Synthesis and characterization of pristine closo-[Ge10]2–†

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The first [Ge10]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 [Ge10]2–, adapting a D4d symmetric closo-structure, were crystallized from a Rb4Ge9/ethylendiamine solution, containing 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yn. The role of the latter on the formation of [Rb(222-crypt)]2[Ge10](en)1.5 is discussed.

The soft oxidation of nido-[E9]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.1–5 By that strategy new element allotropes4–5 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 [E9]4+ clusters in solution has been performed during the last couple of years,1,2 and a broad variety of coupled clusters [[(Ge9)h]m]+ (m = 2–4, ∞) has been obtained by soft oxidation of [Ge9]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 E = Ge a full oxidation to novel germanium allotropes under retention of the polyhedral structure is reasonable.21 The reaction of [E9]4+ with organometallic complexes ML (M = metal, L = ligand) in en, dmf and liquid ammonia yielded a broad variety of endohedrally filled clusters [M@E9]n+ (n ≥ 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 [M@E9]n+ (n > 9), from [E9]+ cages, highlights the ability of these tetrel clusters to structurally reorganize in solution.26,27

The Zintl anions [Pb10]2–26–28 and [(Ge10)Mn(CO)4]3–29 are scarce examples of empty homatomic ten-vertex tetrel clusters, and recently we extended the series of structurally characterized heteroatomic correspondents.26,30,31 In [GeSnGe9]4– a formally closo-[Ge9Sn]2– unit coordinates to a [Ge9]2– cluster.32 In case of [M@E9]n+ a stabilizing effect of the interstitial M atom on the surrounding [E9] 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 [Pb10]2– unit on the one hand and of [(Ge10)Mn(CO)4]3– on the other also suggests the existence of an unbound [Ge10]2– Zintl anion. An earlier report on such a [Ge10]2– cluster13 turned out to be rather questionable because a disordered closo-[Ge10]2– cluster (Fig. S1, ESI†) was unequivocally characterized in similar crystals.4–7 Although the isolation of crystals containing the unbound and empty [Ge10]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 [Rb(222-crypt)]2[Ge10](en)1.5 (1) which contains such an empty and unbound [Ge10]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 Rb4Ge9 (1 eq.) and 7-amino-1-trimethylsilyl-5-aza-hepta-3-en-1-yne (1 eq.) in en after layering of the solution with toluene/cryptand2.2.2 (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 [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). \([Ge_{10}]^{2-}\) (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 mean inter-square Ge–Ge distances \(d_{int}(A)=2.55(1)\) Å is significantly shorter than the mean Ge–Ge distances within A and B \(d_{int}(A)=2.79(2)\) Å, \(d_{int}(B)=2.80(2)\) Å. The two atoms Ge1 and Ge10 cap the quadratic antiprism, whereby \(d_{int}(A)=2.55(1)\) Å is adapted almost perfectly \(D_{4d}\) symmetry. The geometrical parameters of 1a are very similar to those of \([Ge_{10}]^{2-}\) (2a) (Fig. 1b). Like for 1a, the \([Ge_{10}]\) cluster in 2a adapts \(D_{4d}\) symmetry. The mean Ge–Ge distances \(d_{ij}(2a)\) and \(d_{ij}^*(2a)\) are both 2.58(1) Å, suggesting that \(d_{ij}(2a)\) 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 \(d_{ij}(2a)=2.85(2)\) Å compared to B’ \(d_{ij}(2a)=2.77(1)\) 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 \(d_{int}(1a)=2.55(1)\) Å, \(d_{int}(2a)=2.547(8)\) 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.30

In order to study the vibrational behavior of 1a, single crystals of 1 were investigated by Raman spectroscopy. The 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 \([K(222-crypt)]_2[Ge_9]\) 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\([Ge_9]\)\(^{2-}\) cluster. At least one of the medium intensive signals is attributed to vibrations of the central trigonal prism.31 For 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.30–34 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 \([Ge_9]\)\(^{2-}\) clusters, and thus we conclude that the mode at 209 cm\(^{-1}\) corresponds to the “breathing” vibration of 1a.34–39

Crystals of 1 were obtained only from Rb\(_4\)Ge\(_9\)/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\(_4\)Ge\(_9\)/en and Rb\(_4\)Ge\(_9\)/en/3 with a molar ratio Rb\(_4\)Ge\(_9\)/3 = 1 : 1 at an equal concentration of Rb\(_4\)Ge\(_9\) 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...
The occurrence of also Ge_{9}^{2-} and (Ge,Rb)^{−} in ESI-MS most likely is attributed to the cleavage of the Ge–C bonds of [Ge_{9}R]^{3−} under ESI-MS conditions.42

7 G. S. Armatas and M. G. Kanatzidis, Science, 2006, 313, 817.