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# Nonagermanide *Zintl* Clusters with $\text{Mg}^{2+}$ Counter Ions

Christoph Wallach,<sup>[a]</sup> Wilhelm Klein,<sup>[a]</sup> and Thomas F. Fässler<sup>\*[a]</sup>Dedicated to Professor Cameron Jones on the Occasion of his 60<sup>th</sup> Birthday.

Ion exchange processes are rarely investigated with respect to tetrel element *Zintl* clusters. We now discovered that the addition of Mg complexes to nonagermanide anions comprising  $\text{K}^+$  counter cations results in an exchange of the alkali ions by alkaline earth cations. Upon stirring  $\text{K}[\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_3]$  (TMS = trimethylsilyl) and  $\text{Mg}(\text{NacNac}^{\text{Mes}})\text{I}$  ( $\text{NacNac}^{\text{Mes}} = N,N'$ -bis(2,4,6-trimethylphenyl)- $\beta$ -diketiminato) in MeCN the product  $[\text{Mg}(\text{NacNac}^{\text{Mes}})(\text{MeCN})_4][\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_3]\cdot\text{MeCN}$  is formed. Reactions of  $\text{Mg}(\text{NacNac}^{\text{Mes}})\text{I}$  with  $\text{K}_4\text{Ge}_9$  in liquid ammonia as a

solvent yielded  $[\text{K}[2.2.2]\text{crypt}]_4[\text{Mg}(\text{NacNac}^{\text{Mes}})(\text{NH}_3)_4]_2[\text{Ge}_9\text{---}\text{Ge}_9]\cdot 32.58 \text{ NH}_3$  featuring a mixed alkali/alkaline earth metal cationic sphere and an oxidative coupling of the  $[\text{Ge}_9]^{4-}$  clusters. From comparable reactions of  $[\text{Mg}(\text{NacNac}^{\text{Mes}})]_2$  with  $\text{K}_4\text{Ge}_9$  or  $\text{K}_{12}\text{Ge}_{17}$  in liquid ammonia crystals of  $[\text{K}[2.2.2]\text{crypt}][\text{NacNac}^{\text{Mes}}]\cdot\text{NH}_3$  and  $[\text{K}(18\text{-crown-6})][\text{NacNac}^{\text{Mes}}]\cdot 3 \text{ NH}_3$ , respectively, were isolated. All compounds were characterized by means of single crystal structure determination.

## Introduction

The usage of main group element clusters obtained from *Zintl* phases in solution has developed to an attractive synthetic strategy for the generation of extended atom-precise metalloid and intermetalloid clusters.<sup>[1]</sup> *Zintl* phases that contain alkali metals as the electropositive component serve as precursors, and the clusters can be isolated from solution with the help of alkali metal sequestering agents. In case of the tetrel element clusters the phases  $A_4E_9$  and  $A_{12}E_{17}$  comprising an alkali metal (A) matrix with embedded tetrel element clusters  $[\text{E}_9]^{4-}$  ( $E = \text{Ge}, \text{Sn}, \text{Pb}$ ) and a combination of  $[\text{E}_4]^{4-}$  and  $[\text{E}_3]^{4-}$  ( $E = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ ) clusters, respectively, are especially suitable starting materials for further reactions due to the good solubility of the nine-atom clusters.<sup>[1a,2]</sup>

For the nine-atom clusters a prosperous chemistry has evolved, and the discrete polyanions have been used as cornerstones in the synthesis of filled, substituted, and extended cage compounds.<sup>[1-3]</sup> The  $[\text{E}_9]^{4-}$  clusters are transferred into solution without changes concerning their inherent structure.<sup>[4]</sup> In recent years, the protonation of such clusters has been described in species like  $[\text{HE}_9]^{3-}$  ( $E = \text{Si},^{[5]} \text{Ge},^{[6]} \text{Sn}^{[7]}$ ),  $[\text{H}_2\text{Si}_9]^{2-}$ <sup>[8]</sup> and  $[\text{H}_2(\text{Si}/\text{Ge})_9]^{2-}$ <sup>[5a]</sup> bearing the smallest possible ligand. However, the cage compounds also form covalent 2-centre-2-electron bonds to main group element compounds

resulting in multi-decorated species such as  $[\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_2]^{2-}$ ,<sup>[9]</sup>  $[\text{Ge}_9\{R\}_3]^-$  ( $R = \text{Si}(\text{TMS})_3$ ,<sup>[10]</sup>  $\text{SiH}^t\text{Bu}_2$ )<sup>[11]</sup> and  $[\text{Ge}_9\{\text{PRR}\}_3]^-$  ( $R = N^t\text{Pr}_2$ ;  $R^t = ^t\text{Bu}, N^t\text{Pr}_2$ ).<sup>[12]</sup> Particularly the twofold silylated  $[\text{Ge}_9]$  cluster has served as a precursor for the generation of mixed-substituted cluster species, exemplarily enabling the linking of two cluster entities by a bridging silyl ligand,<sup>[13]</sup> and only recently the introduction of Lewis basic phosphanyl<sup>[14]</sup> and Lewis acidic boranyl groups<sup>[15]</sup> to the respective dianion has been reported. Apart from the described reactions, extended cluster species might arise from a partial oxidation of the nine-atom polyanions in solution yielding interconnected cages with covalent  $E\text{---}E$  bonds. The simplest example is the dimeric germanide  $[\text{Ge}_9\text{---}\text{Ge}_9]^{6-}$ , which consists of two bridged  $[\text{Ge}_9]^{3-}$  units.<sup>[4a,16]</sup> A similar connectivity is found in polymeric  $[\text{Ge}_9]^{2-}$ .<sup>[17]</sup> Further oligomeric anions show multi-interconnected cages like  $[\text{Ge}_9\text{---}\text{Ge}_9\text{---}\text{Ge}_9]^{6-}$ <sup>[18]</sup> or  $[\text{Ge}_9\text{---}\text{Ge}_9\text{---}\text{Ge}_9\text{---}\text{Ge}_9]^{8-}$ .<sup>[19]</sup> Despite the many isolated representatives the mechanism of cluster oxidation is not fully understood yet. However, it is postulated that the solutions contain various species  $[\text{Ge}_9]^{n-}$  ( $n = 2\text{---}4$ ) together with solvated electrons, which could account for redox reactions and the formation of the described Ge oligomers.<sup>[2]</sup>

Over the last decades a huge number of solid-state phases containing group 14 element polyanions other than  $[\text{E}_4]^{4-}$  and  $[\text{E}_9]^{4-}$  has been reported. Thus, dumbbells of Si or Ge are described in phases like  $\text{Li}_7\text{Si}_2$ <sup>[20]</sup> or  $\text{Li}_3\text{NaGe}_2$ <sup>[21]</sup> and structure motifs like five-<sup>[22]</sup> or six-membered<sup>[23]</sup> tetrel element rings, as well as a butterfly-like atom arrangement of  $[\text{E}_4]^{6-}$  moieties ( $E = \text{Si},^{[24]} \text{Ge}^{[25]}$ ) in the solids  $\text{Ba}_3\text{E}_4$  have been found. Furthermore, planar polyanionic  $\text{Si}_{12}$  units are observed in the solid state in  $\text{Ca}_7\text{Mg}_{7.5\pm\delta}\text{Si}_{14}$ .<sup>[26]</sup> All of these tetrel element building blocks of the solid-state phases could in principle be used as precursors for subsequent reactions, but reactions with *Zintl* phases comprising alkaline earth metals are rare. As a scarce example, Si and Ge nano-sheets are obtained upon deintercalation of the alkaline earth ions from the phases  $\text{CaE}_2$  ( $E = \text{Si}, \text{Ge}$ ),<sup>[27]</sup> that

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comprise a layer structure, and serve as substrate in following reactions.<sup>[28]</sup>

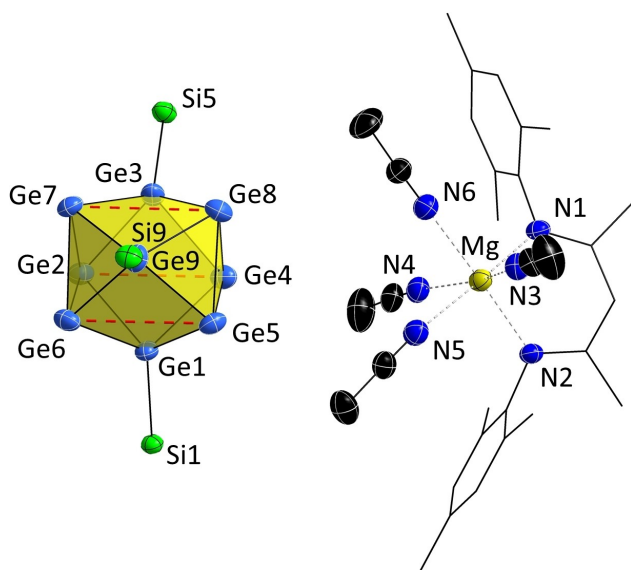
Even though numerous compounds with negatively charged nine-atom tetrel element clusters have been isolated from solution, they all contain to the best of our knowledge alkali metal counter ions. Due to the lack of solid-state precursors with  $[E_9]^{4-}$  anions in combination with alkaline earth metals, we investigated ion exchange reactions starting from the potassium germanides  $K_4Ge_9$  and  $K_{12}Ge_{17}$  and organic Mg salts as ion exchanging reactants.

## Results and discussion

### Reactivity of Mg(II) organyls towards $[Ge_9]$ Zintl clusters

The reaction of  $K[Ge_9\{Si(TMS)_3\}_3]$  (**1 a-K**) with a three-fold excess of the Mg(II) species  $Mg(NacNac^{Mes})I$  in MeCN yields a milky deep orange suspension. After filtration and storage of the concentrated filtrate overnight, crystals of compound **1 a-Mg**,  $[Mg(NacNac^{Mes})(MeCN)_4][Ge_9\{Si(TMS)_3\}_3] \cdot MeCN$ , suitable for single crystal diffraction were obtained. Compound **1 a-Mg** (Figure 1) is the ion-exchanged analogue of the K-containing silylated  $[Ge_9]$  precursor. A full ellipsoid plot of compound **1 a-Mg** can be found in Figure S1.

The structure of the anion  $[Ge_9\{Si(TMS)_3\}_3]^-$  (**1 a**) is best described as a  $C_{2v}$ -symmetric tricapped trigonal prism (Figure 1, dashed red lines) with prism heights  $Ge2-Ge4$ ,  $Ge5-Ge6$  and  $Ge7-Ge8$  of 3.485(1) Å, 3.344(1) Å and 3.415(1) Å, respectively. All Ge-Ge and Ge-Si distances are in agreement with the

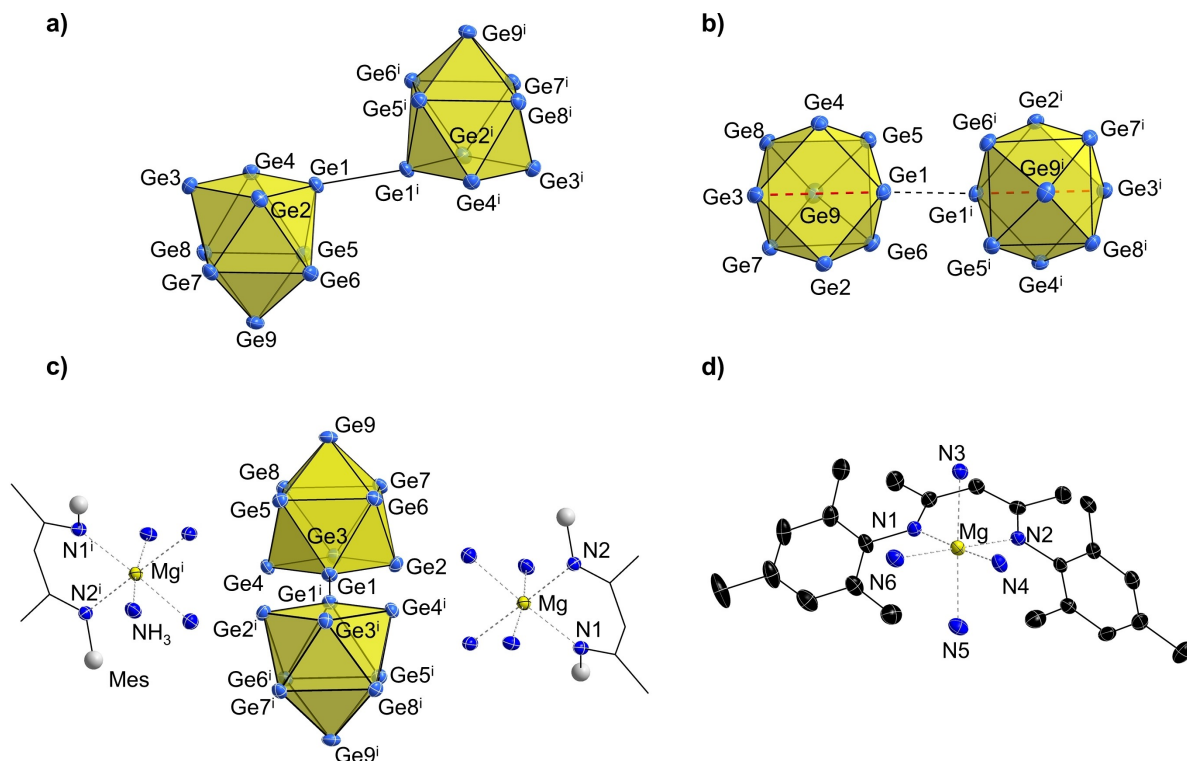


**Figure 1.** Structure of the formula unit of **1 a-Mg**. All ellipsoids are shown at a 50% probability level. The tricapped trigonal prism is indicated by dashed red lines. TMS groups, hydrogen atoms and the co-crystallized MeCN molecule are omitted, and the carbon atoms of the  $[NacNac^{Mes}]^-$  ligand are shown as wire-sticks for clarity. A plot showing all atoms as ellipsoids can be found in the Supporting Information (Figure S1).

reported ones in compound **1 a-K**.<sup>[10]</sup> The  $Mg^{2+}$  ion is embedded in an octahedral matrix of N atoms provided by the  $[NacNac^{Mes}]^-$  ligand and the solvent molecules [2.114(3) Å ( $Mg-N2$ ) to 2.223(3) Å ( $Mg-N6$ )]. The  $Mg-N$  distances are in accordance with those in the octahedral complex  $[Mg(NH_3)_6]^{2+}$  [2.1969(1) Å].<sup>[29]</sup> The octahedral coordination of the  $Mg^{2+}$  cation by polar groups is very common, and also present e.g. in  $[Mg(H_2O)_6]^{2+}$  and in protein chemistry.<sup>[30]</sup> Ge atoms are not located in the first coordination sphere of the  $Mg^{2+}$  ion, and, regarding the shortest distance of 6.305(1) Å between Mg and Ge atoms ( $Mg-Ge4$ ), any direct interactions can be excluded. Compound **1 a-Mg** was further investigated by NMR spectroscopy ( $^1H$ ,  $^{13}C$ ,  $^{29}Si$ ) and by elemental analysis. The  $^1H$  NMR spectrum (Figure S2) unambiguously shows the presence of the  $[NacNac^{Mes}]^-$  ligand and the silylated cluster in a 1:1 ratio, while Mg was monitored in qualitative EDX measurements (Figure S6). The elemental analysis is in accordance with the formula  $C_{56}H_{119}Ge_9MgN_5Si_{12}$ , matching the sum of the single units  $[Ge_9\{Si(TMS)_3\}_3]^-$ ,  $[Mg(NacNac^{Mes})]^+$ , and three MeCN molecules. The different number of solvent molecules is most probably due to excessive drying of the solid in vacuo prior to the analysis.

The reactivity of **1 a-Mg** was tested by dissolving the compound in  $thf-d_8$  and the addition of a  $thf-d_8$  solution of the N-heterocyclic carbene  $NHC^{Dipp}Cu-Cl$  [ $NHC^{Dipp} = 1,3$ -di(2,6-diisopropylphenyl)imidazolyliidene]. The  $^1H$  NMR spectrum revealed the same signals as reported for the reaction of **1 a-K** and  $NHC^{Dipp}Cu-Cl$ , indicating the analogous formation of  $(NHC^{Dipp}Cu)[Ge_9\{Si(TMS)_3\}_3]$ .<sup>[31]</sup> Hence, the counter ion seems to play a minor role in the tested reaction. Despite the straightforward formation of **1 a-Mg**, no clean ion exchange reaction with the closely related dianionic species  $[Ge_9\{Si(TMS)_3\}_3]^{2-}$  could be observed, and the  $^1H$  NMR spectra of the reaction outcome showed a vast, so far unidentified mixture of products.

Further investigations focused on the reactivity of the Mg(II) organyl towards bare  $[Ge_9]^{4-}$  clusters in liquid ammonia. Block-shaped dark brown crystals of  $[K[2.2.2]crypt]_4[Mg(NacNac^{Mes})(NH_3)_4]_2[Ge_9-Ge_9] \cdot 32.58 NH_3$  (**2 a-KMg**) were isolated after several months. Compound **2 a-KMg** crystallizes in the triclinic space group  $P\bar{1}$  with two formula units per unit cell and contains a dimeric  $[Ge_9-Ge_9]^{6-}$  unit (**2 a**, Figure 2a), four cationic  $[K[2.2.2]crypt]^+$  moieties, and two  $[Mg(NacNac^{Mes})(NH_3)_4]^+$  molecules (Figure 2d). Four of the 34 co-crystallizing ammonia molecules are only partially occupied ( $N26: 0.79$  and  $N27: 0.50$ ), resulting in an overall number of 32.58  $NH_3$  molecules per unit cell. The 18-atom  $[Ge_9-Ge_9]^{6-}$  cluster consists of two  $[Ge_9]$  moieties which are interconnected by a Ge-Ge exo-bond between two vertices of the pseudo square planes of the cages [ $d(Ge1-Ge1^i) = 2.531(1)$  Å]. The symmetry of the  $[Ge_9]$  moieties is best described as capped square antiprisms with a slightly distorted  $C_{4v}$  symmetry. The deviation is best expressed by the ratio of the diagonal length of the open square face  $Ge1-Ge2-Ge3-Ge4$  given by  $d_{Ge2-Ge4} : d_{Ge1-Ge3} = 1.09$  and the dihedral angle  $\omega_{Ge1-Ge2-Ge4-Ge3} = 0.5^\circ$ . The exo-bond  $Ge1-Ge1^i$  is almost collinear to the shorter diagonal of the square planes (Figure 2b). Analogous  $[Ge_9]$  dimers have previously been reported in anions isolated from ethylenedi-



**Figure 2.** a) Molecular structure of anion **2a**; b) top view of the molecular structure of **2a** with indication of the collinear arrangement of the cluster-connecting exo-bond (Ge1–Ge1'; dashed black line) and the diagonals of the square planes (indicated by dashed red lines); c) arrangement of **2a** and the counter ions  $[\text{Mg}(\text{NacNac}^{\text{Mes}})(\text{NH}_3)_4]^+$ ; d) molecular structure of the cationic fragment  $[\text{Mg}(\text{NacNac}^{\text{Mes}})(\text{NH}_3)_4]^+$  emphasizing the octahedral coordination of Mg(II). All ellipsoids are shown at a 50% probability level. In c) the backbone of the  $[\text{NacNac}^{\text{Mes}}]^-$  ligand is shown as wire-sticks, and Mes groups as grey spheres for clarity. Hydrogen atoms are omitted in c) and d). Symmetry operation (i): 1–x, 1–y, 1–z.

amine, N,N-dimethylformamide, or liquid ammonia.<sup>[16b,c,e,f]</sup> Ge–Ge distances are in accordance with those in the latter dimeric species.

Compound **2a-KMg** comprises a mixed alkali/alkaline earth metal cationic sphere with four  $[\text{2.2.2}]$ crypt-sequestered  $\text{K}^+$  ions and two  $[\text{Mg}(\text{NacNac}^{\text{Mes}})(\text{NH}_3)_4]^+$  units balancing the negative charge of the germanide dimer. The  $\text{Mg}^{2+}$  cations are found in distances above 4.839(2) Å (Mg–Ge2) to the nearest Ge atoms (Figure 2c), which is approximately double the sum of the covalent radii.<sup>[32]</sup> The  $\text{Mg}^{2+}$  cation is coordinated by two N atoms of the bidentate ligand  $[\text{NacNac}^{\text{Mes}}]^-$ , and the octahedral ligand environment is completed by four additional  $\text{NH}_3$  molecules (Figure 2d). The Mg–N distances range from 2.200(5) Å (Mg–N2) to 2.241(5) Å (Mg–N5) with the shortest bonds between Mg and N atoms of the  $\beta$ -diketiminato ligand. With an almost planar torsion angle of the equatorial plane of the octahedron of coordinating N atoms  $\omega_{\text{N2-N1-N4-N6}} = 175.4^\circ$ , approximate rectangular angles  $\text{N}_x\text{–Mg–N}_y$ , and an almost linear arrangement of  $\text{N3–Mg–N5}$  ( $\angle_{\text{N3–Mg–N5}} = 171.4^\circ$ ), the symmetry deviates only slightly from a perfect octahedron (Supporting information Table S2). However, the reason for the dimerization of the  $[\text{Ge}_9]$  clusters in solution still remains unclear.

### Reactivity of Mg(I) organyls towards $[\text{Ge}_9]$ Zintl clusters

Due to their steric shielding  $\beta$ -diketiminates are often applied as ligands for the stabilization of unusual oxidation states such as in  $[\text{Mg}(\text{NacNac}^{\text{Dipp}})]_2$  (Dipp = 2,6-diisopropylphenyl)<sup>[33]</sup> or  $[\text{Zn}(\text{NacNac}^{\text{Mes}})]_2$ <sup>[34]</sup> and the reaction of the Zn(I) organyl with  $\text{K}_4\text{Ge}_9$  in ethylenediamine yielded the polymeric anion  $[\text{Zn}\{\text{trans-}\mu_2(\eta^3\text{-}\eta^3\text{-Ge}_9)\}]_2^{2-}$ .<sup>[35]</sup> Since  $[\text{Mg}(\text{NacNac}^{\text{Mes}})]_2$  immediately leads to an unidentified, insoluble species when exposed to ethylenediamine, we studied its reactivity towards liquid ammonia. The Mg(I) compound was weighed into a Schenk tube, and two milliliters of ammonia were condensed on top of it. Even though the reactant does not dissolve in liquid ammonia, a color change from initially bright yellow to orange-red was observed, which might be caused by the coordination of  $\text{NH}_3$  molecules to Mg. After storing the suspension for one day at  $-40^\circ\text{C}$  the solvent was evaporated, thereby restoring the former yellow color. The  $^1\text{H}$  NMR spectrum of the product does not significantly differ from that of the initial reactant (Figure S5), thus corroborating the stability of the organo-metallic compound in  $\text{NH}_3$  (l). Subsequently, we investigated the reactivity of  $[\text{Mg}(\text{NacNac}^{\text{Mes}})]_2$  towards Zintl phases in liquid ammonia. After several months the formation of solids was observed. However, attempts to isolate crystals from the

reddish precipitate were hampered by a rapid degradation of the solid material upon opening the reaction flask, indicated by a color change to brown-green. Nevertheless, we were able to isolate the side-products  $[K[2.2.2]crypt][NaCNac^{Mes}] \cdot NH_3$  (**3**) as well as  $[K(18\text{-crown-6})][NaCNac^{Mes}] \cdot 3 NH_3$  (**4**) as yellow or colorless crystals, respectively (Figure 3). Both compounds crystallize in the space group  $P\bar{1}$  with two formula units per unit cell. The C–N distances in the  $[NaCNac^{Mes}]^-$  moieties as well as the K–O distances in the cryptand and crown ether are in agreement with previously reported data.<sup>[36]</sup> The experiment which resulted in the formation of **3** also contained crystals of the known ammoniate  $[K[2.2.2]crypt]_3[Ge_9] \cdot 8 NH_3$  as a by-product, which comprises  $[Ge_9]^{3-}$  anions – the paramagnetic monomer of **2a**.<sup>[37]</sup>

## Conclusion

The two anionic *Zintl* clusters  $[Mg(NaCNac^{Mes})(MeCN)_4][Ge_9\{Si(TMS)_3\}_3] \cdot MeCN$  (**1a-Mg**) and  $[K[2.2.2]crypt]_4[Mg(NaCNac^{Mes})(NH_3)_4]_2[Ge_9-Ge_9] \cdot 32.58 NH_3$  (**2a-KMg**) with either pure alkaline earth metal or mixed alkali/alkaline earth metal counterions were obtained via counter ion exchange starting from potassium germanide precursors by offering a Mg(II) source. In both cases the alkaline earth metal does not directly coordinate to the Ge cluster, which contrasts observations made for analogous Zn compounds. When a Mg(I) compound is used, oxidized  $[Ge_9]^{3-}$  clusters and the side products  $[K[2.2.2]crypt][NaCNac^{Mes}] \cdot NH_3$  (**3**) and  $[K(18\text{-crown-6})][NaCNac^{Mes}] \cdot 3 NH_3$  (**4**) were isolated. The transfer of the herein presented reactions to analogous Si- and Sn-based *Zintl* clusters and the influence of the counter ion on the solubility of the clusters is under current investigation in our laboratories.

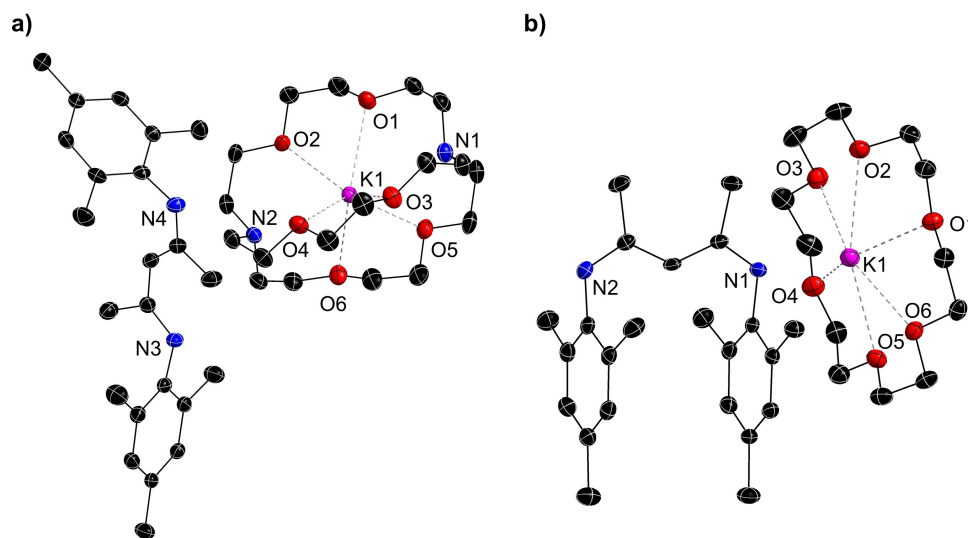
## Experimental details

### General considerations

All experiments were carried out under a dry, oxygen-free atmosphere using standard glove box and Schlenk-line techniques. Glassware was dried by heating it at 650 °C *in vacuo*. MeCN (VWR) was purified in a MBraun solvent purification system and stored over molecular sieves. The solid phases  $K_4Ge_9$  and  $K_{12}Ge_{17}$  were prepared by fusion of stoichiometric amounts of the elements at elevated temperatures in a stainless-steel autoclave and a tantalum ampule, respectively.  $K[Ge_9\{Si(TMS)_3\}_3]$  and  $NHC^{Dipp}Cu-Cl$  were prepared according to literature procedures.<sup>[10,38]</sup> Liquid ammonia was dried over sodium metal, and  $[2.2.2]crypt$  (Merck) was dried overnight applying dynamic vacuum before usage. 18-Crown-6 (Merck) was purified by sublimation before usage.  $Mg(NaCNac^{Mes})I$  was prepared according to modified literature procedures, and  $[Mg(NaCNac^{Mes})]_2$  was generously donated by Prof. C. Jones, Monash University, Australia.<sup>[33,39]</sup>

### Single crystal structure determination

The air- and moisture-sensitive crystals of **2–4** were transferred from the mother liquor into cooled perfluoroalkyl ether oil and isolated from polycrystalline material under a cooled stream of nitrogen.<sup>[40]</sup> Crystals of **1a-Mg** were transferred in and isolated under perfluoroalkyl ether oil at room temperature in a glove box. For diffraction data collection, the single crystals were mounted on a glass capillary and positioned in a 150 K cold  $N_2$  gas stream. Data collection was performed with a STOE StadiVari diffractometer ( $MoK\alpha$  radiation) equipped with a DECTRIS PILATUS 300 K detector. Structures were solved by Direct Methods (SHELXS-97)<sup>[41]</sup> and refined by full-matrix least-squares calculations against  $F^2$  (SHELXL-2014 or SHELXL-2018).<sup>[42]</sup> The positions of the hydrogen atoms were calculated and refined using a riding model. Unless stated otherwise, all non-hydrogen atoms were treated with anisotropic displacement parameters. The supplementary crystallographic data for this paper have been deposited with the Cambridge Structural database and are available free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). The crystallographic data for compounds **1–4** are summarized in Table 1.



**Figure 3.** Structure of the formula unit of a) compound **3** and b) compound **4**. All ellipsoids are shown at a 50% probability level. The co-crystallizing  $NH_3$  molecules and hydrogen atoms are omitted for clarity.



Table 1. Crystallographic data of compounds 1–4.

compound	1 a-Mg	2 a-KMg	3	4
formula	C <sub>60</sub> H <sub>125</sub> Ge <sub>9</sub> MgN <sub>7</sub> Si <sub>12</sub>	C <sub>118</sub> H <sub>323.74</sub> Ge <sub>18</sub> K <sub>4</sub> Mg <sub>2</sub> N <sub>52.58</sub> O <sub>24</sub>	C <sub>41</sub> H <sub>68</sub> KN <sub>5</sub> O <sub>6</sub>	C <sub>35</sub> H <sub>62</sub> KN <sub>5</sub> O <sub>6</sub>
fw [g·mol <sup>-1</sup> ]	1959.70	4376.44	766.10	687.99
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	15.5673(6)	15.8617(3)	12.6685(5)	11.5238(9)
<i>b</i> [Å]	16.2296(7)	17.2066(4)	13.3496(6)	12.7793(9)
<i>c</i> [Å]	20.6144(9)	20.2740(4)	27.8011(13)	13.9201(11)
$\alpha$ [deg]	90.658(3)	89.173(2)	80.259(3)	95.485(6)
$\beta$ [deg]	94.783(3)	70.622(2)	86.359(3)	104.540(6)
$\gamma$ [deg]	108.461(3)	80.298(2)	71.456(3)	92.242(6)
<i>V</i> [Å <sup>3</sup> ]	4919.1(4)	5140.1(2)	4393.1(3)	1971.0(3)
<i>Z</i>	2	2	2	2
<i>T</i> [K]	150(2)	150(2)	150(2)	150(2)
$\lambda$ [Å]	0.71073	0.71073	0.71073	0.71073
$\rho_{\text{calcd}}$ [g·cm <sup>-3</sup> ]	1.323	1.414	1.158	1.159
$\mu$ [mm <sup>-1</sup> ]	2.895	2.738	0.169	0.181
collected reflections	93691	122523	81650	37380
indep. reflections	19301	20152	17271	7735
<i>R</i> <sub>int</sub> / <i>R</i> <sub><math>\sigma</math></sub>	0.0613/0.0433	0.1248/0.0560	0.0539/0.0458	0.0605/0.0479
parameters/restraints	842/0	978/0	989/0	432/0
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )/all data]	0.0376/0.0633	0.0604/0.0846	0.0382/0.0673	0.0423/0.0765
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )/all data]	0.0778/0.0893	0.1365/0.1543	0.0876/0.0982	0.0960/0.1108
goodness of fit	1.032	1.150	1.016	1.017
max./min. diff. el. density [e·Å <sup>-3</sup> ]	0.562/-0.413	1.431/-1.003	0.248/-0.219	0.257/-0.280
deposition no.	CCDC-2117110	CCDC-2117111	CCDC-2117112	CCDC-2117113

### NMR spectroscopy

<sup>1</sup>H and <sup>29</sup>Si INEPT NMR spectra were measured on a Bruker Avance Ultrashield 400 MHz spectrometer; the <sup>13</sup>C NMR spectrum was measured on a Bruker Avance HD 400 MHz spectrometer. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were calibrated using the residual signals of the used deuterated solvent. Chemical shifts are reported in parts per million (ppm) relative to TMS, with the solvent peaks serving as internal reference.<sup>[43]</sup> Singlets are abbreviated with (s).

### Elemental analysis

The elemental analysis was carried out in the microanalytical laboratory of the Chemistry Department of the Technical University of Munich. Analyses of C, H and N were performed in a combustion analyzer (EURO EA, HEKA tech).

### Syntheses

#### [Mg(NacNac<sup>Mes</sup>)(MeCN)<sub>4</sub>][Ge<sub>9</sub>{Si(TMS)<sub>3</sub>}]·MeCN (1 a-Mg)

Solid K[Ge<sub>9</sub>{Si(TMS)<sub>3</sub>}] (28.7 mg, 20.0  $\mu$ mol, 1 equiv.) and Mg(NacNac<sup>Mes</sup>)I (29.1 mg, 60  $\mu$ mol, 3 equiv.) were weighed into a Schlenk tube, and MeCN (1 mL) was added. The orange suspension was stirred for three days, filtered, and after reduction of the volume of the filtrate stored for crystallization at r.t. Overnight, orange needle-shaped crystals suitable for single crystal diffraction were obtained (23.9 mg, 12.2  $\mu$ mol, 61 %).

<sup>1</sup>H NMR (400 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  [ppm] = 6.83 (s, 4H, CH<sub>Mes(m)</sub>), 4.93 (s, 1H, CH<sub>NacNac</sub>), 2.18 (s, 12H, CH<sub>3 Mes</sub>), 1.66 (s, 6H, CH<sub>3 Mes</sub>), 1.45 (s, 6H, CH<sub>3 NacNac</sub>), 0.51 (s, 81H, CH<sub>3 TMS</sub>). <sup>13</sup>C NMR (101 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  [ppm] = 147.30 (s, C<sub>Mes-N</sub>), 133.34 (s, C<sub>Mes(p)</sub>), 132.14 (s, C<sub>Mes(o)</sub>), 129.21 (s, CH<sub>Mes(m)</sub>), 118.07 (s, C<sub>NacNac</sub>), 95.03 (s, CH<sub>NacNac</sub>), 24.29 (s, CH<sub>3 Mes</sub>),

20.89 (s, CH<sub>3 NacNac</sub>), 18.90 (s, CH<sub>3 Mes</sub>), 3.26 (s, CH<sub>3 TMS</sub>). <sup>29</sup>Si-INEPT NMR (79 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  [ppm] = -9.46 (s, Si<sub>TMS</sub>), -107.01 (s, Si<sub>Ge9</sub>). **Elemental analysis:** anal. calcd. for C<sub>56</sub>H<sub>119</sub>Ge<sub>9</sub>MgN<sub>5</sub>Si<sub>12</sub>: C, 35.82; H, 6.39; N, 3.73; found: C, 35.11; H, 6.44; N, 3.51.

#### [K{2.2.2}crypt]<sub>4</sub>[Mg(NacNac<sup>Mes</sup>)(NH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>[Ge<sub>9</sub>-Ge<sub>9</sub>]·32.58 NH<sub>3</sub> (2 a-KMg)

Equimolar amounts of K<sub>4</sub>Ge<sub>9</sub> (80.0 mg, 99.0  $\mu$ mol, 1 equiv.) and Mg(NacNac<sup>Mes</sup>)I (55.2 mg, 99.0  $\mu$ mol, 1 equiv.) were weighed in into a Schlenk tube. After the addition of [2.2.2]crypt (66.9 mg, 178.2  $\mu$ mol, 1.8 equiv.) liquid ammonia (2 mL) was condensed onto the solid mixture, instantly causing the formation of a red solution. The flask was stored at -70 °C. One dark brown, block-shaped single crystal of 2 a-KMg was obtained after 8 months.

#### [K{2.2.2}crypt][NacNac<sup>Mes</sup>]-NH<sub>3</sub> (3)

K<sub>4</sub>Ge<sub>9</sub> (70.0 mg, 90.0  $\mu$ mol, 1 equiv.) and [Mg(NacNac<sup>Mes</sup>)<sub>2</sub>] (32.1 mg, 45.0  $\mu$ mol, 0.5 equiv.) were weighed in into a Schlenk tube. After the addition of [2.2.2]crypt (58.6 mg, 160.0  $\mu$ mol, 1.8 equiv.) liquid ammonia (2 mL) was condensed onto the solid mixture, instantly causing the formation of a red solution with remaining yellow solids. The flask was stored at -40 °C. Several colorless spherical crystals of 3 were obtained after 18 months. Due to the experimental setup an exact yield could not be determined.

#### [K(18-crown-6)][NacNac<sup>Mes</sup>]-3 NH<sub>3</sub> (4)

K<sub>12</sub>Ge<sub>17</sub> (100.0 mg, 59.0  $\mu$ mol, 1 equiv.), 18-crown-6 (31.0 mg, 117.0  $\mu$ mol, 2 equiv.) and [Mg(NacNac<sup>Mes</sup>)<sub>2</sub>] (25.2 mg, 35.0  $\mu$ mol, 0.6 equiv.) were weighed in into a Schlenk tube. Subsequently, liquid ammonia (2 mL) was condensed onto the solid mixture,

instantly causing the formation of a red solution with remaining yellow solids. The flask was stored at  $-70^{\circ}\text{C}$ . Several colorless spherical crystals of **4** were obtained after 24 months. Due to the experimental setup an exact yield could not be determined.

## Author contributions

C. W. performed experiments and authored the manuscript. W. K. refined the single crystal structure data. T. F. F. supervised the project.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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