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Rational Synthesis of $[Ge_9\{Si(SiMe_3)_3\}_3]^-$ from Its Parent Zintl Ion $Ge_9{}^{4-}$

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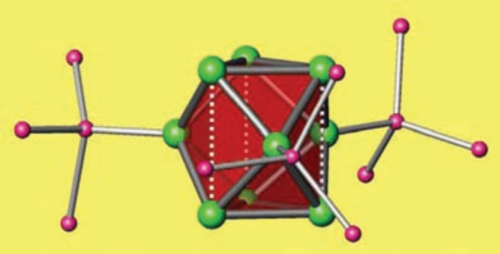
S Supporting Information

ABSTRACT: Reported is the first rational synthesis of a trisubstituted deltahedral Zintl ion, $[Ge_9\{Si(SiMe_3)_3\}_3]^-$ in this case, by the addition of the three substituents in a reaction of the parent naked deltahedral Zintl ion $Ge_9{}^{4-}$ with $\{(Me_3Si)_3Si\}Cl$. The new species were crystallized and structurally characterized in $[K(2,2,2\text{-crypt})]_2[Ge_9\{Si(SiMe_3)_3\}_3]$ (monoclinic, $P2_1/c$, $a = 26.497(3)$ Å, $b = 24.090(2)$ Å, $c = 29.268(3)$ Å, $\beta = 113.888(2)°$, $V = 17082(3)$ Å^3, $Z = 8$, R1/wR2 = 0.0436/0.0812 for the observed data and 0.1023/0.1010 for all data).



INTRODUCTION

The title trisubstituted Zintl ion is not new (Figure 1);[1,2] what is new is its rational synthesis starting from the parent Zintl ion $Ge_9{}^{4-}$ and reacting it with $\{Si(SiMe_3)_3\}Cl$ to add the three substituents. Why is this important? First, because after seeing for a long time only mono- and disubstituted clusters in all previous studies, it seemed that two was the maximum number of substituents the clusters could add. Showing that they are capable of adding a third ligand is in many ways similar to the earlier discovery of the oxidatively coupled dimers $[Ge_9-Ge_9]^{6-}$, which proved that nine-atom clusters can have at least one external bond.[3] This led to the synthesis of numerous functionalized clusters and opened up a whole new research field dealing with the redox chemistry of deltahedral Zintl ions.[4] Second, the synthesis of the title species from naked Zintl ions makes them more readily accessible and provides a path to similar species with other substituents. Third, the capability of adding three substituents to the clusters strongly suggests that the ultimate tetrasubstituted and neutral species $Ge_9R_4{}^0$ might be accessible as well.

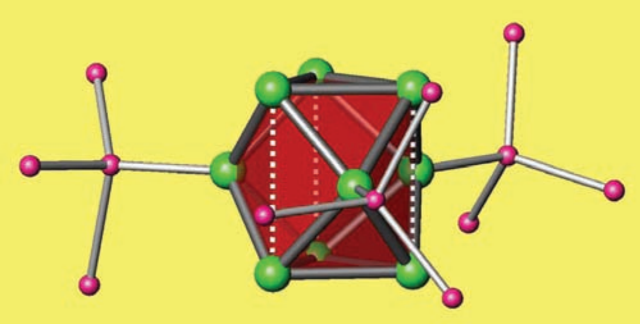


Figure 1. General view of **1** with the approximate shape of a tricapped trigonal prism elongated along the vertical 3-fold axis (the three elongated prismatic edges are shown with broken lines). Color code: Ge, green; Si, purple. All C and H atoms are omitted for clarity. The substituents are exo-bonded to the three capping atoms.

$[Ge_9\{Si(SiMe_3)_3\}_3]^-$ (**1**) was previously reported by Schnepf.[1] However, its synthesis is quite complex, requires specialized equipment, is not readily accessible to the broader synthetic community, and cannot be readily rationalized. The starting material is GeBr made by a reaction of liquid Ge with HBr at 1550 °C in a very specific apparatus. The gas product is then condensed in toluene/R_3N mixtures at −196 °C and is subsequently reacted with $Li\{Si(SiMe_3)_3\}$ at −78 °C. Allegedly, these reactions produce multiple products that need further separation, for example, by extraction with various solvents. It is very likely that the reaction does not proceed via the initial formation of a Ge_9 cluster but is rather an assembly of $Ge\{Si(SiMe_3)_3\}$ fragments, some of which lose their ligands at some point in the process.[5] Despite the difficult synthesis, however, reactions with the trisubstituted anion have already been carried out, and they show interesting chemistry.[6]

Here we report the rational synthesis of the same anion but in high yield and as the single product by a method that is logical and very accessible. Thus, it starts with the standard synthesis of an air-sensitive intermetallic compound, something practiced in many laboratories. This involves heating of the constituting elements in inert containers under vacuum (or an inert atmosphere) at moderately high temperatures. The specific compound in this case is K_4Ge_9 made from K and Ge heated at 950 °C. This intermetallic precursor is then reacted with $\{(Me_3Si)_3Si\}Cl$ dissolved in acetonitrile, and the title anion is crystallized in $(K\text{-}2,2,2\text{-crypt})[Ge_9\{Si(SiMe_3)_3\}_3]$ by layering the reaction mixture with a hexane solution of 2,2,2-crypt.

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RESULTS AND DISCUSSION

Hints for the existence of trisubstituted nine-atom Zintl ions initially came from the electrospray mass spectrometry (ES-MS) spectra of reactions of the clusters with a large excess of the organometallic halides R_3EX (E = Ge, Sn) of the heavier congeners of group 14 carried out in ethylenediamine. In addition to the known mono- and disubstituted clusters $[Ge_9(ER_3)]^{3-}$ and $[Ge_9(ER_3)_2]^{2-}$, respectively,[7] the spectra showed peaks corresponding to $[Ge_9(ER_3)_3]^-$ (Figure S1 in the Supporting Information). However, because all attempts to crystallize the species were unsuccessful, it was not completely clear whether the peaks corresponded to real trisubstituted species or were either artifacts or due to some sort of ion pairing. At the time, reactions with organosilicon halides R_3SiX were not carried out simply because they react with the ethylenediamine solvent. Thus, silicon was passed over in favor of the lightest element in the group, C, and its halides R_3CX, which provided a number of interesting organo-Zintl ions.[8] However, a recent reevaluation of the reactions with R_3SiX was carried out by replacing the ethylenediamine solvent with acetonitrile. The mass spectrum of the reaction with a 10-fold excess of $\{(Me_3Si)_3Si\}Cl$ showed almost pure trisubstituted species (Figure S2 in the Supporting Information), and this led to the attempted crystallization of these anions. Also, recently, the existence of trivinylated clusters $[Ge_9(CH{=}CH_2)_3]^-$ was suggested based on ^1H NMR studies.[9]

The structure of the new compound contains two crystallographically unique anions $[Ge_9\{Si(SiMe_3)_3\}_3]^-$, **2a** and **2b**. Both of them are very similar to the previously reported species **1** in that the Ge_9 cores are tricapped trigonal prisms elongated along the 3-fold axes and the three silyl groups are bonded to the three capping atoms (Figure 1). Most of the distances are also very similar. The bases of the trigonal prisms have distances in the ranges 2.649(1)−2.690(1) Å in **1** and 2.6272(7)−2.7056(8) Å in **2**, and the distances from the bases to the capping atoms are in the ranges 2.5251(9)−2.5347(9) Å in **1** and 2.5073(7)−2.5635(9) Å in **2**. The Ge−Si distances are also nearly identical: 2.363(2)−2.369(1) Å in **1** and 2.365(1)−2.385(2) Å in **2**. The only significant difference is in the way the trigonal prisms of the core clusters are elongated. This is simply measured by the lengths of the three vertical prismatic edges (broken lines in Figure 1), which are quite different for the three clusters: 3.325(2), 3.443(1), and 3.443(1) Å in **1**; 3.1382(8), 3.5174(8), and 3.5291(8) Å in **2a**; 3.2196(9), 3.4904(9), and 3.4966(9) Å in **2b**. Despite these very different distances, however, the overall degrees of elongation of the trigonal prisms are nearly identical. Thus, the averages of the three vertical edges in each core are 3.404(2), 3.395(1), and 3.402(1) Å in **1**, **2a**, and **2b**, respectively.

It is this average elongated distance that defines the electronic structure of the core cluster as a *nido* species that requires $2n + 4 = 22$ electrons ($n = 9$) for cluster bonding.[10] The six naked and three exo-bonded Ge atoms provide $6 \times 2 + 3 \times 3 = 21$ such electrons, and thus the charge of 1− for the trisubstituted clusters. It has already been discussed elsewhere[4a] that these deltahedral clusters can be viewed in a first approximation as made of triangular panels with rigid bonding within the panels (the two trigonal-prismatic bases and the two sets of three triangles that are edge-fused to them; see Figure 6 in ref 4a) but with flexible connections (hinges) between the panels. Without elongation, the tricapped trigonal prism is a *closo* species with $2n + 2 = 20$ cluster-bonding electrons. The lowest unoccupied molecular orbital for this geometry is bonding within each of the two triangular prismatic bases but antibonding between them. Increasing the distance between the two bases by elongation of one or more of the vertical edges of the prism naturally reduces the antibonding character of this orbital, and it becomes bonding and occupied for the *nido* species, as observed in the title anions and in many other mono- and disubstituted clusters.[4] Thus, the geometric flexibility of the clusters results in a flexible electronic structure and electron counts.

In light of the structurally determined $[Ge_9\{Si(SiMe_3)_3\}_3]^-$ and its observation by ES-MS, we can assume that the trisubstituted species observed in the MS spectra of the reactions with Ph_3GeCl and Me_3SnCl, i.e., $[Ge_9\{GePh_3\}_3]^-$ and $[Ge_9\{SnMe_3\}_3]^-$, respectively, are real and most likely structurally similar to $[Ge_9\{Si(SiMe_3)_3\}_3]^-$. We can safely assume that these three examples are only the "tip of the iceberg", and many more examples of trisubstituted and perhaps neutral tetrasubstituted nine-atom deltahedral clusters will be accessible by similar reactions. Stabilization of the neutral species may require the use of very nonpolar solvents such as toluene or even hexane.

EXPERIMENTAL SECTION

Materials and Synthesis. All manipulations were carried out under nitrogen using a glovebox. The Zintl precursor, K_4Ge_9, was synthesized from stoichiometreic mixtures of the elements (K, Strem, 99+%; Ge, Alfa-Aesar, 99.999%) heated at 950 °C over 2 days in sealed niobium containers jacketed in evacuated fused silica tubes. Hexane (Alfa-Aesar, 98.5+%) was dried by passage over a copper-based catalyst and 4 Å molecular sieves and was stored in a gastight ampule under nitrogen. Ethylenediamine (Alfa-Aesar, 99%) was distilled over sodium metal and stored in a gastight ampule under nitrogen. Acetonitrile (Acros, anhydrous, 99.9%) was stored over molecular sieves. $\{(Me_3Si)_3Si\}Cl$ [chlorotris(trimethylsilyl)silane, TCI, 95+%], Ph_3GeCl (triphenylgermanium chloride, Strem Chemicals, 99%), Me_3SnCl (trimethyltin chloride, Aldrich, 96%+), and 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, Acros, 98%) were used as received.

Synthesis of (K-2,2,2-crypt)[$Ge_9\{Si(SiMe_3)_3\}_3$]. K_4Ge_9 (85 mg, 0.105 mmol) was weighed out in a test tube in the glovebox, and an acetonitrile (3.0 mL) solution of $\{(Me_3Si)_3Si\}Cl$ (288 mg, 1.019 mmol) was added to the test tube. The reaction mixture was stirred for 2 h, filtered, layered with hexane containing 2,2,2-crypt (134 mg, 0.362 mmol), and left for crystallization. Although hexane and acetonitrile do not mix, the layering allows for slow crystal growth by the slow diffusion of 2,2,2-crypt into acetonitrile. As it turns out, naked potassium countercations give the anion solubility in acetonitrile, while their sequestered version makes it insoluble. Large, red-orange, blocklike single crystals were obtained after 2 weeks (ca. 75−80% yield). After washing with hexane in order to remove any possible neutral molecules, the ES-MS spectrum of the crystalline material dissolved in tetrahydrofuran showed the presence of only $[Ge_9\{Si(SiMe_3)_3\}_3]^-$ (Figure S3 in the Supporting Information). This confirms the single-phase nature of the product as well as its elemental composition.

Synthesis of $[Ge_9\{SnMe_3\}_n]^{(4-n)-}$ and $[Ge_9\{GePh_3\}_n]^{(4-n)-}$. K_4Ge_9 (88 mg, 0.109 mmol) was mixed with $SnMe_3Cl$ (190 mg, 0.954 mmol) or $GePh_3Cl$ (260 mg, 0.768 mmol) in two test tubes in the glovebox. Subsequently, 2.5 mL of ethylenediamine was added to each tube, and the reaction mixtures were stirred for 4 h. After filtration, aliquots were taken for MS using a gastight syringe. ES-MS (m/z): 818 $[Ge_9\{SnMe_3\}]^-$, 857 $\{[K^+][Ge_9\{SnMe_3\}]\}^-$, 981 $[Ge_9\{SnMe_3\}_2]^-$, 1020 $\{[K^+][Ge_9\{SnMe_3\}_2]\}^-$, 1146 $[Ge_9\{SnMe_3\}_3]^-$, 958 $[Ge_9\{GePh_3\}_3]^-$, 1261 $[Ge_9\{GePh_3\}_3]^-$, 1566 $[Ge_9\{GePh_3\}_3]^-$.

MS. ES-MS spectra were recorded on a Micromass Quattro-LC triple-quadropole mass spectrometer (125 °C source temperature, 150 °C desolvation temperature, 3.0 kV capillary voltage, and 45−75 V cone voltages). The samples were introduced by direct infusion with a Harvard syringe pump at 10 μL/min.

Structure Determination. Single-crystal X-ray diffraction data of (K-2,2,2-crypt)[$Ge_9\{Si(SiMe_3)_3\}_3$] were collected on a Bruker X8 APEX-II diffractometer with a CCD area detector and Mo Kα radiation at 120 K. The crystal was selected under Paratone-N oil, mounted on a Mitegen micromount loop, and positioned in the cold stream of the diffractometer. The structure was solved by direct methods and refined on F^2 against all reflections using the *SHELXTL*, version 6.21, package.[11] Crystal data: monoclinic, $P2_1/c$, $a = 26.497(3)$ Å, $b = 24.090(2)$ Å, $c = 29.268(3)$ Å, $\beta = 113.888(2)°$, $V = 17082(3)$ Å^3, $Z = 8$, R1/wR2 = 0.0436/0.0812 for the observed data and 0.1023/0.1010 for all data.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic file in CIF format and ES-MS spectra in negative ion mode. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor John D. Corbett on the occasion of his 85th birthday.

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