The Reduced Nitridogermanates(III) $\text{Ca}_6[\text{Ge}_2\text{N}_6]$ and $\text{Sr}_6[\text{Ge}_2\text{N}_6]$ with Ge–Ge Bonds

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Dedicated to Prof. Wolfgang Kaim on the occasion of his 70th birthday
Abstract: The first nitridogermanates(III) $\text{Ca}_6[\text{Ge}_6\text{N}_{12}]$ and $\text{Sr}_6[\text{Ge}_6\text{N}_{12}]$ were synthesized from sodium flux and structurally characterized by powder and single crystal X-ray diffraction, respectively. They crystallize isostructurally to each other and homeotypic to $\text{Ca}_6[\text{Cr}_6\text{N}_{12}]$ in space group $\text{R}3$. They feature unprecedented, mutually isolated, etheane-like $[\text{Ge}^{6\text{II}}\text{N}_{6}]^{12-}$ anions in a staggered conformation. The compounds are semiconductors according to resistivity measurements and electronic structure calculations, yielding band gaps of 1.1 eV for $\text{Ca}_6[\text{Ge}_6\text{N}_{12}]$ and 0.2 eV for $\text{Sr}_6[\text{Ge}_6\text{N}_{12}]$.

Introduction

The binary nitrides of the heavier tetrels silicon, germanium, tin and lead show a clear trend with respect to the stability of the tetrel-nitrogen bond. Silicon nitride $\text{Si}_3\text{N}_4$ is a well-known, highly inert compound that undergoes significant thermal decomposition only at temperatures above 1500°C.[1] It has a large number of industrial and specialty applications due to its high hardness and thermal stability. Germanium nitride $\text{Ge}_3\text{N}_4$ is still a rather stable nitride, however, it decomposes around 600°C in vacuum.[2] The crystal structures of the low-pressure modifications of both silicon and germanium nitride consist of three-dimensional networks of corner-sharing $\text{Si}_4\text{N}_4$ or $\text{Ge}_4\text{N}_4$ tetrahedra. There also exists a high-pressure spinel modification of both,[3,4] in which two thirds of the tetrel atoms are coordinated octahedrally by nitrogen. Tin nitride $\text{Sn}_3\text{N}_4$ was so far exclusively observed in this modification. It is obtainable at atmospheric pressure, but starts to decompose around 300°C.[5] Lead nitride, to the best of our knowledge, has not been shown to exist as of yet.

Due to the intermediate stability of the germanium-nitrogen bond, Ge is unique among the group 14 elements when it comes to ternary nitrides. As discussed above, the heavier elements tin and lead are very reluctant to form bonds with nitrogen at all, with $\text{NaSn}_3\text{N}_4$ currently being the only known ternary nitridostannate.[6] Silicon on the other hand is so strongly attracted to nitrogen that $[\text{Si}^\text{IV}\text{N}_6]^4-$ tetrahedra and their condensates are usually the only structural units found in nitridosilicates.[7] Exceptions from this rule include the (oxido)nitridosilicate $\text{Ce}_6[(\text{Si}_6\text{O})_3\text{N}_6]$ containing $\text{Si}_6\text{N}_6$ octahedra and particularly $\text{SrSi}_6\text{N}_6$ and $\text{BaSi}_6\text{N}_6$, which feature $\text{Si}^{3\text{II}}$-$\text{Si}^{3\text{III}}$ bonds next to dominating vertex-sharing $\text{Si}_6\text{N}_6$ tetrahedra.[8-10] Nitridogermanates exhibit a much richer structural chemistry than known for nitridosilicates or -stannates. Building blocks can include bent $[\text{Ge}^{6\text{II}}\text{N}_{6}]^{12-}$ anions,[11-13] trigonal planar $[\text{Ge}^{4\text{IV}}\text{N}_{4}]^{10-}$ units,[14] as well as $[\text{Ge}^{4\text{IV}}\text{N}_{4}]^{4-}$ tetrahedra.[15,16] As with the silicates, these latter tetrahedra can condense via corner-sharing to yield extended units or via edge-sharing, resulting in $[\text{Ge}^{4\text{IV}}\text{N}_{6}]^{10-}$ units.[16] Instances of nitridogermanate units coexisting with both isolated nitride ions and germanide Zintl ions have also been shown to exist.[13,17,18]

Here we present a hitherto unknown structural unit, the $[\text{Ge}^{3\text{II}}\text{N}_{6}]^{12-}$ anion, featuring two germanium(III) atoms connected by a direct covalent bond and three nitride ligands each. In the title compounds, the $[\text{Ge}^{3\text{II}}\text{N}_{6}]^{12-}$ anion is arranged in a staggered conformation, consistent with point group 3, within the crystal structure arrangement it retains full $3m$ ($D_{3d}$) symmetry, even though the crystal structure as a whole does not. This anion is notably distinct from the $[\text{Ge}^{4\text{IV}}\text{N}_{6}]^{10-}$ unit formed by two edge-sharing tetrahedra found in $\text{Sr}_6[\text{Ge}_6\text{N}_{12}]$.[10] Similar anionic units were revealed, for example, in a class of alkali metal chlorocenidotetrelates with the general formula $\text{A}_n[\text{Te}_6\text{Cl}_{18}]$ and $\text{A} = \text{Si}, \text{Ge, Sn; } \text{Ch} = \text{S, Se, Te}$[10-23] Each of those compounds features etheane-analogue $[\text{Te}_6\text{Ch}_{18}]^{10-}$ ions. Related compounds in the nitridometalate chemistry of transition metals include the homeotypic hydride $\text{Ca}_6[\text{Cr}_6\text{N}_{12}]\text{H}_4$[24] as well as $\text{Sr}_6\text{Li}_6[\text{Mn}_6\text{N}_{12}]$ and $\text{Ca}_6\text{Li}_6[\text{Mn}_6\text{N}_{12}]$[25,26] which contain $[\text{Mn}^{IV}_8\text{N}_{12}]^{10-}$ anions in a similar rhombohedral packing motif.

Results and Discussion

Dark grey single phase microcrystalline $\text{Ca}_6[\text{Ge}_6\text{N}_{12}]$ was obtained from calcium nitride $\text{Ca}_3\text{N}_4$, elemental Ge and sodium azide in a molar ratio $n(\text{Ca}_3\text{N}_4):(\text{Ge}):(\text{N})$ of 3:1:3.7 in sealed tantalum ampoules at 800°C. $\text{Sr}_6[\text{Ge}_6\text{N}_{12}]$ was synthesized by reacting strontium nitride $\text{Sr}_6\text{N}_6$ germanium powder and sodium azide in a molar ratio $n(\text{Sr}_6\text{N}_6):(\text{Ge}):(\text{N})$ of 3:1:3.5 in sealed niobium ampoules at 720°C, using molten sodium flux. In each of three batches using this method, a small quantity of black $\text{Sr}_6[\text{Ge}_6\text{N}_{12}]$ single crystals was found, alongside mostly black, rod-shaped $\text{Sr}_6[\text{Ge}_6\text{N}_{12}]$ crystals, yellow platelets of $\text{Sr}_6[\text{Ge}_6\text{N}_{12}]$ and red $\text{Sr}_6[\text{Ge}_6\text{N}_{12}]$ crystals.[12,15,16] In a later attempt to synthesize $\text{Sr}_6[\text{Ge}_6\text{N}_{12}]$, elemental germanium was replaced in the synthesis by germanium nitride $\text{Ge}_3\text{N}_4$ while keeping the overall nitrogen amount identical by reducing the sodium azide quantity. All other products resulted in similar proportions as before, but no $\text{Sr}_6[\text{Ge}_6\text{N}_{12}]$ was found in this batch. This suggests that $\text{Sr}_6[\text{Ge}_6\text{N}_{12}]$ might form as an intermediate during intercalation of strontium and concomitant nitridation of elemental germanium, retaining an isolated Ge–Ge bond. More detailed information on

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synthesis and crystal structure determinations can be found in the supporting information.

The title compounds crystallize homeotypic to \( \text{Ca}_2[\text{CrN}_2]\text{H}_6 \) [24] which features ethane-like \( \text{CrN}_2 \) anions as well as hydride anions. The hydride ions are coordinated octahedrally by six calcium atoms. However, the site at (0, 0, 0), where hydride is found in \( \text{Ca}_2[\text{CrN}_2]\text{H}_6 \), is unoccupied in the title compounds. The distance from the vacant site to each neighboring cation amounts to 2.96 Å for \( \text{Sr}_2[\text{GeN}_2]\text{N}_6 \) and 2.85 Å for \( \text{Ca}_2[\text{GeN}_2]\text{N}_6 \), which would leave ample space for an anion such as \( \text{N}^3^- \) or \( \text{H}^- \). However, no significant residual electron density was found in this position, which is consistent with the charge balance of the compounds leaving no room for additional charged constituents. As depicted in Figure 1, this arrangement leads to a distorted square pyramidal coordination for the alkaline earth metal ions, where a distorted octahedral coordination complemented by \( \text{H}^- \) was reported for \( \text{Ca}_2[\text{CrN}_2]\text{H}_6 \).

Table 1 lists the most characteristic bond distances and angles in the title compounds. Perhaps unexpectedly, the Ge–Ge bond distances are significantly longer in \( \text{Sr}_2[\text{GeN}_2]\text{N}_6 \) than in \( \text{Ca}_2[\text{GeN}_2]\text{N}_6 \). Though the difference may seem rather large, both values are within the range of Ge–Ge single bond distances reported for similar germanium(III) compounds, for example, the alkali metal chalcogenido-germanates with Ge–Ge bond distances as short as 2.43 Å in \( \text{Na}_2[\text{GeS}_2]\text{N}_6 \) or as long as 2.58 Å in \( \text{K}_2[\text{GeS}_2]\text{N}_6 [22, 23] \). Even longer distances are found in \( \text{SrGe} \), a Zintl phase featuring infinite \( \text{Ge}^- \) chains with a bond length of 2.63 Å [27]. Lastly, the distance between two germanium atoms bridged by two nitrogen atoms in \( \text{Sr}_2[\text{GeN}_2]\text{N}_6 \) is reported at 2.61 Å [16], which makes it only slightly longer than the Ge–Ge distance in \( \text{Sr}_2[\text{GeN}_2]\text{N}_6 \).

The Ge–N bond distances found for the title compounds are similar to those of nitridogerhanates(IV) with a tetrahedral coordination of germanium, such as \( \text{Sr}_2[\text{GeN}_2]\text{N}_6 \) with \( d(\text{Ge-N}) = 1.92 \) Å [15], \( \text{Sr}_2[\text{GeN}_2]\text{N}_6 \) with \( 1.84 < d(\text{Ge-N}) < 1.99 \) Å [16], and \( \text{Ca}_2[\text{GeN}_2]\text{N}_6 \) with \( 1.89 < d(\text{Ge-N}) < 1.95 \) Å [11]. Nitridogerhanates(II) generally contain slightly shorter Ge-N distances, typically ranging between 1.84 Å and 1.89 Å [13, 17, 18] with \( \text{Sr}_2[\text{GeN}_2]\text{N}_6 \) being the only outlier with a reported Ge-N distance of 1.94 Å [12].

Figure 2 depicts IR and Raman spectra of \( \text{Ca}_2[\text{GeN}_2]\text{N}_6 \) and \( \text{Sr}_2[\text{GeN}_2]\text{N}_6 \). In accordance to point group \( D_{3h} \) of the ethane-like anion, three clearly distinguishable regions are visible: the \( v(\text{GeN}) \) mode \( (A_g) \), two Raman active modes for \( \delta(\text{GeN}) \) \((A_{1g}, E_g)\), and four \( v(\text{Ge-N}) \) modes in IR \((A_{2g}, E_g)\) and Raman \((A_{1g}, E_g)\) spectra. The Ge–Ge stretching mode is close to 300 cm\(^{-1}\) which was reported for elemental germanium [29] despite the different bond lengths. Deformation modes \( \delta(\text{Ge-N}) \) agree well with those of various Ge-N

\[
\begin{array}{|c|c|c|}
\hline
\text{Bond} & \text{Ca}_2[\text{GeN}_2]\text{N}_6 & \text{Sr}_2[\text{GeN}_2]\text{N}_6 \\
\hline
\text{Ge-N} & 1.95 & 1.92 \\
\hline
\end{array}
\]

Table 1: Selected distances (Å) and angles (deg.) found in the title compounds (A=Ca, Sr). [27]


Figure 1. Two projections of the extended unit cell of the title compounds (left, center) and coordination of the alkaline earth metal ions (right). [29]
In contrast, stretching modes $\nu(\text{GeN})$ are shifted to lower frequencies in comparison to Ge$_6$N$_8$. This corresponds well to the longer Ge–N bonds of terminal N atoms in [Ge$_6$N$_8$]$^{12-}$ and shorter bonds for the Ge–N–Ge bridging unit in Ge$_6$N$_4$.$^{[31]}$ A similar situation is observed for other isolated molecular anions such as [GeN$_2$]$^{3-}$ and [GeN$_2$]$^{8-}$ whose $\nu(\text{GeN})$ modes accord well with the title compounds (Figure S2, Table S3).

Measurements of the temperature dependence of the magnetization were performed via SQUID magnetometry for magnetic fields up to 7 T and temperatures between 1.8 and 350 K. They indicate that Ca$_6$[Ge$_6$N$_8$] is diamagnetic—see the supplementary material for details—which is consistent with what can be expected from the constituent elements and bonding. Electrical resistivity measurements were performed with a sapphire pressure cell from about 150 K to room temperature. Measurements of the resistivity of a Ca$_6$[Ge$_6$N$_8$] sample exhibit activated semiconducting-like behavior consistent with the sample being diamagnetic.

The electronic structure calculations show that both Ca$_6$[Ge$_6$N$_8$] and Sr$_6$[Ge$_6$N$_8$] are semiconductors with band gaps of 1.1 and 0.2 eV, respectively (see Figure 3). The densities of states (DOS) of both compounds are very similar throughout the whole valence band region. There are two very narrow bands at around −7.5 and −6.0 eV, respectively. The largest contributions to the former are from germanium and nitrogen $s$ states, while N 2p is the largest contributor to the latter ahead of the $s$ states. The higher energy regions are structured into three segments with the following approximate boundaries: [−4.4, −3.1], [−2.9, −1.0] and [−1.0, 0.0] eV (top of the valence band is set to 0 eV). The largest contributions come from the N 2p states, with Ca or Sr contributions (mainly from the 3d or 4d states, respectively) becoming significant in the last two segments. Most of the Ge 4p contributions are in the segment ranging from −4.4 to −3.1 eV. In both phases, the alkaline earth metal elements dominate the conduction bands.

The similarities between the two compounds extend to their effective charges and chemical bonding situation, as well. The effective charges computed based on the QTAIM approach yield positive charges amounting to 1.37 for calcium, 1.36 for strontium and 1.14 for germanium, in both cases. Hence, nitrogen atoms hold an effective charge of −1.75 in Ca$_6$[Ge$_6$N$_8$] and −1.74 in Sr$_6$[Ge$_6$N$_8$]. These high effective charge values imply significant ionic interaction contribution to the cohesion in the title compounds. The topological analysis of the ELI reveals the chemical bonding situation in the hexagonal unit cell as depicted in Figure 4. The organization of the two types of bonds in the [Ge$_6$N$_8$]$^{12-}$-ion is shown in Figure 5. The two-center Ge–Ge bond has an electron population of $n_{\text{Ge-Ge}} = 2.72$ and 2.70 in Ca$_6$[Ge$_6$N$_8$] and Sr$_6$[Ge$_6$N$_8$], respectively. The volume of the Ge–Ge bond basin, $V_{\text{b}}$, in Sr$_6$[Ge$_6$N$_8$] (13.67 Å$^3$) is larger than that in Ca$_6$[Ge$_6$N$_8$] (11.91 Å$^3$), however when expressed as a fraction of the unit cell volume, these values become comparable, 1.73% versus 1.75%, respectively. Additionally, if we define density of bonding electrons as $\rho_{\text{b}} = n_{\text{Ge-Ge}} / V_{\text{b}}$, then we find that $\rho_{\text{b}}$ in Ca$_6$[Ge$_6$N$_8$] (0.228 e Å$^{-3}$) is higher than that in Sr$_6$[Ge$_6$N$_8$] (0.198 e Å$^{-3}$) reflecting, essentially, the effect of difference in unit cell volumes rather than difference in Ge–Ge bond distances. The other bond is a highly polar Ge–N bond at which each of the five alkaline earth metal atoms coordinating to the nitrogen atom participates at a level less than 1%. There are six such bonds per formula unit.
(alternatively one per N atom). The electron population of the bond basin is 7.50 in Ca$_2$[Ge$_6$N$_6$] and 7.48 in Sr$_2$[Ge$_6$N$_6$] with the largest contributions coming from the N atoms, at 6.62 and 6.59 electrons, respectively. Ge contributions are 0.57 and 0.58 electrons, while individual alkaline earth metal atoms provide only about 0.06 electrons so that total Ca or Sr contribution amounts to 0.30 and 0.31, respectively.

ELI valence region attractors and the associated basins involve the genuine valence electrons of the atoms. The electrons occupying the Ca 3d or Sr 4d states belong to the penultimate shell (principal quantum number equal to 3 and 4, respectively). The participation of these electrons in the chemical bonding can be concluded if the distribution of the ELI in the penultimate shell deviates from spherical symmetry, a situation referred to as structuring.$^{[3]}$ Based on the electronic DOS (Figure 3), the occupancies of the Ca 3d and Sr 4d states are computed as 0.54 and 0.65 electrons, respectively. The implied participation of these electrons in chemical bonding is identified in Figure 4 for the exemplary case of Sr$_2$[Ge$_6$N$_6$].

**Conclusion**

Ca$_2$[Ge$_6$N$_6$] and Sr$_2$[Ge$_6$N$_6$] are two new compounds containing the hitherto unknown molecular anion [Ge$_N$]$^{2-}$ and particularly the first nitridogermanates(III), a novel class of compounds virtually unknown in nitride chemistry of the tetrels. Both compounds crystallize homoeotypic to Ca$_2$[Cr$_N$]H, although the hydride site is left unoccupied. Like the majority of nitridogermanates reported so far, the anions in Ca$_2$[Ge$_6$N$_6$] and Sr$_2$[Ge$_6$N$_6$] are isolated from each other and do not condense to form chains, layers or three-dimensional networks, as would be very typical for the related nitridosilicates.

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** germanium - nitrides - nitridogermanates - sodium flux

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[33] 2052482 (Ca₆[Ge₂N₆]) and 1972766 (Sr₆[Ge₂N₆]) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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