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The first $[\text{Ge}_{10}]^{2-}$ 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 $[\text{Ge}_{10}]^{2-}$, adapting a D_{4d} symmetric *closo*-structure, were crystallized from a Rb_4Ge_9 /ethylenediamine solution, containing 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne.

The role of the latter on the formation of $[\text{Rb}(\text{222-crypt})]_2[\text{Ge}_{10}](\text{en})_{1.5}$ is discussed.

The soft oxidation of *nido*- $[\text{E}_9]^{4-}$ Zintl anions ($\text{E} = \text{Ge, Sn, Pb}$) 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.^{1–5} By that strategy new element allotropes^{4–5} as well as ordered, (nano)porous forms of germanium have been obtained.^{6–8} 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 $[\text{E}_9]^{4-}$ clusters in solution has been performed during the last couple of years,^{1,2} and a broad variety of coupled clusters $\{[\text{Ge}_9]_m\}^{q-}$ ($m = 2–4, \infty$) has been obtained by soft oxidation of $[\text{Ge}_9]^{4-}$ in ethylenediamine (en), *N,N*-dimethylformamide (dmf) and liquid ammonia. Even though in most cases the reactions are not understood in detail,^{9–16} mild oxidative properties have been ascribed to the involved solvents,^{5,17–19} and recently we have shown that the solvent en indeed plays an important role in the cluster formation.⁸

It has been found that oxidative reaction conditions not only can trigger the coupling but also the growth of clusters.²⁰ Theoretical investigations showed that for $\text{E} = \text{Ge}$ a full oxidation to novel germanium allotropes under retention of the polyhedral structure is reasonable.²¹ The reaction of $[\text{E}_9]^{4-}$ with organometallic complexes ML_a ($\text{M} = \text{metal, L} = \text{ligand}$) in en, dmf and liquid ammonia yielded a broad variety of endohedrally filled

clusters $[\text{M}@\text{E}_n]^{q-}$ ($n \geq 9$),^{1–3} which in special cases adapt non-deltahedral structures and transition metal complexes of clusters with up to 45 covalently connected Ge atoms.^{22–25} The formation of $[\text{M}@\text{E}_n]^{q-}$ ($n > 9$), from $[\text{E}_9]^{4-}$ cages, highlights the ability of these tetrel clusters to structurally reorganize in solution.^{26,27}

The Zintl anions $[\text{Pb}_{10}]^{2-}$ ²⁸ and $[(\text{Ge}_{10})\text{Mn}(\text{CO})_4]^{3-}$ ²⁹ are scarce examples of empty homoatomic ten-vertex tetrel clusters, and recently we extended the series of structurally characterized heteroatomic correspondents.^{26,30,31} In $[\text{Ge}_9\text{SnGe}_9]^{4-}$ a formally *closo*- $[\text{Ge}_9\text{Sn}]^{2-}$ unit coordinates to a $[\text{Ge}_9]^{2-}$ cluster.³² In case of $[\text{M}@\text{E}_n]^{q-}$ a stabilizing effect of the interstitial M atom on the surrounding $[\text{E}_n]$ cage has been evidenced by quantum-chemical calculations, indicating the preferred formation of endohedrally filled clusters with $n > 9$ instead of their empty correspondents.^{1,3,20}

The formation of the empty pristine $[\text{Pb}_{10}]^{2-}$ unit on the one hand and of $[(\text{Ge}_{10})\text{Mn}(\text{CO})_4]^{3-}$ on the other also suggests the existence of an unbound $[\text{Ge}_{10}]^{2-}$ Zintl anion. An earlier report on such a $[\text{Ge}_{10}]^{2-}$ cluster³³ turned out to be rather questionable because a disordered *closo*- $[\text{Ge}_9]^{2-}$ cluster (Fig. S1, ESI†) was unequivocally characterized in similar crystals.[‡]³⁴ Although the isolation of crystals containing the unbound and empty $[\text{Ge}_{10}]^{2-}$ 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.^{29,32,35,36}

Herein we report on the synthesis and characterization of $[\text{Rb}(\text{222-crypt})]_2[\text{Ge}_{10}](\text{en})_{1.5}$ (**1**) which contains such an empty and unbound $[\text{Ge}_{10}]^{2-}$ 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_4Ge_9 (1 eq.) and 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne (1 eq.)³⁷ in en after layering of the solution with toluene/cryptand[2.2.2] (4,7,13,16,21,24-hexaoxa-1,10-diaza-bicyclo[8.8.8]hexacosane; for experimental details see ESI†).

Crystals of **1** (Fig. S2, ESI†) contain two $[\text{Rb}(\text{222-crypt})]^+$ 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



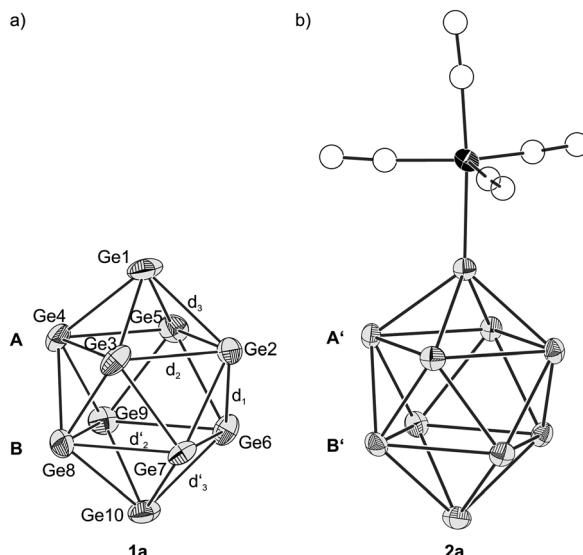


Fig. 1 (a) *closo*-[Ge₁₀]²⁻ (**1a**) and (b) [(Ge₁₀)Mn(CO)₄]³⁻ (**2a**)²⁹ for comparison. Square planes of **1a** and **2a** are labeled with A/B and A'/B', respectively. (a and b) Ge and Mn atoms are shown as grey and black ellipsoids, respectively, at a probability level of 50%. C and O atoms are shown as empty spheres.

to the anionic cluster entity (Fig. 1a). [Ge₁₀]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 (**1a**) = 2.55(1) Å is considerably shorter than the mean Ge-Ge distances within A and B [d_2 (**1a**) = 2.79(2) Å, d_2' (**1a**) = 2.80(2) Å]. The two atoms Ge₁ and Ge₁₀ cap the quadratic antiprism, whereby d_3 (**1a**) = 2.583(7) Å and d_3' (**1a**) = 2.59(2) Å are slightly longer than d_1 (**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 [(Ge₁₀)Mn(CO)₄]³⁻ (**2a**) (Fig. 1b). Like for **1a**, the [Ge₁₀] 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)₄ fragment. However, in contrast to the square planes in **1a**, **A'** is significantly widened [d_2 (**2a**) = 2.85(2) Å] compared to **B'** [d_2' (**2a**) = 2.77(1) Å], which might be attributed to the neighboring Mn(CO)₄ fragment. The inter-square Ge-Ge distances are almost identical for **1a** and **2a** [d_1 (**1a**) = 2.55(1) Å, d_1 (**2a**) = 2.547(8) 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.³⁸

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

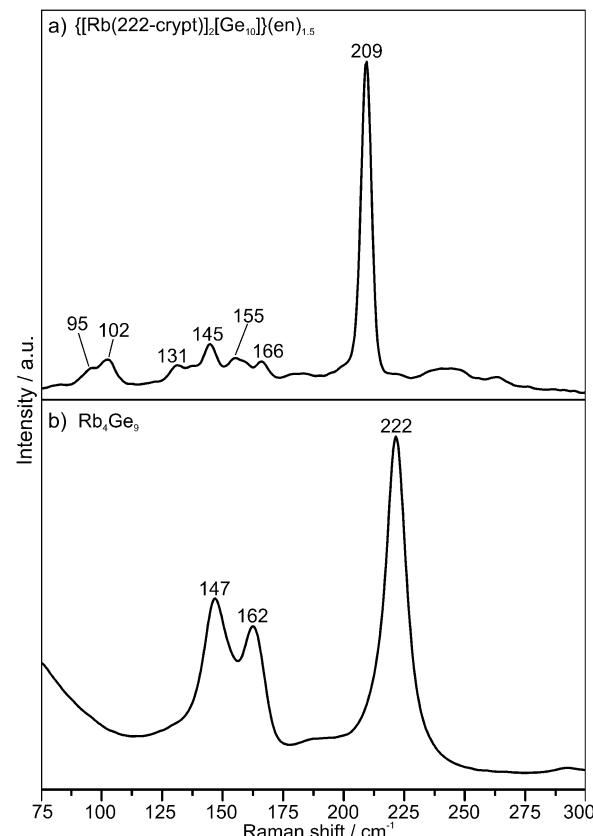


Fig. 2 Raman spectrum of (a) **1** and (b) Rb₄Ge₉. Characteristic modes are labeled with the corresponding Raman shifts.

spectrum (Fig. 2a) shows a very strong signal at 209 cm⁻¹ and several very weak bands in the range from 95 to 166 cm⁻¹. In comparison, the Raman spectrum of the compound [K(222-crypt)₂][Ge₉] exhibits one very intensive peak at 212 cm⁻¹ and three signals below 200 cm⁻¹ of medium intensity. Quantum-chemical calculations showed that the most intensive mode at 212 cm⁻¹ corresponds to the "breathing" of the *closo*-[Ge₉]²⁻ cluster. At least one of the medium intensive signals is attributed to vibrations of the central trigonal prism.³⁴ For *nido*-[Ge₉]⁴⁻ clusters (Fig. 2b) the "breathing" mode appears at higher wavenumbers of ca. 222 cm⁻¹, and below 150 cm⁻¹ medium-intensive signals are visible.³⁹⁻⁴¹ 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⁻¹ evidences, that **1** does not contain [Ge₉]²⁻ clusters, and thus we conclude that the mode at 209 cm⁻¹ corresponds to the "breathing" vibration of **1a**.^{34,39-41}

Crystals of **1** were obtained only from Rb₄Ge₉/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 Rb₄Ge₉/en and Rb₄Ge₉/en/**3** with a molar ratio Rb₄Ge₉/**3** = 1 : 1 at an equal concentration of Rb₄Ge₉ 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

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 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 $\{\text{H}_x\text{Ge}_9\}^-$ ($x = 0\text{--}2$; $m/z = 653, 654, 655$), $\{\text{HGe}_{10}\}^-$ ($m/z = 726$) 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 Rb_4Ge_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 $\{\text{H}_x\text{Ge}_9\}^-$ ($x = 0\text{--}2$), $\{\text{Ge}_9\text{Rb}\}^-$ ‡¶ 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 $[\text{Ge}_{10}]^{2-}$.^{37,42} 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 Rb_4Ge_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 $[\text{Ge}_9]^{y-}$ ($y = 2\text{--}4$) 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 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 Åkerstedt 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 $[\text{Ge}_{10}]^{2-}$. Åkerstedt *et al.* re-investigated the same compound (identical unit cell and cell volume) at 100 K, and observed a fully ordered *closو*- $[\text{Ge}_9]^{2-}$ cluster.^{33,34}

§ 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) Ge_9 clusters, but none comprising **1a**.¹⁷

|| The occurrence of also 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.⁴²

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