Synthesis and characterization of pristine closo-[Ge_{10}]^{2–}\dagger

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

It has been found that oxidative reaction conditions not only can trigger the coupling but also the growth of clusters.\textsuperscript{20} Theoretical investigations showed that for E = Ge a full oxidation to novel germanium allotropes under retention of the polyhedral structure is reasonable.\textsuperscript{21} The reaction of [E_{9}]^{4+} with organo-metallic complexes ML\textsubscript{q} (M = metal, L = ligand) in en, dmf and liquid ammonia yielded a broad variety of endohedrally filled clusters [M@E_{n}]^{q–} (n ≥ 9),\textsuperscript{1,2} which in special cases adapt non-deltahedral structures and transition metal complexes of clusters with up to 45 covalently connected Ge atoms.\textsuperscript{22–25} The formation of [M@E_{n}]^{q–} (n > 9), from \[E_{n}\]^{4+} cages, highlights the ability of these tetrel clusters to structurally reorganize in solution.\textsuperscript{26,27}

The Zintl anions [Pb_{10}]^{3–}\dagger and \[[Ge_{9}Mn(CO)_{9}]^{3–}\dagger\] are scarce examples of empty homatomic ten-vertex tetrel clusters, and recently we extended the series of structurally characterized heteroatomic correspondents.\textsuperscript{26,30,31} In \[Ge_{9}SnGe_{9}\] a formally closo-[Ge_{9}Sn]^{4–} unit coordinates to a \[Ge_{10}]^{2–} cluster.\textsuperscript{32} In case of \[M@E_{9}]^{q–}\dagger a stabilizing effect of the interstitial M atom on the surrounding \[E_{9}\] cage has been evidenced by quantum-chemical calculations, indicating the preferred formation of endohedrally filled clusters with n > 9 instead of their empty counterparts.\textsuperscript{1–3,20}

The formation of the empty pristine \[Pb_{10}]^{3–}\dagger unit on the one hand and of \[[Ge_{9}Mn(CO)_{9}]^{3–}\dagger\] on the other also suggests the existence of an unbound \[Ge_{10}]^{2–} Zintl anion. An earlier report on such a \[Ge_{10}]^{2–}\dagger cluster\textsuperscript{13} turned out to be rather questionable because a disordered closo-[Ge_{9}]^{2–} cluster (Fig. S1, ESI\textsuperscript{†}) was unequivocally characterized in similar crystals.\textsuperscript{4,14} Although the isolation of crystals containing the unbound and empty \[Ge_{10}]^{2–}\dagger 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.\textsuperscript{29,32,35,36}

Herein we report on the synthesis and characterization of \[Rb(222-crypt)]_{2}[Ge_{10}](en)_{1.5} (1) which contains such an empty and unbound \[Ge_{10}]^{2–}\dagger 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 RbGe_{9} (1 eq.) and 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne (1 eq.)\textsuperscript{37} in en after layering of the solution with toluene/cryptand\textsuperscript{[2.2.2]} (4,7,13,16,21,24-hexaoxa-1,10-diaza-bicyclo[8.8.8]hexacosen; for experimental details see ESI\textsuperscript{†}).

Crystals of 1 (Fig. S2, ESI†) contain two \[Rb(222-crypt)]^{2+} cations per cluster unit, and thus a formal charge of –2 can be assigned
to the anionic cluster entity (Fig. 1a). \([\text{Ge}_{10}]^{2-}\) (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, the narrow ranges of 2.760(1) Å (Ge2–Ge3) to 2.799(1) Å (Ge4–Ge5) and 2.777(1) Å (Ge4–Ge9) indicate that A and B are in parallel. The mean inter-square Ge–Ge distances \(d_{\text{A}}(1\text{a}) = 2.55(1)\) Å is considerably shorter than the mean Ge–Ge distances within A and B \([d_{\text{A}}(1\text{a}) = 2.79(2)\ \text{Å}, d_{\text{A}}'(1\text{a}) = 2.80(2)\ \text{Å}].\) The two atoms Ge1 and Ge10 cap the quadratic antiprism, whereby one of the medium intensive signals is attributed to vibrations of the \([\text{Ge}_{10}]^{2-}\) fragment. At least one of the medium intensive signals is attributed to vibrations of the central trigonal prism. For \([\text{nido-Ge}_{9}]^{3+}\) 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. However, the latter appear in a neat solid with stronger alkali metal–Ge interactions. In the spectrum of 1 the absence of intensive signals below 200 cm\(^{-1}\) evidences that 1 does not contain \([\text{Ge}_{9}]^{3+}\) clusters, and thus we conclude that the mode at 209 cm\(^{-1}\) corresponds to the "breathing" vibration of 1a.44

Crystals of 1 were obtained only from Rb4Ge9/en mixtures in the presence of 7-aminono-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 \([\text{K}(222-crypt)][\text{Ge}_{9}]\) 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-\([\text{Ge}_{9}]^{2-}\) cluster. At least one of the medium intensive signals is attributed to vibrations of the central trigonal prism. For \([\text{nido-Ge}_{9}]^{3+}\) 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. However, the latter appear in a neat solid with stronger alkali metal–Ge interactions. In the spectrum of 1 the absence of intensive signals below 200 cm\(^{-1}\) evidences that 1 does not contain \([\text{Ge}_{9}]^{3+}\) clusters, and thus we conclude that the mode at 209 cm\(^{-1}\) corresponds to the "breathing" vibration of 1a.44

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
The occurrence of also Ge$_{10}^-$ and (Ge$_{10}$Rb)$^-$ in ESI-MS most likely is attributed to the cleavage of the Ge–C bonds of [Ge$_{10}$R]$^-$ under ESI-MS conditions.\textsuperscript{42}

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