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## Synthesis and characterization of pristine *closo*-[Ge<sub>10</sub>]<sup>2-</sup>†

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The first  $[Ge_{10}]^{2-}$  Zintl anion, which is neither filled nor connected to another metal atom is presented in terms of X-ray structure, Raman-spectrum and ESI-MS. Pure  $[Ge_{10}]^{2-}$ , adapting a  $D_{4d}$  symmetric *closo*-structure, were crystallized from a Rb<sub>4</sub>Ge<sub>9</sub>/ethylendiamine solution, containing 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne. The role of the latter on the formation of  $[Rb(222-crypt)]_2[Ge_{10}](en)_{1.5}$  is discussed.

The soft oxidation of *nido*- $[E_9]^{4-}$  Zintl anions (E = Ge, Sn, Pb) with 22 skeleton electrons (SE) is a powerful method for the synthesis of new types of the heavier representatives of group 14 clusters and led to a large variety of cage-like structures.<sup>1-5</sup> By that strategy new element allotropes<sup>4–5</sup> as well as ordered, (nano)porous forms of germanium have been obtained.<sup>6-8</sup> Although a comprehensive understanding of the cluster oxidation and thus a control over the reaction outcome is still lacking, a large number of investigations on the oxidation of  $[E_q]^{4-}$  clusters in solution has been performed during the last couple of years,<sup>1,2</sup> and a broad variety of coupled clusters  $\{[(Ge_9)_m]\}^{q-}$   $(m = 2-4, \infty)$ has been obtained by soft oxidation of  $[Ge_9]^{4-}$  in ethylenediamine (en), N,N-dimethylformamide (dmf) and liquid ammonia. Even though in most cases the reactions are not understood in detail,<sup>9-16</sup> mild oxidative properties have been ascribed to the involved solvents,<sup>5,17–19</sup> and recently we have shown that the solvent en indeed plays an important role in the cluster formation.<sup>8</sup>

It has been found that oxidative reaction conditions not only can trigger the coupling but also the growth of clusters.<sup>20</sup> Theoretical investigations showed that for E = Ge a full oxidation to novel germanium allotropes under retention of the polyhedral structure is reasonable.<sup>21</sup> The reaction of  $[E_9]^{4-}$  with organometallic complexes  $ML_a$  (M = metal, L = ligand) in en, dmf and liquid ammonia yielded a broad variety of endohedrally filled clusters  $[M@E_n]^{q-}$   $(n \ge 9)$ ,<sup>1-3</sup> which in special cases adapt nondeltahedral structures and transition metal complexes of clusters with up to 45 covalently connected Ge atoms.<sup>22–25</sup> The formation of  $[M@E_n]^{q-}$  (n > 9), from  $[E_9]^{4-}$  cages, highlights the ability of these tetrel clusters to structurally reorganize in solution.<sup>26,27</sup>

The Zintl anions  $[Pb_{10}]^{2-28}$  and  $[(Ge_{10})Mn(CO)_4]^{3-29}$  are scarce examples of empty homoatomic ten-vertex tetrel clusters, and recently we extended the series of structurally characterized heteroatomic correspondents.<sup>26,30,31</sup> In  $[Ge_9SnGe_9]^{4-}$  a formally *closo*- $[Ge_9Sn]^{2-}$  unit coordinates to a  $[Ge_9]^{2-}$  cluster.<sup>32</sup> In case of  $[M@E_n]^{q-}$ a stabilizing effect of the interstitial M atom on the surrounding  $[E_n]$ cage has been evidenced by quantum-chemical calculations, indicating the preferred formation of endohedrally filled clusters with n > 9instead of their empty correspondents.<sup>1-3,20</sup>

The formation of the empty pristine  $[Pb_{10}]^{2-}$  unit on the one hand and of  $[(Ge_{10})Mn(CO)_4]^{3-}$  on the other also suggests the existence of an unbound  $[Ge_{10}]^{2-}$  Zintl anion. An earlier report on such a  $[Ge_{10}]^{2-}$ cluster<sup>33</sup> turned out to be rather questionable because a disordered *closo*- $[Ge_9]^{2-}$  cluster (Fig. S1, ESI<sup>†</sup>) was unequivocally characterized in similar crystals.<sup>‡ 34</sup> Although the isolation of crystals containing the unbound and empty  $[Ge_{10}]^{2-}$  Zintl anion has been unsuccessful so far, the latter is a frequently observed species in mass spectra obtained by laser desorption experiments or from solutions of Zintl phases in polar organic solvents.<sup>29,32,35,36</sup>

Herein we report on the synthesis and characterization of  $[Rb(222\text{-}crypt)]_2[Ge_{10}](en)_{1.5}$  (1) which contains such an empty and unbound  $[Ge_{10}]^{2-}$  Zintl anion. Compound 1 was characterized by single crystal X-ray structure analysis, Raman-spectroscopy and electrospray ionization mass spectrometry (ESI-MS). Further, we present an ESI-MS investigation on the involved reaction solutions in order to shed some light on the formation of 1.

Dark purple pillars of **1** were obtained (yield *ca.* 10–20%) from a solution of Rb<sub>4</sub>Ge<sub>9</sub> (1 eq.) and 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne (1 eq.)<sup>37</sup> in en after layering of the solution with toluene/cryptand[2.2.2] (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; for experimental details see ESI†).

Crystals of 1 (Fig. S2, ESI<sup> $\dagger$ </sup>) contain two [Rb(222-crypt)]<sup>+</sup> cations per cluster unit, and thus a formal charge of -2 can be assigned

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Experimental details, crystallographic details, ESI-MS spectra. CCDC 1479637. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc04143d



Fig. 1 (a)  $closo-[Ge_{10}]^{2-}$  (**1a**) and (b)  $[(Ge_{10})Mn(CO)_4]^{3-}$  (**2a**)<sup>29</sup> for comparison. Square planes of **1a** and **2a** are labeled with **A/B** and **A'/B'**, respectively. (a and b) Ge and Mn atoms are shown as grey and black ellipsoids, respectively, at a probability level of 50%. C and O atoms are shown as empty spheres.

to the anionic cluster entity (Fig. 1a).  $[Ge_{10}]^{2-}$  (1a) consists of ten symmetry-independent germanium atoms and adapts the shape of a bi-capped square antiprism. The atoms of the planes A (Ge2 to Ge5) and B (Ge6 to Ge9) are nearly perfect squares with ratios of the face diagonals of 1.01 and 1.00 and torsion angles of 179.8° and 179.9°, respectively. The side lengths of **A** and **B** are in the narrow ranges of 2.760(1) Å (Ge2–Ge3) to 2.799(1) Å (Ge4–Ge5) and 2.780(1) Å (Ge7-Ge8) to 2.822(1) Å (Ge6-Ge9). Moreover, similar inter-square Ge-Ge distances from 2.535(1) Å (Ge3-Ge7) to 2.566(1) Å (Ge4–Ge9) indicate that A and B are in parallel. The mean inter-square Ge–Ge distance  $d_1(1\mathbf{a}) = 2.55(1)$  Å is considerably shorter than the mean Ge-Ge distances within A and B  $[d_2(1\mathbf{a}) = 2.79(2) \text{ Å}, d_2'(1\mathbf{a}) = 2.80(2) \text{ Å}]$ . The two atoms Ge1 and Ge10 cap the quadratic antiprism, whereby  $d_3(1a) = 2.583(7)$  Å and  $d_3'(\mathbf{1a}) = 2.59(2)$  Å are slightly longer than  $d_1(\mathbf{1a}) = 2.55(1)$  Å. In summary 1a adopts a nearly perfect  $D_{4d}$  symmetry.

The geometrical parameters of **1a** are very similar to those of  $[(Ge_{10})Mn(CO)_4]^{3-}$  (**2a**) (Fig. 1b). Like for **1a**, the  $[Ge_{10}]$  cluster in **2a** adapts  $D_{4d}$  symmetry. The mean Ge–Ge distances  $d_3(2a)$  and  $d_3'(2a)$  are both 2.58(1) Å, suggesting that  $d_3(2a)$  is not influenced by the coordination of the Mn(CO)<sub>4</sub> fragment. However, in contrast to the square planes in **1a**, **A**' is significantly widened  $[d_2(2a) = 2.85(2) \text{ Å}]$  compared to **B**'  $[d_2'(2a) = 2.77(1) \text{ Å}]$ , which might be attributed to the neighboring Mn(CO)<sub>4</sub> fragment. The inter-square Ge–Ge distances are almost identical for **1a** and **2a**  $[d_1(1a) = 2.55(1) \text{ Å}, d_1(2a) = 2.57(8) \text{ Å}].^{29}$ 

According to Wade's rules, **1a** can be described as a *closo*deltahedron with 22 skeleton electrons (SE), whereby each vertex atom contributes two electrons, plus two extra electrons due to the two-fold negative charge.<sup>38</sup>

In order to study the vibrational behavior of **1a**, single crystals of **1** were investigated by Raman spectroscopy. The



Fig. 2 Raman spectrum of (a)  ${\bf 1}$  and (b)  ${\rm Rb}_4{\rm Ge}_9.$  Characteristic modes are labeled with the corresponding Raman shifts.

spectrum (Fig. 2a) shows a very strong signal at 209 cm<sup>-1</sup> and several very weak bands in the range from 95 to 166  $\text{cm}^{-1}$ . In comparison, the Raman spectrum of the compound [K(222- $(rypt)]_2[Ge_9]$  exhibits one very intensive peak at 212 cm<sup>-1</sup> and three signals below 200 cm<sup>-1</sup> of medium intensity. Quantum-chemical calculations showed that the most intensive mode at 212 cm<sup>-1</sup> corresponds to the "breathing" of the closo-[Ge<sub>9</sub>]<sup>2-</sup> cluster. At least one of the medium intensive signals is attributed to vibrations of the central trigonal prism.<sup>34</sup> For *nido*- $[Ge_9]^{4-}$  clusters (Fig. 2b) the "breathing" mode appears at higher wavenumbers of *ca.* 222 cm<sup>-1</sup>, and below 150 cm<sup>-1</sup> medium-intensive signals are visible.<sup>39-41</sup> However, the latter appear in a neat solid with stronger alkaline metal-Ge interactions. In the spectrum of 1 the absence of intensive signals below 200 cm<sup>-1</sup> evidences, that 1 does not contain  $[Ge_q]^{2-}$ clusters, and thus we conclude that the mode at 209 cm<sup>-1</sup> corresponds to the "breathing" vibration of 1a.34,39-41

Crystals of **1** were obtained only from Rb<sub>4</sub>Ge<sub>9</sub>/en mixtures in the presence of 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne (3), but not in the absence of **3**. Therefore we investigated several solutions by ESI-MS, namely **1** in acetonitrile (acn) (Fig. S3, ESI<sup>†</sup>) as well as Rb<sub>4</sub>Ge<sub>9</sub>/en and Rb<sub>4</sub>Ge<sub>9</sub>/en/3 with a molar ratio Rb<sub>4</sub>Ge<sub>9</sub>/3 = 1 : 1 at an equal concentration of Rb<sub>4</sub>Ge<sub>9</sub> in en for both mixtures (Fig. S4, ESI<sup>†</sup>).

Crystals of 1 readily dissolve in acn (denoted as 1/acn) giving a deep brown solution. Immediate injection of this solution into the mass spectrometer leads to peaks indicative for the presence of

 $\operatorname{Ge_{10}}^{-}$  (*m*/*z* = 725), { $\operatorname{Ge_{10}Rb}$ }<sup>-</sup> (*m*/*z* = 812), and { $\operatorname{Ge_{10}Rb}$ (222-crypt)}<sup>-</sup> (m/z = 1188), with the latter one as the most prominent species. The occurrence of solely Ge10 units hints for an enhanced stability of this cluster. By contrast, the ESI-MS of Rb<sub>4</sub>Ge<sub>9</sub>/en (Fig. S4a, ESI<sup>+</sup>) reveals the presence of  $\{H_xGe_9\}^-$  (x = 0-2; m/z = 653, 654, 655),  $\{HGe_{10}\}^-$ (m/z = 726) and  $\{\text{Ge}_{9}\text{Rb}\}^{-}$  (m/z = 738) with an approximate ratio of intensities of 3:1:1. The high abundance of  $\{HGe_{10}\}^{-}$  indicates that 1a is readily formed upon solution of Rb<sub>4</sub>Ge<sub>9</sub> in en, by a not yet understood fragmentation of the original  $[Ge_9]^{4-}$  cluster.§¶

Interestingly, the mass spectrum of the solution of Rb<sub>4</sub>Ge<sub>9</sub>/3/en (Fig. S4b, ESI<sup>†</sup>), from which the crystals of **1a** were obtained, shows dominant signals of  $\{Ge_9R\}^-$  (*m*/*z* = 764),  $\{Ge_8R\}^-$  (*m*/*z* = 692) and  $\{\text{Ge}_{7}R\}^{-}$  (m/z = 618) (R = 7-amino-5-aza-hepta-2,4-dien-2-yl) as well as the non-alkenylated species  $\{H_xGe_9\}^-$  (x = 0-2),  $\{Ge_9Rb\}^- \parallel^{42}$ and  $\{HGe_{10}\}^{-}$ . The high abundance of clusters bearing organic ligands R, that arise from the nucleophilic addition of one and two molecules of 3 to the  $[Ge_9]^{4-}$  unit, documents the higher reactivity of the  $[Ge_9]^{4-}$  unit compared to that of  $[Ge_{10}]^{2-}$ .<sup>37,42</sup> The appearance of  $\{HGe_{10}\}^{-}$  suggests that a fraction of the initial  $[Ge_{9}]^{4-}$  clusters reacts to 1a prior to the reaction with 3. Thus, layering of a Rb<sub>4</sub>Ge<sub>9</sub>/3/en solution with cryptand[2.2.2] in toluene preferably produces crystals of **1** since the functionalized species  $[Ge_9R]^{3-}$  obviously do not crystalize under these conditions. The binding mode of the organic group R to the cluster is shown in Fig. S5 (ESI<sup>†</sup>).

Our investigations shed some light onto the formation of the  $[Ge_{10}]^{2-}$  Zintl anion. ESI-MS investigations revealed that the  $[Ge_{10}]^{2-}$ unit is readily formed upon simple dissolution of Rb<sub>4</sub>Ge<sub>9</sub> in en, highlighting the flexibility of the dissolved tetrel element  $[Ge_0]^{4-}$ clusters which can grow and thereby change their shape. It turned out that the crystallization of the bare  $[Ge_9]^{y-}$  (y = 2-4) clusters is favored over the crystallization of  $[Ge_{10}]^{2-}$ , both of which are present in Rb<sub>4</sub>Ge<sub>9</sub>/en solutions. Obviously, the  $[Ge_{10}]^{2-}$  unit can only be obtained when the Ge<sub>9</sub> clusters are "masked" by the reaction with 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne, leading to  $[RGe_9]^{3-}$ , which remains in solution and does not crystalize by layering with cryptand[2.2.2] in toluene. By adjusting the experimental conditions, it might be possible to obtain even larger empty germanium cages, and it also is feasible that other representatives of the  $[E_{10}]^{2-}$  series can be synthesized by this method.

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## Notes and references

- $\ddagger$  Both Belin and Akerstedt isolated  $[K(222\mbox{-}crypt)]_2[Ge_9]\mbox{, which under-}$ goes a disorder/order transition between 250 K and 100 K. Belin et al. performed single-crystal X-ray structure analysis at 250 K, and described the disordered  $[Ge_9]^{2-}$  clusters as  $[Ge_{10}]^{2-}$ . Akerstedt *et al.* reinvestigated the same compound (identical unit cell and cell volume) at 100 K, and observed a fully ordered closo- $[Ge_9]^{2-}$  cluster.<sup>33,34</sup>
- § The formation of 1a is an oxidative process (Scheme S1, ESI<sup>†</sup>), as the formal number of valence electrons per Ge atom, reduces from 22/9 in case of  $[Ge_9]^{4-}$  to 22/10 for 1a.  $\P$  Layering of such solutions with cryptand[2.2.2] or 18-crown-6
- (1,4,7,10,13,16-hexaoxacyclooctadecane) in toluene has yielded a variety of crystals containing (connected) Ge<sub>9</sub> clusters, but none comprising 1a.<sup>1</sup>

|| The occurrence of also Ge<sub>9</sub><sup>-</sup> and (Ge<sub>9</sub>Rb)<sup>-</sup> in ESI-MS most likely is attributed to the cleavage of the Ge-C bonds of [Ge<sub>9</sub>R]<sup>3-</sup> under ESI-MS conditions.42

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