held at that temperature for 10 h, and then slowly cooled down to room temperature with a rate of 0.5 K/min.

Compound 1: $K_{12}Si_{12}Ge_5$ (88 mg; 0.075 mmol), [2.2.2]crypt (51 mg, 0.135 mmol) and Ph$_2$Zn (17 mg; 0.075 mmol) were weighed into a Schlenk tube and dissolved in approximately 1 mL liquid ammonia at $−78$ °C. The resulting red reaction mixture, still containing an insoluble, not further characterized residue, was kept at $−70$ °C. 1 crystallized as dark red plates which were isolated after 14 weeks with low yield. Crystal size: 0.15 x 0.15 x 0.1 mm$^3$; unit cell parameters: $a = 9.0694(5)$ Å, $b = 11.4274(5)$ Å, $c = 15.8894(8)$ Å, $\alpha = 77.468(4)$ °, $\beta = 81.547(4)$ °, $\gamma = 87.070(4)$ °, $V = 1589.8(2)$ Å$^3$; triclinic, space group $P\bar{1}$ (No. 2), $Z = 2$, $\rho_{\text{calc}} = 1.794$ g cm$^{-3}$, $\mu = 4.802$ mm$^{-1}$, $\theta_{\text{max}} = 27.50$ °, 14501 measured reflections, 7193 independent reflections, $R_{\text{int}} = 0.059$, $R_1 = 0.041$ and $wR_2 = 0.079$ for reflections with $I \geq 2\sigma(I)$, $R_1 = 0.090$ and $wR_2 = 0.086$ for all data. EDX analysis confirmed the presence of Zn, Si, Ge and K in single crystals of 1. Observed ratio for Zn/Si/Ge/K: 6(2)/34(4)/19(5)/41(4) atom-%.

Compound 2: $K_{12}Si_{12}Ge_5$ (88 mg; 0.075 mmol), [18]-crown-6 (36 mg, 0.135 mmol) and Ph$_2$Zn (17 mg; 0.075 mmol) were weighed into a Schlenk tube and dissolved in approximately 1 mL liquid ammonia at $−78$ °C. The resulting red solution, still containing an insoluble, not further characterized residue, was kept at $−70$ °C. 2 crystallized as red plates which were isolated after 16 weeks with low yield. Crystal size: 0.2 x 0.15 x 0.1 mm$^3$; unit cell parameters: $a = 9.5430(3)$ Å, $b = 12.2351(4)$ Å, $c = 13.8927(4)$ Å, $\beta = 103.145(3)$ °, $V = 1579.60(8)$ Å$^3$; monoclinic, space group $P2_1$ (No. 4), $Z = 2$, $\rho_{\text{calc}} = 1.858$ g cm$^{-3}$, $\mu = 5.334$ mm$^{-1}$, $\theta_{\text{max}} = 26.25$ °, 12970 measured reflections, 5149 independent reflections, $R_{\text{int}} = 0.055$, $R_1 = 0.036$ and $wR_2 = 0.075$ for reflections with $I \geq 2\sigma(I)$, $R_1 = 0.066$ and $wR_2 = 0.079$ for all data. BASF = 0.55(3). EDX analysis confirmed the presence of Zn, Si, Ge and K in single crystals of 2. Observed ratio for Zn/Si/Ge/K: 7(2)/44(5)/6(2)/43(5) atom-%.
Figure S1: X-ray powder diagram of K$_{12}$Si$_{12}$Ge$_5$ (2θ = 10 – 90 °) with the smaller picture showing an enlarged section (2θ = 10 – 20 °). Theoretical powder diagram of K$_{12}$Si$_{17}$ colored in red. The theoretical diagram for KSi is colored in green. The reflections resulting from the diamond powder are marked with *.
**Figure S2:** Structure of the novel dimeric tetrahedral Zintl cluster [(η^2-E4)Zn(η^2-E4)]^6− (1a). Displacement ellipsoids are drawn at the 70% probability level. Si amounts at atomic sites E in % (standard deviation): E1 37.9(4), E2 39.5(4), E3 78.5(4), E4 72.8(4), E5 68.3(4), E6 82.4(4), E7 53.9(4), E8 36.9(4). Selected bond lengths / Å: E1 - E2 = 2.564(1), E1 - E3 = 2.471(2), E1 - E4 = 2.457(1), E2 - E3 = 2.452(1), E2 - E4 = 2.471(1), E3 - E4 = 2.621(2), Zn - E3 = 2.509(1), Zn - E4 = 2.535(1), Zn - E5 = 2.545(1), Zn - E6 = 2.468(1), E5 - E6 = 2.640(2), E5 - E7 = 2.459(1), E5 - E8 = 2.483(1), E7 - E8 = 2.549(1), E6 - E7 = 2.450(2), E6 - E8 = 2.449(1), K2 - E7 = 3.292(2). K - E distances longer than 3.4 Å are shown as dotted lines.
**Figure S3a:** Unit cell of 1 (triclinic space group $P\overline{1}$; view along the crystallographic [100] direction). Heteroatomic tetrahedra are shown as grey polyhedra, K and Zn atoms are shown as ellipsoids with 70 % probability. Ammonia molecules are schematically shown for clarity.

**Figure S3b:** Unit cell of 1 (triclinic space group $P\overline{1}$; view along the crystallographic [001] direction). Heteroatomic tetrahedra are shown as grey polyhedra, K and Zn atoms are shown as ellipsoids with 70 % probability. Ammonia molecules are schematically shown for clarity.
Figure S4: Structure of the novel dimeric tetrahedral Zintl cluster \([(\eta^2-E_4)Zn(\eta^2-E_4)]^{6-} \) (2a). Displacement ellipsoids are drawn at the 70% probability level. Si amounts at atomic sites \( E \) in % (standard deviation): \( E1 \) 30.5(9), \( E2 \) 32.9(9), \( E3 \) 63.6(5), \( E4 \) 71.8(5), \( E5 \) 70.8(8), \( E6 \) 75.1(8), \( E7 \) 38.2(5), \( E8 \) 31.9(5). Selected bond lengths / Å: \( E1 - E2 = 2.549(1) \), \( E1 - E3 = 2.481(3) \), \( E1 - E4 = 2.467(3) \), \( E2 - E3 = 2.465(3) \), \( E2 - E4 = 2.478(2) \), \( E3 - E4 = 2.639(2) \), \( Zn - E3 = 2.510(1) \), \( Zn - E4 = 2.511(2) \), \( Zn - E5 = 2.494(3) \), \( Zn - E6 = 2.516(3) \), \( E5 - E6 = 2.622(2) \), \( E5 - E7 = 2.457(3) \), \( E5 - E8 = 2.475(3) \), \( E7 - E8 = 2.572(1) \), \( E6 - E7 = 2.449(3) \), \( E6 - E8 = 2.484(3) \). K - E distances longer than 3.4 Å are shown as dotted lines.
Figure S5: Unit cell of 2 (monoclinic space group $P2_1$; view along the crystallographic [100] direction). Heteroatomic tetrahedra are shown as grey polyhedra, K and Zn atoms are shown as ellipsoids with 70% probability. Ammonia molecules are schematically shown for clarity.
Computational Details:

DFT-calculations on $[\text{Si}_4]^{4-}$, $[\text{Si}_2\text{Ge}_2]^{4-}$ and $[\text{Ge}_4]^{4-}$ were performed in the Gaussian09. program package. For all calculations the exchange correlation hybrid functional after Perdew, Burke, and Ernzerhof (PBE0) was used together with triple-zeta-valence + polarization quality basis set (Def2-TZVP). For compensation of the negative cluster charges, a solvation model (Polarizable Continuum Model, PCM) was used. Harmonic vibration frequencies were calculated to characterize the nature of the stationary point on the potential energy surface.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E$/kJ·mol⁻¹</th>
<th>$\Delta G$/kJ·mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Si}_4]^{4-} + [\text{Ge}_4]^{4-}$</td>
<td>1.0</td>
<td>4.6</td>
</tr>
<tr>
<td>$2[\text{Si}_2\text{Ge}_2]^{4-}$</td>
<td>0</td>
<td>0</td>
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Scheme S1:
The HOMO-LUMO gap of the mixed cluster \([\text{Si}_2\text{Ge}_2]^{4-}\) is very close to the \([\text{Si}_4]^{4-}\) tetrahedron (Table S2). Additionally the difference to \([\text{Ge}_4]^{4-}\) is very small (range from 4.04 eV to 4.49 eV).

**Table S2:** HOMO-LUMO gaps for the homoatomic and the mixed \([\text{Si}_2\text{Ge}_2]^{4-}\) tetrahedral clusters formed of Si and Ge, calculated with Gaussian09\(^4\) after structure optimization.

<table>
<thead>
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<th>Compound</th>
<th>gap /eV</th>
</tr>
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<tbody>
<tr>
<td>([\text{Si}_4]^{4-})</td>
<td>4.05</td>
</tr>
<tr>
<td>([\text{Si}_2\text{Ge}_2]^{4-})</td>
<td>4.04</td>
</tr>
<tr>
<td>([\text{Ge}_4]^{4-})</td>
<td>4.29</td>
</tr>
</tbody>
</table>

**Table S3:** Comparison of resulting bond lengths in molecular \([\text{Si}_4]^{4+}\), \([\text{Si}_2\text{Ge}_2]^{4+}\) and \([\text{Ge}_4]^{4+}\) clusters after their structure optimization with Gaussian09, using the functional PBE0 and def2-TZVP type basis sets for all elements. Bond length differences \(d\) are given in percent.

<table>
<thead>
<tr>
<th></th>
<th>(d_{\text{Si-Si}})/Å</th>
<th>(d_{\text{relat.}})</th>
<th>(d_{\text{Si-Ge}})/Å</th>
<th>(d_{\text{relat.}})</th>
<th>(d_{\text{Ge-Ge}})/Å</th>
<th>(d_{\text{relat.}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Si}_4]^{4+})</td>
<td>2.429</td>
<td>1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>([\text{Si}_2\text{Ge}_2]^{4+})</td>
<td>2.424</td>
<td>1.00</td>
<td>2.513</td>
<td>1.04</td>
<td>2.569</td>
<td>1.06</td>
</tr>
<tr>
<td>([\text{Ge}_4]^{4+})</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.580</td>
<td>1.06</td>
</tr>
</tbody>
</table>
Literature:

(2) Sheldrick, G. M. SHELXS-97; Program for the Solution of Crystal Structures; Universität Göttingen 1997.