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

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**The first [Ge<sub>10</sub>]<sup>2−</sup> 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<sub>10</sub>]<sup>2−</sup>, adapting a *D*<sub>4d</sub> symmetric *closo*-structure, were crystallized from a Rb<sub>4</sub>Ge<sub>9</sub>/ethylenediamine 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)]<sub>2</sub>[Ge<sub>10</sub>](en)<sub>1.5</sub> is discussed.**

The soft oxidation of *nido*-[E<sub>9</sub>]<sup>4−</sup> 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<sub>9</sub>]<sup>4−</sup> clusters in solution has been performed during the last couple of years,<sup>1,2</sup> and a broad variety of coupled clusters {[(Ge<sub>9</sub>)<sub>m</sub>]<sup>q−</sup> (m = 2–4, ∞)} has been obtained by soft oxidation of [Ge<sub>9</sub>]<sup>4−</sup> 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<sub>9</sub>]<sup>4−</sup> with organometallic complexes ML<sub>a</sub> (M = metal, L = ligand) in en, dmf and liquid ammonia yielded a broad variety of endohedrally filled

clusters [M@E<sub>n</sub>]<sup>q−</sup> (n ≥ 9),<sup>1–3</sup> which in special cases adapt non-deltahedral structures and transition metal complexes of clusters with up to 45 covalently connected Ge atoms.<sup>22–25</sup> The formation of [M@E<sub>n</sub>]<sup>q−</sup> (n > 9), from [E<sub>9</sub>]<sup>4−</sup> cages, highlights the ability of these tetrel clusters to structurally reorganize in solution.<sup>26,27</sup>

The Zintl anions [Pb<sub>10</sub>]<sup>2−</sup><sup>28</sup> and [(Ge<sub>10</sub>)Mn(CO)<sub>4</sub>]<sup>3−</sup><sup>29</sup> 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<sub>9</sub>SnGe<sub>9</sub>]<sup>4−</sup> a formally *closo*-[Ge<sub>9</sub>Sn]<sup>2−</sup> unit coordinates to a [Ge<sub>9</sub>]<sup>2−</sup> cluster.<sup>32</sup> In case of [M@E<sub>n</sub>]<sup>q−</sup> a stabilizing effect of the interstitial M atom on the surrounding [E<sub>n</sub>] cage has been evidenced by quantum-chemical calculations, indicating the preferred formation of endohedrally filled clusters with n > 9 instead of their empty correspondents.<sup>1–3,20</sup>

The formation of the empty pristine [Pb<sub>10</sub>]<sup>2−</sup> unit on the one hand and of [(Ge<sub>10</sub>)Mn(CO)<sub>4</sub>]<sup>3−</sup> on the other also suggests the existence of an unbound [Ge<sub>10</sub>]<sup>2−</sup> Zintl anion. An earlier report on such a [Ge<sub>10</sub>]<sup>2−</sup> cluster<sup>33</sup> turned out to be rather questionable because a disordered *closo*-[Ge<sub>9</sub>]<sup>2−</sup> cluster (Fig. S1, ESI†) was unequivocally characterized in similar crystals.<sup>34</sup> Although the isolation of crystals containing the unbound and empty [Ge<sub>10</sub>]<sup>2−</sup> 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>1–3,20,29,32,35,36</sup>

Herein we report on the synthesis and characterization of [Rb(222-crypt)]<sub>2</sub>[Ge<sub>10</sub>](en)<sub>1.5</sub> (**1**) which contains such an empty and unbound [Ge<sub>10</sub>]<sup>2−</sup> 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**.

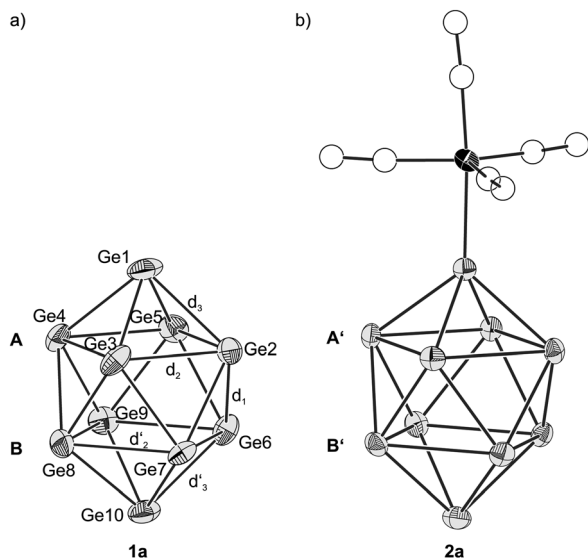
Dark purple pillars of **1** were obtained (yield ca. 10–20%) from a solution of Rb<sub>4</sub>Ge<sub>9</sub> (1 eq.) and 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne (1 eq.)<sup>37</sup> in en after layering of the solution with toluene/cryptand[2.2.2] (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane;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

Crystals of **1** (Fig. S2, ESI†) 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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† 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





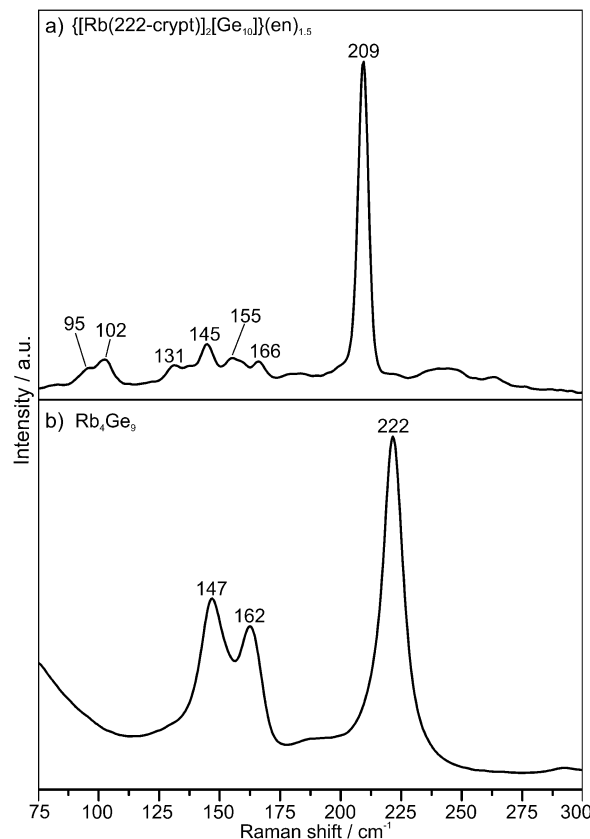
**Fig. 1** (a) *closo*-[Ge<sub>10</sub>]<sup>2-</sup> (**1a**) and (b) [(Ge<sub>10</sub>)Mn(CO)<sub>4</sub>]<sup>3-</sup> (**2a**)<sup>29</sup> for comparison. Square planes of **1a** and **2a** are labeled with **A/B** and **A'/B'**, respectively. (a and b) Ge and Mn atoms are shown as grey and black 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<sub>10</sub>]<sup>2-</sup> (**1a**) consists of ten symmetry-independent germanium atoms and adopts 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  $d_1(\mathbf{1a}) = 2.55(1)$  Å is considerably shorter than the mean Ge–Ge distances within **A** and **B** [ $d_2(\mathbf{1a}) = 2.79(2)$  Å,  $d'_2(\mathbf{1a}) = 2.80(2)$  Å]. The two atoms Ge1 and Ge10 cap the quadratic antiprism, whereby  $d_3(\mathbf{1a}) = 2.583(7)$  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*<sub>4d</sub> symmetry.

The geometrical parameters of **1a** are very similar to those of [(Ge<sub>10</sub>)Mn(CO)<sub>4</sub>]<sup>3-</sup> (**2a**) (Fig. 1b). Like for **1a**, the [Ge<sub>10</sub>] cluster in **2a** adopts *D*<sub>4d</sub> symmetry. The mean Ge–Ge distances  $d_3(\mathbf{2a})$  and  $d'_3(\mathbf{2a})$  are both 2.58(1) Å, suggesting that  $d_3(\mathbf{2a})$  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 [ $d_2(\mathbf{2a}) = 2.85(2)$  Å] compared to **B'** [ $d'_2(\mathbf{2a}) = 2.77(1)$  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** [ $d_1(\mathbf{1a}) = 2.55(1)$  Å,  $d_1(\mathbf{2a}) = 2.547(8)$  Å].<sup>29</sup>

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) **1** and (b) Rb<sub>4</sub>Ge<sub>9</sub>. 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 cm<sup>-1</sup>. In comparison, the Raman spectrum of the compound [K(222-crypt)]<sub>2</sub>[Ge<sub>9</sub>] 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<sub>9</sub>]<sup>4-</sup> 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<sub>9</sub>]<sup>2-</sup> clusters, and thus we conclude that the mode at 209 cm<sup>-1</sup> corresponds to the “breathing” vibration of **1a**.<sup>34,39–41</sup>

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†) 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†).

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



$\text{Ge}_{10}^-$  ( $m/z = 725$ ),  $\{\text{Ge}_{10}\text{Rb}\}^-$  ( $m/z = 812$ ), and  $\{\text{Ge}_{10}\text{Rb}(222\text{-crypt})\}^-$  ( $m/z = 1188$ ), with the latter one as the most prominent species. The occurrence of solely  $\text{Ge}_{10}$  units hints for an enhanced stability of this cluster. By contrast, the ESI-MS of  $\text{Rb}_4\text{Ge}_9/\text{en}$  (Fig. S4a, ESI†) reveals the presence of  $\{\text{H}_x\text{Ge}_9\}^-$  ( $x = 0-2$ ;  $m/z = 653, 654, 655$ ),  $\{\text{HGe}_{10}\}^-$  ( $m/z = 726$ ) and  $\{\text{Ge}_9\text{Rb}\}^-$  ( $m/z = 738$ ) with an approximate ratio of intensities of 3 : 1 : 1. The high abundance of  $\{\text{HGe}_{10}\}^-$  indicates that **1a** is readily formed upon solution of  $\text{Rb}_4\text{Ge}_9$  in en, by a not yet understood fragmentation of the original  $[\text{Ge}_9]^{4-}$  cluster.†

Interestingly, the mass spectrum of the solution of  $\text{Rb}_4\text{Ge}_9/3/\text{en}$  (Fig. S4b, ESI†), from which the crystals of **1a** were obtained, shows dominant signals of  $\{\text{Ge}_9\text{R}\}^-$  ( $m/z = 764$ ),  $\{\text{Ge}_8\text{R}\}^-$  ( $m/z = 692$ ) and  $\{\text{Ge}_7\text{R}\}^-$  ( $m/z = 618$ ) ( $\text{R} = 7\text{-amino-5-aza-hepta-2,4-dien-2-yl}$ ) as well as the non-alkenylated species  $\{\text{H}_x\text{Ge}_9\}^-$  ( $x = 0-2$ ),  $\{\text{Ge}_9\text{Rb}\}^-$  and  $\{\text{HGe}_{10}\}^-$ . The high abundance of clusters bearing organic ligands R, that arise from the nucleophilic addition of one and two molecules of **3** to the  $[\text{Ge}_9]^{4-}$  unit, documents the higher reactivity of the  $[\text{Ge}_9]^{4-}$  unit compared to that of  $[\text{Ge}_{10}]^{2-}$ .<sup>37,42</sup> The appearance of  $\{\text{HGe}_{10}\}^-$  suggests that a fraction of the initial  $[\text{Ge}_9]^{4-}$  clusters reacts to **1a** prior to the reaction with **3**. Thus, layering of a  $\text{Rb}_4\text{Ge}_9/3/\text{en}$  solution with cryptand[2.2.2] in toluene preferably produces crystals of **1** since the functionalized species  $[\text{Ge}_9\text{R}]^{3-}$  obviously do not crystallize under these conditions. The binding mode of the organic group R to the cluster is shown in Fig. S5 (ESI†).

Our investigations shed some light onto the formation of the  $[\text{Ge}_{10}]^{2-}$  Zintl anion. ESI-MS investigations revealed that the  $[\text{Ge}_{10}]^{2-}$  unit is readily formed upon simple dissolution of  $\text{Rb}_4\text{Ge}_9$  in en, highlighting the flexibility of the dissolved tetrel element  $[\text{Ge}_9]^{4-}$  clusters which can grow and thereby change their shape. It turned out that the crystallization of the bare  $[\text{Ge}_9]^{y-}$  ( $y = 2-4$ ) clusters is favored over the crystallization of  $[\text{Ge}_{10}]^{2-}$ , both of which are present in  $\text{Rb}_4\text{Ge}_9/\text{en}$  solutions. Obviously, the  $[\text{Ge}_{10}]^{2-}$  unit can only be obtained when the  $\text{Ge}_9$  clusters are “masked” by the reaction with 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne, leading to  $[\text{RGe}_9]^{3-}$ , which remains in solution and does not crystallize 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  $[\text{E}_{10}]^{2-}$  series can be synthesized by this method.

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## Notes and references

‡ Both Belin and Akerstedt isolated  $[\text{K}(222\text{-crypt})]_2[\text{Ge}_9]$ , which undergoes 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  $[\text{Ge}_9]^{2-}$  clusters as  $[\text{Ge}_{10}]^{2-}$ . Akerstedt *et al.* reinvestigated the same compound (identical unit cell and cell volume) at 100 K, and observed a fully ordered *closol*- $[\text{Ge}_9]^{2-}$  cluster.<sup>33,34</sup>

§ The formation of **1a** is an oxidative process (Scheme S1, ESI†), as the formal number of valence electrons per Ge atom, reduces from 22/9 in case of  $[\text{Ge}_9]^{4-}$  to 22/10 for **1a**.

¶ 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)  $\text{Ge}_9$  clusters, but none comprising **1a**.<sup>17</sup>

|| The occurrence of also  $\text{Ge}_9^-$  and  $(\text{Ge}_9\text{Rb})^-$  in ESI-MS most likely is attributed to the cleavage of the Ge–C bonds of  $[\text{Ge}_9\text{R}]^{3-}$  under ESI-MS conditions.<sup>42</sup>

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