

## Intermetalloid clusters: The retention of the Zn-Zn bond in [Ge<sub>9</sub>Zn-ZnGe<sub>9</sub>]<sup>6-</sup> and formation of [(Ge<sub>9</sub>Zn)-(Ge<sub>9</sub>)-(ZnGe<sub>9</sub>)]<sup>8-</sup> as well as polymeric <sup>1</sup><sub>∞</sub>[-(Ge<sub>9</sub>Zn)<sup>2-</sup>]<sup>1</sup>

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### Abstract

The reactions of Zn(I) compounds of the type Zn<sub>2</sub>L<sub>2</sub> (L = Cp\* = 1,2,3,4,5-pentamethylcyclopentadienyl; L = [HC(PhN=PPh<sub>2</sub>)]<sup>-</sup>, Ph = phenyl) with solutions of the Zintl phase K<sub>4</sub>Ge<sub>9</sub> in liquid ammonia and ethylenediamine (en) have been investigated. For L = [HC(PhN=PPh<sub>2</sub>)]<sup>-</sup> the reaction leads under retention of the Zn-Zn bond to the anion [(η<sup>4</sup>-Ge<sub>9</sub>)Zn-Zn(η<sup>4</sup>-Ge<sub>9</sub>)]<sup>6-</sup> (**1a**) as the first complex with a Zn–Zn unit carrying two cluster entities. The trimeric anion [(η<sup>4</sup>-Ge<sub>9</sub>)Zn{μ<sub>2</sub>(η<sup>1</sup>:η<sup>1</sup>Ge<sub>9</sub>)}Zn(η<sup>4</sup>-Ge<sub>9</sub>)]<sup>8-</sup> (**2a**) occurs as side product, indicating that also oxidation reactions take place in these solutions. The reaction of Zn<sub>2</sub>Cp\*<sub>2</sub> with K<sub>4</sub>Ge<sub>9</sub> in ethylenediamine yielded the linear polymeric unit <sup>∞</sup><sub>1</sub>{Zn(μ<sub>2</sub>(η<sup>4</sup>:η<sup>1</sup>Ge<sub>9</sub>))<sup>2-</sup> (**3a**) with the first head-to-tail arrangement of ten-atomic *closo*-clusters. All anions are obtained and structurally characterized as [A(2.2.2-crypt)]<sup>+</sup> salts (A = K, Rb). Copious computational analyses on a DFT-PBE0/def2-TZVPP/PCM level of theory confirm the experimental structures and support the stability of the two hypothetical ten vertex clusters fragments *closo*-[Ge<sub>9</sub>Zn]<sup>2-</sup> and (paramagnetic) [Ge<sub>9</sub>Zn]<sup>3-</sup>.

<sup>1</sup> Supporting information for this article (including detailed synthetic procedures, crystallographic data and computational details for all described compounds) is available on the WWW under ...

The reactions of Zn(I) compounds of the type  $Zn_2L_2$  with solutions of the Zintl phase  $K_4Ge_9$  in liquid ammonia and ethylenediamine (en) lead for  $L = [HC(PhN=PPh_2)]^-$  under retention of the Zn-Zn bond to the anion  $[(\eta^4-Ge_9)Zn-Zn(\eta^4-Ge_9)]^{6-}$  representing the first complex with a Zn-Zn unit carrying two cluster entities. The trimeric anion  $[(\eta^4-Ge_9)Zn\{\mu_2(\eta^1:\eta^1Ge_9)\}Zn(\eta^4-Ge_9)]^{8-}$  occurs as side product, indicating that also oxidation reactions take place. The reaction of  $Zn_2Cp^*_2$  ( $Cp^* = 1,2,3,4,5$ -pentamethylcyclopentadienyl) with  $K_4Ge_9$  in ethylenediamine yielded the linear polymeric unit  ${}^\infty_1\{Zn(\mu_2(\eta^4:\eta^1Ge_9))\}^{2-}$  with the first head-to-tail arrangement of ten-atomic *closo*-clusters. All anions are obtained and structurally characterized as  $[A(2.2.2-crypt)]^+$  salts ( $A = K, Rb$ ). Copious computational analyses on a DFT-PBE0/def2-TZVPP/PCM level of theory confirm the experimental structures and support the stability of the two hypothetical ten vertex clusters fragments *closo*- $[Ge_9Zn]^{2-}$  and (paramagnetic)  $[Ge_9Zn]^{3-}$ .

Since Carmona's discovery of the first Zn(I) compound  $\text{Zn}_2\text{Cp}^*_2$  with a covalent Zn-Zn bond, tremendous activities toward the synthesis of compounds with low-valent Zn atoms have been started.<sup>[1]</sup> The  $\eta^5$ -bonded  $\text{Cp}^*$  ligand can be substituted by either monodentated, neutral donor ligands, i. e. 4-dimethylaminopyridine (dmap),  $\text{Et}_2\text{O}$  or THF,<sup>[2]</sup> as well as by monoanionic monodentated and chelating substituents.<sup>[3]</sup> The reactivity of  $\text{Zn}_2\text{Cp}^*_2$  towards transition metal compounds under formation of intermetallic clusters has also been investigated.<sup>[4]</sup> In addition, the insertion of a formal Zn(0) atom into the Zn-Zn bond under formation of a linear  $[\text{Zn-Zn-Zn}]^{2+}$  fragment<sup>[5]</sup> and the synthesis of cyclic  $(\text{ZnCp}^*)_3^{3+}$ <sup>[6]</sup> as well as reduction reactions with organic azides, which yielded zinc hexazene complexes,<sup>[7]</sup> demonstrated that Zn(I) chemistry is a fertile field to get access to molecules with unusual bonding situations.<sup>[8]</sup> Examples of  $\text{Zn}_2$  units coordinated by p-block metals that support the Zn-Zn bond are less frequent. A  $[\text{Zn}_2(\text{GaCp}^*)_6]^{2+}$  unit with an unsupported Zn-Zn bond has been observed in solution in an equilibrium with a two-fold  $\text{Cp}^*\text{Ga}$ -bridged species as it has also been found in the molecular solid state structure.<sup>[9]</sup>

Up to now, beside  $\text{Cp}^*$  no other donor ligand with a higher hapticity that stabilizes the Zn-Zn bond has been reported. Triggered by the observation that traces of the anion  $[(\eta^4\text{-Pb}_9)\text{Cd-Cd}(\eta^4\text{-Pb}_9)]^{6-}$  with an unsupported Cd-Cd bond are formed in the reaction of the Zintl ion  $[\text{Pb}_9]^{4-}$  with a Cd(II) compound,<sup>[10]</sup> we investigated the reaction of Zn(I) and Zn(II) compounds with the homologous  $[\text{Ge}_9]^{4-}$  unit. The open square of the mono-capped anti-prismatic  $C_{4v}$  symmetric  $[\text{Ge}_9]^{4-}$  cluster possesses donor capabilities that resemble those of  $\text{Cp}^*$  as shown by the formation of  $[(\eta^4\text{-Ge}_9)\text{ZnPh}]^{3-}$ <sup>[11]</sup> and  $[(\eta^4\text{-Ge}_9)\text{Cu}(\text{PR}_3)]^{3-}$  ( $\text{R} = \text{iPr}, \text{Cy}$ ).<sup>[12, 13]</sup>

Recently, we found that reaction of Zn(I) compounds in ethylenediamine (en) and liquid ammonia can lead to a cleavage of the Zn-Zn bond either by disproportionation or oxidative processes. Although species like  $[\text{Bi-Zn-Bi}]^{6-}$ <sup>[14]</sup>,  $[(\eta^4\text{-Ge}_9)\text{-Zn}(\eta^3\text{-Ge}_9)]^{4-}$ ,  $[(\eta^3\text{-Ge}_9)\text{-Zn}(\eta^3\text{-Ge}_9)]^{4-}$ <sup>[15]</sup> and polymeric  $\infty_1\{\text{Zn}(\mu_2(\eta^3:\eta^3\text{Ge}_9))\}^{2-}$ <sup>[16]</sup> have been obtained from reactions with Zintl anions, a retention of the Zn-Zn bond indicative for a Zn(I) compound has not been achieved yet.

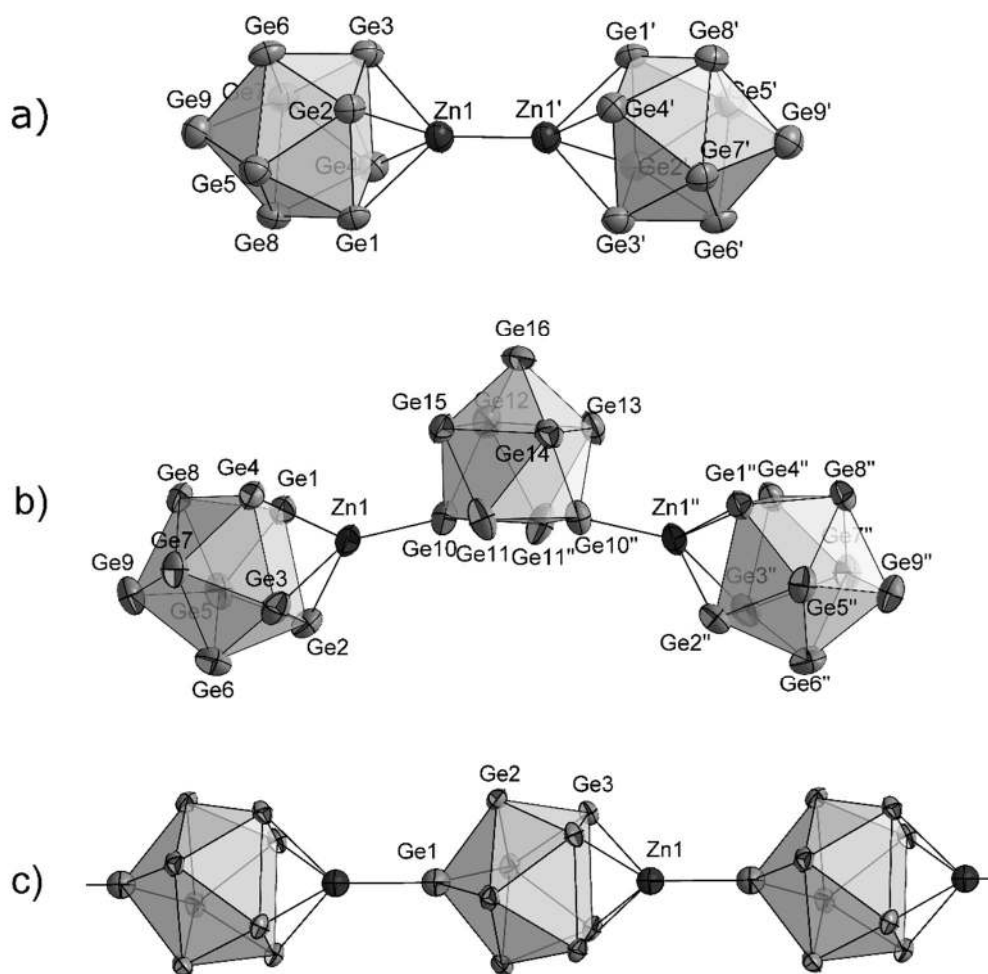
We now have systematically investigated reactions of Zn(I) and Zn(II) compounds with  $[\text{Ge}_9]^{4-}$  in amine solvents ( $\text{NH}_3$ , en) and show that these, depending on the reaction conditions, proceed either under retention of the Zn-Zn bond or oxidation/disproportionation of  $\text{Zn}_2\text{L}_2$ , respectively. The resulting complexes, the

dimeric  $[(\eta^4\text{-Ge}_9)\text{-Zn-Zn-(}\eta^4\text{-Ge}_9)]^{6-}$  (**1a**) – which is the first example with an unsupported Zn-Zn bond that coordinates solely to semimetals – the trimeric species  $[(\eta^4\text{-Ge}_9)\text{Zn}\{\mu_2(\eta^1:\eta^1\text{Ge}_9)\}\text{Zn}(\eta^4\text{-Ge}_9)]^{8-}$  (**2a**) and the polymeric unit  ${}_{\infty}^1\{\text{Zn}(\mu_2(\eta^4:\eta^1\text{Ge}_9))\}^{2-}$  (**3a**) were characterized by single-crystal X-ray structure analysis. The presence of Zn in all compounds was verified by EDX measurements (Supp. Inform.). All anions can be described on the basis of  $[\text{Ge}_9\text{Zn}]^{3-/2-}$  *closo*-clusters which is also supported by computational analyses on a DFT-PBE0/def2-TZVPP/PCM level of theory. The isolobal analogy of  $[\text{Ge}_9\text{Zn}]^{3-}$ ,  $\text{Cp}^*\text{Zn}$  and H is highlighted.

$\text{Zn}_2\text{Cp}^*_2$  immediately turns black in the presence of liquid ammonia under formation of  $\text{Cp}^*\text{H}$ , whereas  $[\text{HC}(\text{PhN}=\text{PPh}_2)_2]_2\text{Zn}_2$  remains stable over weeks. The reaction of a suspension with an excess of  $\text{K}_4\text{Ge}_9$  (atomic ratio  $\text{Zn}:\text{Ge}_9 = 1:2$ ) yielded the  $\text{Zn}^{2+}$ -bridged anion  $[\text{Ge}_9\text{-Zn-Ge}_9]^{6-}$ ,<sup>[15]</sup> whereas the reaction with an equimolar  $\text{Zn}:\text{Ge}_9$  ratio under similar reaction conditions proceeded with formation of orange crystals, which were identified as  $\text{K}_2[\text{K}(2.2.2\text{-crypt})]_4[\text{Ge}_9\text{-Zn-Zn-Ge}_9](\text{NH}_3)_{26}$  (**1**).

In the anion **1a** the iminophosphorane ligands of the starting material are substituted by  $\eta^4\text{-}[\text{Ge}_9]^{4-}$  clusters, and most remarkably, the Zn-Zn bond is retained (Figure 1a). Anion **1a** is only the second example of a sandwich complex of a  $\text{Zn}(\text{I})_2$  unit beside the pristine  $(\eta^5\text{-Cp}^*)\text{Zn-Zn}(\eta^5\text{-Cp}^*)$ . Despite of the high electrostatic repulsion within the six-fold negatively charged ion, the Zn-Zn bond in **1a** of 2.420(1) Å is only slightly longer than those in  $\text{Zn}_2[\text{HC}(\text{Ph}_2\text{P}=\text{NPh})_2]_2$  (2.34 Å<sup>[3c]</sup>) and  $\text{Zn}_2\text{Cp}^*_2$  (2.30 Å<sup>[1]</sup>).<sup>[17]</sup> The  $\text{Ge}_9$  clusters, which are connected in a  $\eta^4$  mode to each Zn atom, possess almost perfect  $\text{C}_{4v}$  symmetry ( $d_1/d_2 = 1.01$ ;  $\alpha_1 = 1.42^\circ$ )<sup>[18]</sup>.

At a first glance the  $6\pi$ -electron donor  $\text{Cp}^*$  is replaced by another  $6\pi$ -electron donor, *nido*- $[\text{Ge}_9]^{4-}$ ,<sup>[19]</sup> however, the Zn atom in **1a** becomes also a part of the deltahedral cluster “ $\text{Ge}_9\text{Zn}$ ” which in consequence appears as dimer connected via the Zn atoms. Tetrel clusters that are connected by *exo*-bonds are indeed known for *nido*- $\text{Ge}_9$  and *nido*- $\text{Sn}_9$  clusters in  $[\text{Ge}_9\text{-Ge}_9]^{6-}$  and  $[\text{Sn}_9\text{-Sn}_9]^{6-}$ .<sup>[20]</sup> For both cases, also the corresponding paramagnetic  $[\text{Ge}_9]^{3-}$  and  $[\text{Sn}_9]^{3-}$  clusters, respectively, are known.<sup>[21]</sup> Thus,  $[(\eta^4\text{-Ge}_9)\text{-Zn-Zn-(}\eta^4\text{-Ge}_9)]^{6-}$  (**1a**) can formally be described as the dimerization product of two *closo*-clusters  $[\text{Ge}_9\text{Zn}]^{3-}$  bearing an unpaired electron at the Zn vertex.



**Figure 1.** Structure details of the molecular anions. a)  $[\text{Ge}_9\text{-Zn-Zn-Ge}_9]^{6-}$  (**1a**). b)  $[\text{Ge}_9\text{Zn-Ge}_9\text{-ZnGe}_9]^{8-}$  (**2a**). c) Cut out of three repeating cluster units of  $[\text{Zn}(\mu_2(\eta^4:\eta^1\text{Ge}_9))]^{2-}$  (**3a**). Ellipsoids for all atoms are shown at a probability level of 70%. Ge atoms are drawn in grey, Zn atoms in dark grey.

Upon the formation of **1** beside hypothetical  $[\text{Ge}_9\text{Zn}]^{3-}$  apparently also anionic units  $[\text{Ge}_9\text{Zn}]^{2-}$  appear in solution as a side product, and orange needles of  $\text{K}_4[\text{K}(\text{2.2.2-crypt})]_4(\text{2a})(\text{NH}_3)_{29}$  (**2**) containing the complex anion  $[(\eta^4\text{-Ge}_9)\text{Zn}\{\mu_2(\eta^1:\eta^1\text{Ge}_9)\}\text{Zn}(\eta^4\text{-Ge}_9)]^{8-}$  (**2a**) were isolated (Figure 1b). The eight-fold negatively charged anion consists of three Ge<sub>9</sub> clusters that formally are bridged by two Zn<sup>2+</sup> ions. As it was observed in **1**, each Zn atom coordinates to the open square of a Ge<sub>9</sub> cluster (2.581(1) – 2.612(2) Å) and to one Ge atom of the central Ge<sub>9</sub> cluster with a Ge10-Zn1 distance of 2.424(1) Å. The almost perfect C<sub>4v</sub>-symmetrical structure (d<sub>1</sub>/d<sub>2</sub> = 1.01) of the Ge<sub>9</sub> cluster unit in **2a** is similar to that in  $[\text{Ge}_9\text{-Zn-Zn-Ge}_9]^{6-}$ . The Ge<sub>9</sub>-Zn bonds with an average value of 2.60 Å (2.581(1) – 2.612(2) Å) are slightly shorter than in **1a** (2.63 Å).

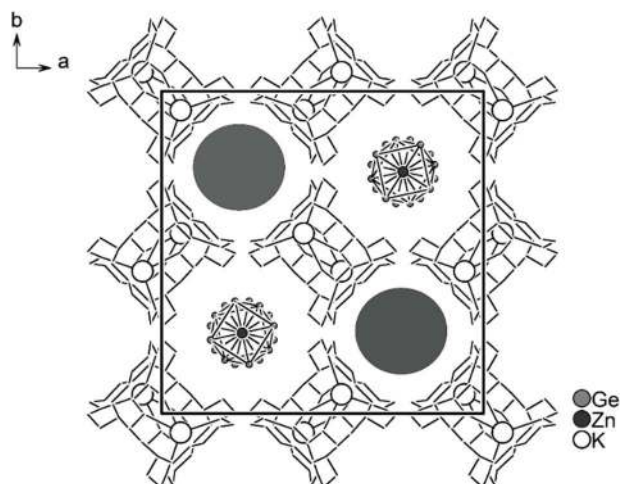
The central Ge<sub>9</sub> cluster possesses C<sub>2v</sub> symmetry (d<sub>1</sub>/d<sub>2</sub> = 1.11, α<sub>1</sub> = 6.2°) and is slightly disordered.<sup>[22]</sup> **2a** can formally be described as an adduct of two [Ge<sub>9</sub>Zn]<sup>2-</sup> units – the formal oxidation product of [Ge<sub>9</sub>Zn]<sup>3-</sup> – that coordinate via an acceptor orbital at each Zn atom to the lone pairs of two Ge atoms of the central Ge<sub>9</sub> cluster.<sup>[23]</sup>

Upon layering a K<sub>4</sub>Ge<sub>9</sub>/en solution with Zn<sub>2</sub>Cp\*<sub>2</sub>/tol, compounds containing polymeric strands of the composition  $\infty_1\{(\text{Zn} - \text{Ge}_9)\}^{2-}$  are formed. Crystallization of the product in the presence of 2.2.2-crypt leads to [K(2.2.2-crypt)]<sub>2</sub>(ZnGe<sub>9</sub>)(en)<sub>0.9</sub> (**3**), which contains the new polymeric anionic unit  $\infty_1\{\text{Zn}(\mu_2(\eta^4:\eta^1\text{Ge}_9))\}^{2-}$  (**3a**).<sup>[24]</sup> By contrast the addition of 18-crown-6 to the solution resulted in the formation of [K(18-crown-6)]<sub>2</sub>(ZnGe<sub>9</sub>)(en) with the polymeric unit  $\infty_1\{\text{Zn}(\mu_2(\eta^3:\eta^3\text{Ge}_9))\}^{2-}$ ,<sup>[16]</sup> in which the Zn atoms coordinate to two triangular faces of the D<sub>3h</sub> symmetric Ge<sub>9</sub> cluster. During the reaction, a greyish precipitate was formed and identified as elemental Zn(0) via EDX measurements (Supp. Inform.). The anion **3a** can be described as a polymeric strand of *closo*-[Ge<sub>9</sub>Zn]<sup>2-</sup> clusters with ideal C<sub>4v</sub> symmetry (d<sub>1</sub>/d<sub>2</sub> = 1) (Figure 1c). The cluster units are linked through the two heteroatomic opposing cap atoms of the bicapped square antiprism. Since the two different forms of the polymeric units can be understood as the coordination of [Ge<sub>9</sub>]<sup>4-</sup> clusters to Zn<sup>2+</sup> we also performed the reaction starting from the Zn(II) compound ZnCp\*<sub>2</sub> (Supp. Inform.) and we obtained both types of polymers under similar reaction conditions in better yields and higher purity.

In the crystal, strands of the anions **3a** are located in 50% of the channels that are formed by the tetragonal primitive packing of the [K(2.2.2-crypt)]<sup>+</sup> units (Figure 2). The remaining channels of equivalent size are filled with disordered solvent molecules, and thermogravimetric experiments show a stepwise release of these en molecules (Supp. Inform.).

The anions **1a** and **2a** / **3a** can be regarded as cluster aggregates of the building blocks [Ge<sub>9</sub>Zn]<sup>3-</sup> and [Ge<sub>9</sub>Zn]<sup>2-</sup>, respectively. [Ge<sub>9</sub>Zn]<sup>2-</sup> formally corresponds to a 22 skeleton electron (SE) ten atom *closo*-cluster<sup>[19]</sup> assuming lone pairs at the Ge atoms and an empty acceptor orbital at the Zn atom, whereas in [Ge<sub>9</sub>Zn]<sup>3-</sup> an unpaired electron is located at the Zn atom. In analogy to Cp\*<sub>2</sub>Zn<sub>2</sub>, which has been described as a combination of two Cp\*Zn fragments with unpaired electrons forming a covalent σ-bond between the two Zn atoms,<sup>[25]</sup> **1a** is the result of a dimerization of two [Ge<sub>9</sub>Zn]<sup>3-</sup> units, however with the difference that the paramagnetic monomers might exist as

stable cluster anions. In view of the pseudo-atom concept of clusters the spherical  $[\text{Ge}_9\text{Zn}]^{3-}$  unit is analogous to an H atom, and **1a** thus corresponds to the  $\text{H}_2$  molecule.



**Figure 2.** Unit cell of  $[\text{K}(2.2.2\text{-crypt})]_2(\text{Zn-Ge}_9)(\text{en})_{0.9}$ , (**3**) shown along the crystallographic  $c$  axis. The K-sequestering 2.2.2-crypt molecules build a framework with four channels per unit cell. The strands of the  $[\text{ZnGe}_9]^{2-}$  *closo* clusters fill two of these channels, whereas the other two are filled with disordered ethylenediamine molecules (drawn as grey spheres). The 2.2.2-crypt molecules are shown schematically as a wire-and-stick model.

These considerations are confirmed by quantum-chemical calculations at a DFT-PBE0<sup>[26]</sup>/def2-TZVPP<sup>[27]</sup>/PCM<sup>[28]</sup> level of theory (Figure 3a). The optimization of the  $[\text{Ge}_9\text{Zn}]^{3-}$  fragment (**1A<sup>opt</sup>**) reveals a stable radical (energetic minimum structure, HOMO-LUMO gap 2.13 eV) with a dimerization energy of  $\Delta E = -2.04$  eV (comparison of the total energies of  $2 \times [\text{Ge}_9\text{Zn}]^{3-}$  versus  $[\text{Ge}_9\text{-Zn-Zn-Ge}_9]^{6-}$ ) and an enlarged HOMO-LUMO gap of 3.32 eV. Structurally, the optimized clusters are in good agreement with the experimental findings (Supp. Inform.). The Zn–Zn bond vector is not perfectly perpendicular to the open squares of the coordinating  $\text{Ge}_9$  clusters ( $179.3^\circ$  to  $179.8^\circ$ ), which is also observed for both, the optimized<sup>[29]</sup> and the experimental<sup>[1, 25]</sup> structures of the analogous  $\text{Cp}^*_2\text{Zn}_2$  compound. Other than for  $\text{Cp}^*_2\text{Zn}_2$ , appears the  $\sigma$ -bond in **1a** in the HOMO (Figure 4a) and does not energetically lie below orbitals with exclusively ligand contributions.<sup>[1,2]</sup>

The  $[\text{Ge}_9\text{Zn}]^{2-}$  unit also represents a minimum on the energy hyper surface.<sup>[30]</sup> Due to the similar X-ray scattering factors of Zn and Ge, the position of the Zn atom in the cluster units cannot be determined unambiguously, but isomers with a Zn atom at a vertex of the square antiprism are energetically less favorable and not of minimum character (for details see Supp. Inform.).<sup>[31]</sup>

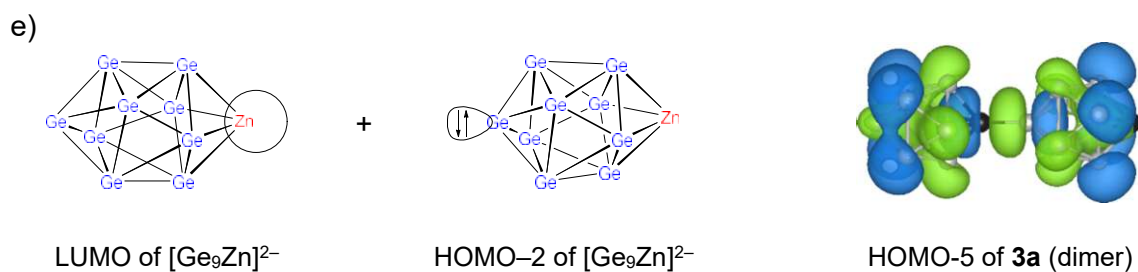
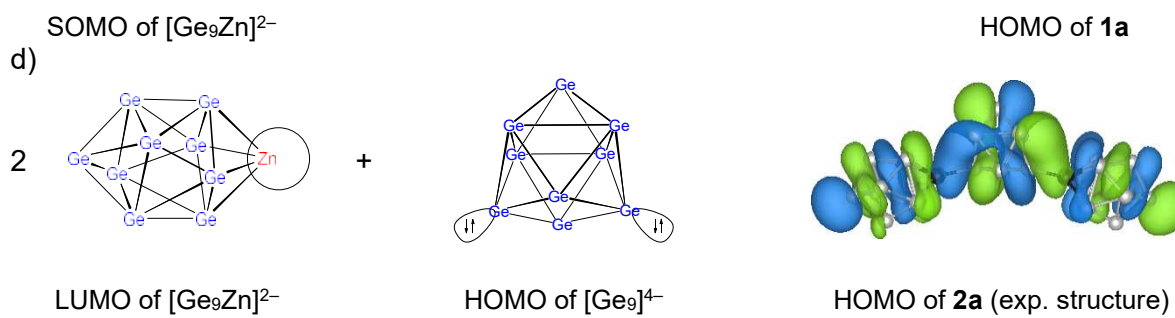
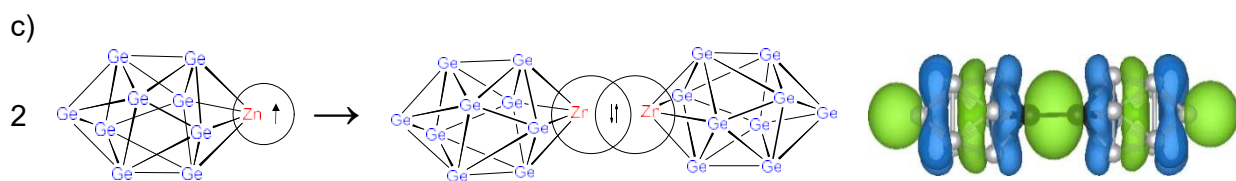
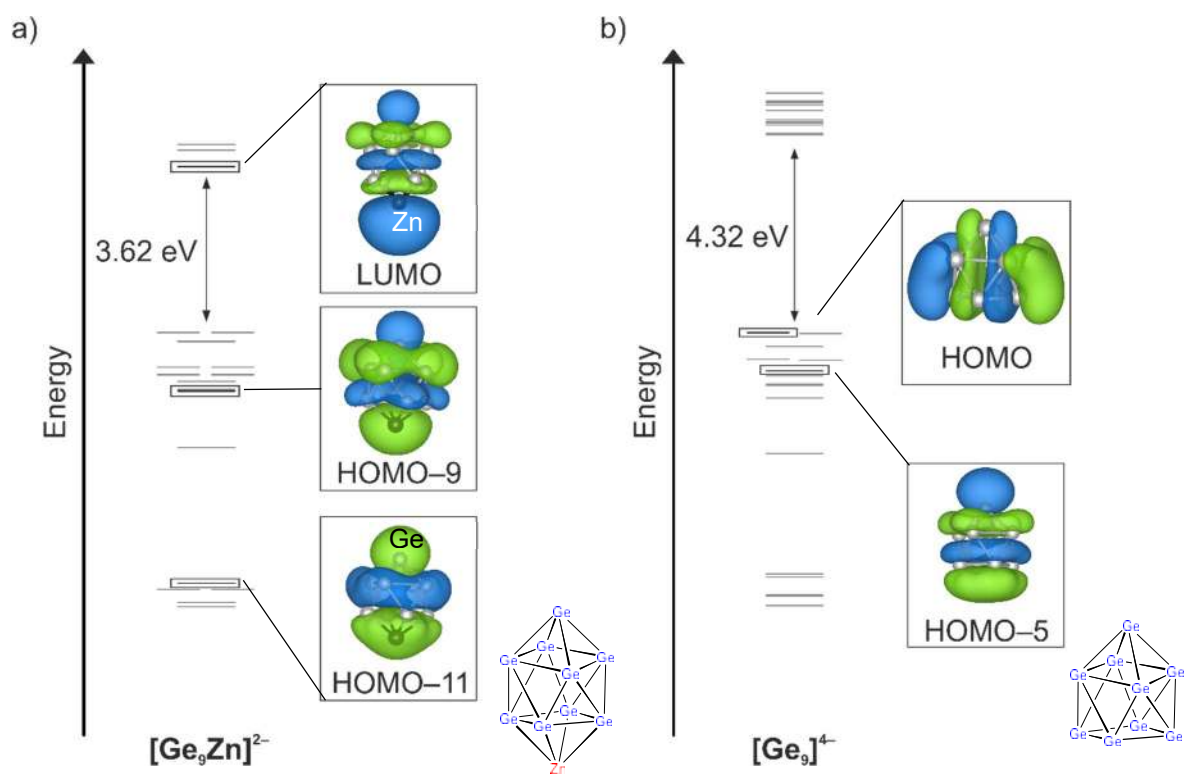




Figure 3. The molecular orbitals of a)  $[\text{Ge}_9\text{Zn}]^{2-}$  including lone pair at the apex Ge (HOMO-11) and acceptor orbital at Zn (LUMO) and b)  $[\text{Ge}_9]^{4-}$  with a lone pair at the apex atom (HOMO-5) and lone pairs at Ge atoms of the open square (HOMO) (b). The arrows with the calculated HOMO-LUMO gaps mark the highest occupied orbitals. Molecular orbitals with significant Zn amount are shown. Representations of iso-surfaces of all filled valence orbitals for both clusters are shown in Supporting Information. c) The HOMO of **1a** as a result of the interaction of two SOMOs forming a covalent Zn-Zn  $\sigma$ -bond. d) The LUMOs of two  $[\text{Ge}_9\text{Zn}]^{2-}$  units and the HOMO of  $[\text{Ge}_9]^{4-}$  form the HOMO of **2a**. e) "Head-to-tail" arrangement of two  $[\text{Ge}_9\text{Zn}]^{2-}$  units forming the *exo*-Zn-Ge bond in the polymer **3a** by repeating interactions. The iso-value for all wave functions is 0.1.

The 40 valence electrons fill the cluster shells 1S, 1P, 1D, 2S, 1F, and 2P corresponding to a spherical  $\sigma$ - and  $\pi$ -aromatic system.<sup>[32]</sup> Similarly the electron count matches a superatom approach.<sup>[33]</sup> Alternatively the deltahedral cluster  $[\text{Ge}_9\text{Zn}]^{2-}$  can be considered as the product of the addition of a  $\text{Zn}^{2+}$  to the open square of a  $[\text{Ge}_9]^{4-}$  unit. The stability then arises from the interaction of the  $F_0$ -cluster orbital of the  $[\text{Ge}_9]^{4-}$  (HOMO-5) and the empty 4s-orbital of  $\text{Zn}^{2+}$  to build the  $F_0$ -cluster orbital (HOMO-9) and the LUMO of  $[\text{Ge}_9\text{Zn}]^{2-}$ . Consequently  $[\text{Ge}_9\text{Zn}]^{2-}$  represents a 22-skeleton electron Wade-cluster with one acceptor-orbital at the Zn atom<sup>[15]</sup> (see s-type orbital at the Zn atom in the LUMO of  $[\text{Ge}_9\text{Zn}]^{2-}$  in Figure 3).

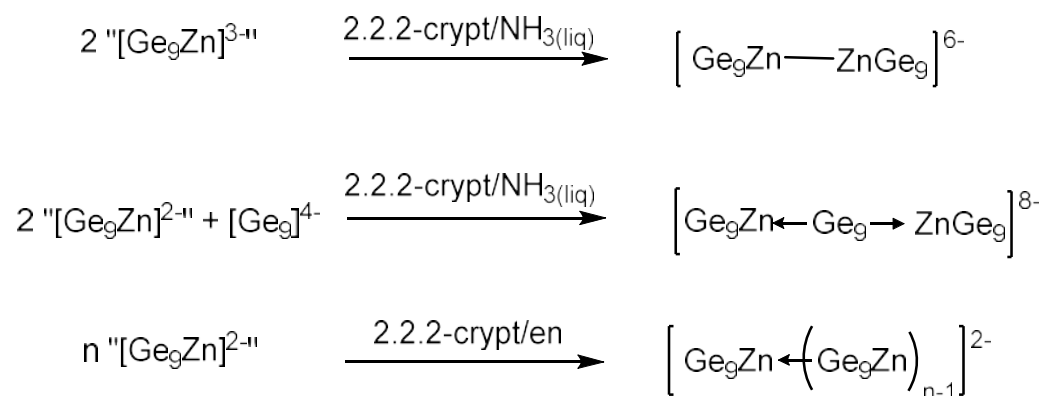
The charge distribution based on population analyses according to Mulliken and Hirshfeld<sup>[34]</sup> and the natural population analysis<sup>[35]</sup> (NPA, Table S1, Supp. Inform.) reveal considerable electron density at the Zn atom. This supports a delocalized electron system including the Zn atom typical of a hetero-atomic *closo*- $[\text{Ge}_9\text{Zn}]^{2-}$  unit rather than an electrostatic interaction between a *nido*- $[\text{Ge}_9]^{4-}$  unit and a  $\text{Zn}^{2+}$ .

The addition of one electron to form  $[\text{Ge}_9\text{Zn}]^{3-}$  (with the shape of **3A<sup>opt</sup>**) leads to a strong increase of the electron density at the Zn vertex (according to NPA, the charge of the Zn atom in the  $[\text{Ge}_9\text{Zn}]^{x-}$  unit is +0.88 and -0.03 for  $x = 2$  and 3, respectively), whereas the average charges of the neighboring Ge atoms remain almost unaffected (-0.44 and -0.40 for  $x = 2$  and 3, respectively). This finding is independent of the applied quantum chemical method (Supp. Inform., Table 1). As a result a classical ten-vertex 42-electron *closo*-cluster  $[\text{Ge}_9\text{Zn}]^{4-}$  with a lone pair at each vertex atom is not stable, and the optimization results in a *nido*- $[\text{Ge}_9]^{4-}$  unit and  $\text{Zn}(0)$ . The empty orbital at the Zn vertex of  $[\text{Ge}_9\text{Zn}]^{2-}$  (LUMO) allows for a coordination of a Lewis base at the Zn vertex, as seen for both anions **2a** and **3a** (Scheme 1). In a fragment orbital approach, the HOMO of **2a** (Figure 4b) can be understood as an

interaction of the two LUMOs of two  $[\text{Ge}_9\text{Zn}]^{2-}$  entities and the HOMO of the  $[\text{Ge}_9]^{4-}$  unit (Figure 3).

Similarly, polymer **3a** is formed by the interaction of the LUMO at the Zn vertex with the lone pair of the Ge atom capping the opposing square in  $[\text{Ge}_9\text{Zn}]^{2-}$  (Figure 4c). The dimerization energy of the structurally optimized polyhedra as the first step of the polymer formation amounts to  $\Delta E = -0.38$  eV ( $2 [\mathbf{3A}^{\text{opt}}]^{2-} \rightarrow [(\mathbf{3A}-\mathbf{3A})^{\text{opt}}]^{4-}$ ).<sup>[36]</sup>

In summary, the formation of  $[\text{Ge}_9\text{-Zn-Zn-Ge}_9]^{6-}$  (**1a**) shows that under appropriate reaction conditions, the  $[\text{Zn-Zn}]^{2+}$  unit of the Zn(I) precursor is retained even upon the reaction with highly charged main-group clusters and in strongly polar solvents. As side reactions, disproportion or oxidation can occur leading to the cluster anions **2a** and **3a**. The protonation of the ligands of the precursors and thus the acidity of ethylenediamine if used as solvent plays a crucial role for the formation of  $\text{Zn}^{2+}$ . The formal description of **1a** as a dimerization product of two  $[\text{Ge}_9\text{Zn}]^{3-}$  units mirrors the simplest example of the superatom concept of clusters – namely the formation of  $\text{H}_2$  from two hydrogen atoms.



**Scheme 1.** Different reaction pathways of the *clos*o cluster  $[\text{Ge}_9\text{Zn}]^{2-/3-}$ .

The stability of the hypothetical  $[\text{Ge}_9\text{Zn}]^{2-}$  unit and thus a cluster expansion by the integration of  $\text{Zn}^{2+}$  in cluster core of  $[\text{Ge}_9]^{4-}$  allows for a concept of intermetalloid cluster growth by Lewis acid / Lewis base principles. The 22-skeletal electron *clos*o- $[\text{Ge}_9\text{Zn}]^{2-}$  cluster possesses an acceptor orbital at the Zn vertex which discloses the formation of the 29-atom cluster  $[\text{Ge}_9\text{Zn-Ge}_9\text{-ZnGe}_9]^{8-}$  and polymeric  $\infty_1\{\text{Zn}(\mu_2(\eta^4:\eta^1\text{Ge}_9))\}^{2-}$  by the interaction with the lone pairs of Ge vertex atoms. The significance of lone pairs at

tetrel clusters appeared before in anions such as  $[\eta^1\text{-Ge}_{10}\text{Mn}(\text{CO})_4]^{3-}$ <sup>[37]</sup> or  $[\text{Ge}_6\{\text{Cr}(\text{CO})_5\}_6]^{2-}$ ,<sup>[38]</sup> whereas examples for acceptor properties of such deltahedral clusters are less frequent. Cluster aggregation through donor-acceptor interactions is not described as a general growth principle yet, even though observed. Upon the formation of  $[(\eta^4\text{-Ge}_9)\text{-Cu}-(\eta^1\text{-Ge}_9)]^{7-}$ , the  $\text{PR}_3$  ligand of known  $[(\eta^4\text{-Ge}_9)\text{-Cu-PR}_3]^{3-}$  is replaced by a second  $[\text{Ge}_9]^{4-}$  cluster. The latter acts as a two-electron donor through the lone pair of one Ge atom.<sup>[12]</sup> Notice, the resulting  $[\text{Ge}_9\text{Cu}]^{3-}$  unit also corresponds to a 22-skeletal electron cluster with an acceptor function at the Cu atom.

**Supporting Information.** The Supporting Information contains experimental procedures and crystallographic and computational details.

CCDC 1514918 (**1**), CCDC 1514921 (**2**), and CCDC 1514920 (**3**) 1514919 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

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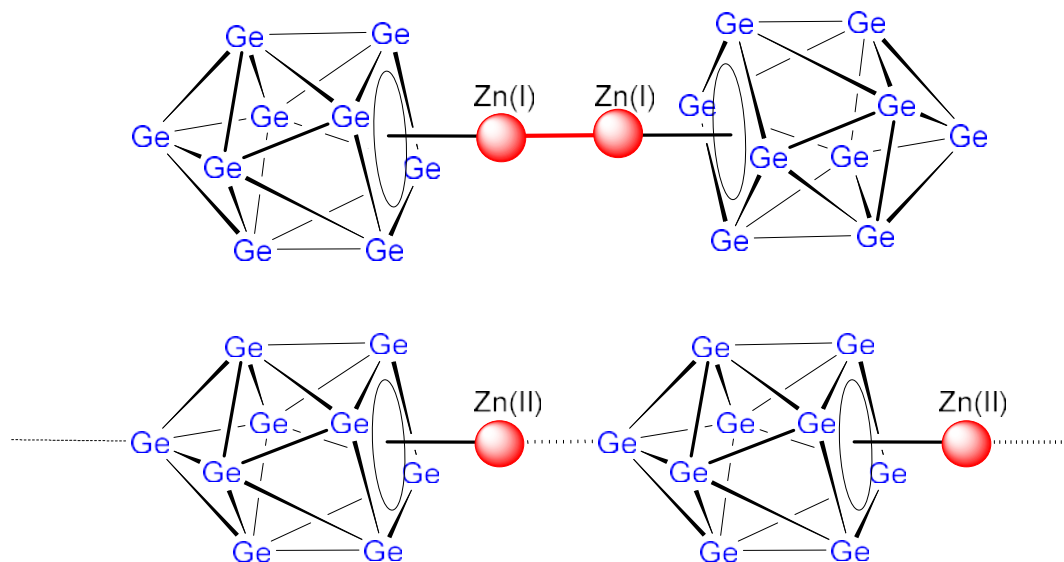
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## TOC

**Zn atoms serve for both.** Either covalent coupling at the Zn vertex atom or acting as a Lewis acid for the interaction with a Lewis base leads to novel Intermetalloid clusters.



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