

## Synthesis and Crystal Structure of a Salt Containing

# $\infty^1$ {Zn[*trans*- $\mu_2(\eta^3:\eta^3\text{-Ge}_9)$ ]}<sup>2-</sup> Anions – A new Polymer with Ge<sub>9</sub> Zintl Clusters Bridged by Zn Atoms

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Zintl ion – Germanium – Zinc – Cluster compounds – Polymer – Crystal structure

## Abstract:

The reaction of an ethylenediamine (en) solution of  $K_4Ge_9$  with  $Zn_2(Mesnacnac)_2$  ( $Mesnacnac = [(2,4,6-Me_3C_6H_2)NC(Me)]_2CH$ ) in the presence of [18]crown-6 ([18]crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) leads to the formation of the new compound  $[K([18]crown-6)]_2\{Zn[trans-\mu_2(\eta^3:\eta^3-Ge_9)]\}(en)$ . A single crystal structure determination reveals that the salt contains  ${}^\infty [Zn(Ge_9)]^{2-}$  polyanions in which each Zn atom bridges two  $Ge_9$  clusters by coordinating to opposite triangular faces of the  $Ge_9$  deltahedra. The polymeric chain can formally be described as a *trans*-Zn(II) complex with two  $[\eta^3:\eta^3-Ge_9]^{4-}$  ligands.  ${}^1H$  NMR spectroscopic investigations indicate that the protonation of the  $Mesnacnac^-$  ligand by the solvent ethylenediamine plays a crucial role in the disproportionation of the Zn(I) starting material and thus in the formation of the polymeric Zn(II) complex. In contrast, the reaction of  $ZnPh_2$  instead of  $Zn_2(Mesnacnac)_2$  under the same conditions leads to the known complex  $[PhZn(\eta^4-Ge_9)]^{3-}$ .

## Introduction

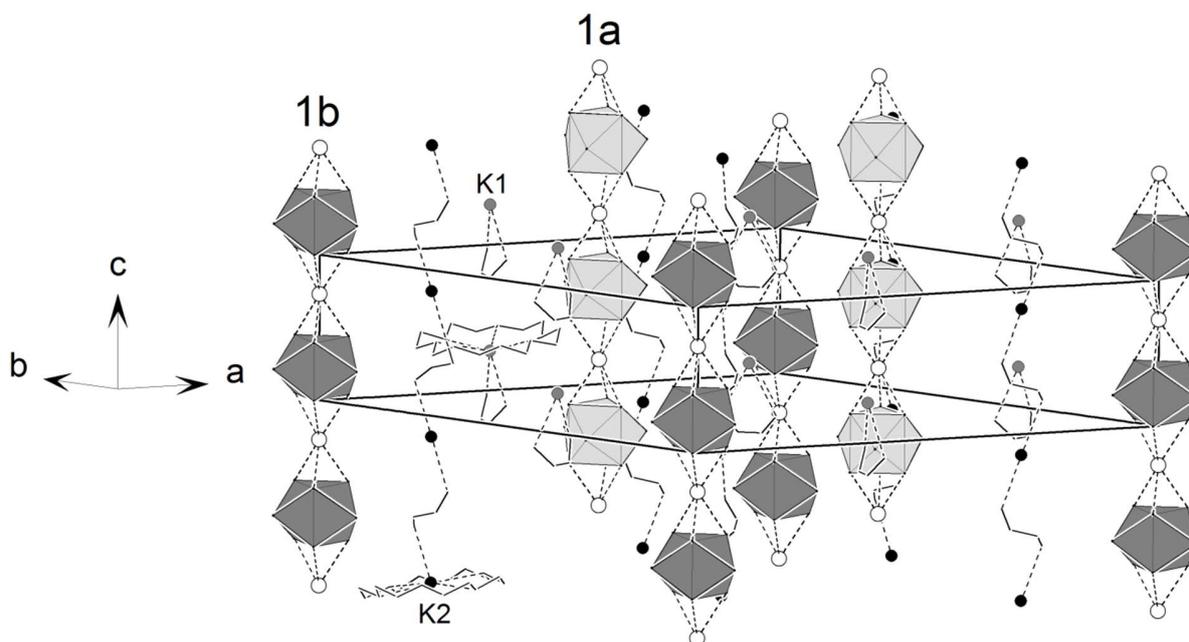
A huge number of different reactions with deltahedral homoatomic group 14 Zintl cluster compounds have been reported up to date. Beside the crystallization of solvates of the  $[E_9]^{4-}$  clusters ( $E = Si-Pb$ ), confirming the existence of these clusters in solid phases, the self-condensation especially of the  $Ge_9$  cluster has been observed in the dimeric  $[Ge_9-Ge_9]^{6-}$  [1-4], trimeric  $[Ge_9=Ge_9=Ge_9]^{6-}$  [5-6], tetrameric  $[Ge_9=Ge_9=Ge_9=Ge_9]^{8-}$ , [7-8] and polymeric  ${}^\infty [Ge_9]^{2-}$  units. [9-10] The very first reaction of Zintl clusters in solution with transition metal complexes was reported by Eichhorn.  $[Sn_9]^{4-}$  was found to replace the Mes ligand ( $Mes = 2,4,6-Me_3C_6H_2$ ) in the complex  $Cr(CO)_3(Mes)$ , yielding the first isolated "cluster complex"  $[Sn_9Cr(CO)_3]^{4-}$ . [11] Up to date a huge number of reactions in solution of deltahedral Zintl ions with a variety of transition metal complexes and main group compounds have been performed, and the results have been summarized in several review articles. [12-16] Whereas disproportionation plays a dominant role in the reaction of the heavier homologues  $[E_9]^{4-}$  ( $E = Sn, Pb$ ), numerous examples of group 11 metal complexes have been reported in which  $Ge_9$  clusters serve as ligands. The examples include  $[Ge_9-CuPR_3]^{3-}$  with  $R = isopropyl (iPr)$  and cyclohexyl (Cy),  $[Ge_9-Cu(Ge_9)]^{7-}$  [17],  $[Ge_9Au_3Ge_9]^{5-}$  [18],  $[M(Ge_9R_3)_2]^-$  with  $M = Cu, Ag, Au$  [19-20] and  $[M(Ge_9R_3)_2]$  with  $M = Zn, Cd, Hg$  and  $R = Si(SiMe_3)_3$ , [21] and the giant 45 atom cluster  $[Ge_{45}]^{12-}$  which consists of five connected  $Ge_9$  cluster that coordinate to three  $Au^+$  ions. [22] In all cases metal organic compounds such as  $CuMes$ ,  $Cu(PR_3)Cl$  ( $R = iPr, Cy, Ph$ ) and  $Au(PPh_3)Cl$  were found to be very reactive

starting materials. For the formation of group 12 metal complexes, solutions of  $K_4Ge_9$  in ethylenediamine have been reacted with  $ZnPh_2$  to form  $[PhZn(\eta^4-Ge_9)]^{3-}$ .<sup>[23]</sup> For this reaction the reductive cleavage of a phenyl group from  $ZnPh_2$ , the formation of the anion  $(C_6H_5)^-$  and its protonation by ethylenediamine has been postulated. The presence of benzene was confirmed by  $^1H$  NMR spectroscopy.<sup>[24]</sup> The fragment  $[ZnPh]^+$  coordinates to the open square face of a mono-capped square antiprism  $[E_9]^{4-}$ .<sup>[23]</sup> The derivatives  $ZnR_2$  with  $R = iPr$  and  $Mes$  similarly react with  $K_4Ge_9$  solutions to form  $[RZn(\eta^4-Ge_9)]^{3-}$ .<sup>[25]</sup>

In order to get a deeper insight in the reactivity of  $[Ge_9]^{4-}$  clusters, we investigated reactions with Zn(I) compounds containing a  $[Zn-Zn]^{2+}$  unit and chose  $Zn_2(Mesnacnac)_2$  as a precursor.<sup>[26-36]</sup>

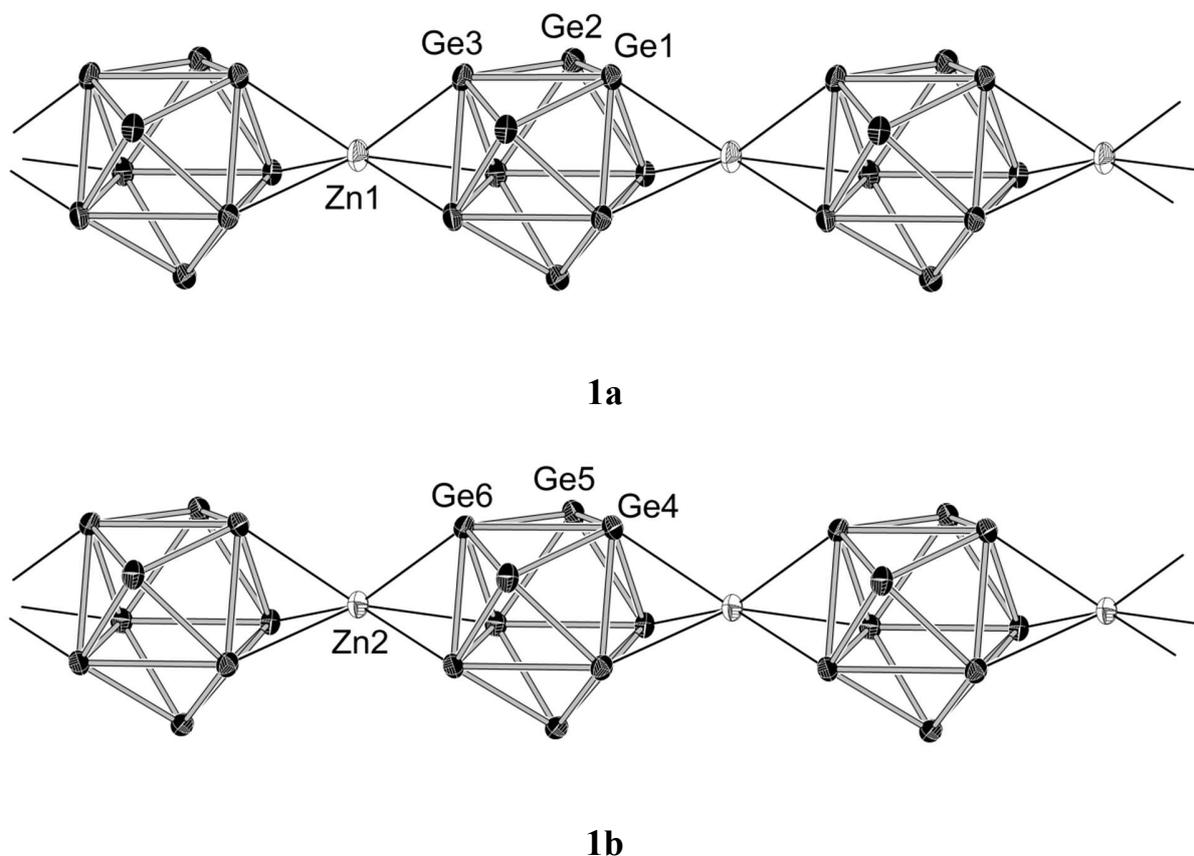
## Results

The reaction of  $K_4Ge_9$  in ethylenediamine with  $Zn_2(Mesnacnac)_2$  leads to the novel polymeric anion  ${}^1_{\infty}\{Zn[trans-\mu_2(\eta^3:\eta^3-Ge_9)]\}^{2-}$  which was obtained in form of  $[K([18]crown-6)]_2\{Zn[trans-\mu_2(\eta^3:\eta^3-Ge_9)]\}(en)$  (**1**). Compound **1** crystallizes in the trigonal space group  $P3_1m$  (no. 157). The unit cell consists of three  $Ge_9$  clusters (two clusters **1a** with Ge1, Ge2 and Ge3, each at Wyckoff site  $6d$ , and one cluster **1b** with Ge4, Ge5 and Ge6 each at Wyckoff site  $3c$ ), three zinc atoms (2 x Zn1, each at  $1a$ , and 1 x Zn2 at Wyckoff site  $2b$ ) and six potassium atoms (K1 and K2 at Wyckoff site  $3c$ ) each sequestered by [18]crown-6 molecules. Ethylenediamine molecules (en) act either as chelating ligands ( $\eta^2$ ) as in the case of K1 or link two potassium atoms as in the case of K2 which is further sequestered by [18]crown-6. Figure 1 illustrates the unit cell consisting of strands of  ${}^1[K([18]crown-6)(\eta^1:\eta^1-en)]^+$  and  ${}^1_{\infty}\{Zn[trans-\mu_2(\eta^3:\eta^3-Ge_9)]\}^{2-}$  which are orientated parallel to the crystallographic  $c$  axis.



**Figure 1.** Extended unit cell of compound **1** with emphasis on the chains of  ${}^1_{\infty}[\text{K}([\text{18}]\text{crown-6})(\eta^1:\eta^1\text{-en})]^+$  and  ${}^1_{\infty}\{\text{Zn}[\text{trans-}\mu_2(\eta^3:\eta^3\text{-Ge}_9)]\}^{2-}$  along the crystallographic  $c$  axis.  $\text{Ge}_9$  clusters are drawn as polyhedra (grey for **1a** and dark grey for **1b**), Zn atoms are depicted as white balls. K1 and K2 are drawn as grey and black balls, respectively. [18]Crown-6 and ethylenediamine molecules are drawn as wire-and-stick model. For clarity only two [18]crown-6 molecules that coordinate to K1 and K2 atoms are shown. H atoms are omitted.

In the polymeric anions  ${}^1_{\infty}\{\text{Zn}[\text{trans-}\mu_2(\eta^3:\eta^3\text{-Ge}_9)]\}^{2-}$  (**1a** and **1b**) the Zn atoms are located at a threefold rotation axis and are coordinated each by two opposite deltahedral faces of two  $\text{Ge}_9$  polyhedra. The  $\text{Ge}_9$  clusters fully adopt a three-fold symmetry. The Zn atom is linearly coordinated by two  $\text{Ge}_9$  clusters with respect to the center of gravity of the neighboring  $\text{Ge}_9$  clusters ( $180^\circ$  in **1a** and **1b**), and *vice versa* the clusters are linearly coordinated by two Zn atoms through two coplanar opposite triangular faces. Thus, the structure of clusters **1a** and **1b** can be described as tricapped trigonal prisms with perfect  $D_{3h}$  symmetry (Figure 2).



**Figure 2.** Section of the molecular structure of the linear strands  ${}^1_{\infty} \{ \text{Zn}[\text{trans-}\mu_2(\eta^3:\eta^3\text{-Ge}_9)] \}^{2-}$  **1a** and **1b**. The displacement ellipsoids of the atoms are drawn at the 50 % probability level at 100 K. Selected bond lengths (Å) and angles (deg). **1a**: Ge1-Ge1 2.710(1), Ge1-Ge2 2.568(1), Ge1-Ge3 2.943(1), Ge2-Ge3 2.580(1), Ge3-Ge3 2.684(1), Zn1-Ge1 2.704(1), Zn1-Ge3 2.711(1); Ge1-Ge1-Ge1 60.0, Ge3-Ge3-Ge3 60.0, Ge1-Ge1-Zn1 59.93(1), Ge3-Ge3-Zn1 60.34(1), Ge1-Zn1-Ge1 60.15(3), Ge3-Zn1-Ge3 59.32(3). **1b**: Ge4-Ge4 2.713(1), Ge4-Ge5 2.564(1), Ge4-Ge6 2.927(1), Ge5-Ge6 2.572(1), Ge6-Ge6 2.693(1), Zn2-Ge4 2.716, Zn2-Ge6 2.717(1); Ge4-Ge4-Ge4 60.0, Ge6-Ge6-Ge6 60.0, Ge4-Ge4-Zn2 60.03(2), Ge6-Ge6-Zn2 60.29(2), Ge4-Zn2-Ge4 59.94(4), Ge6-Zn2-Ge6 59.42(4).

Since the atoms Ge1 and Ge3 of **1a** as well as Ge4 and Ge6 of **1b** are situated around the crystallographic  $C_3$  rotation axis, perfect trigonal prisms are formed, which, together with the capping atoms of the rectangular prism faces Ge2 and Ge5, respectively, leads to  $\text{Ge}_9$  clusters with perfect  $D_{3h}$  symmetry (Figure 2). The prism heights  $h$  are rather similar with 2.943(1) Å (Ge1-Ge3) in **1a** and 2.927(1) Å (Ge4-Ge6) in **1b** and reflect the longest Ge-Ge bonds. The Ge-Ge distances within the trigonal faces of  $d(\text{Ge1-Ge1}) = 2.710(1)$  Å and  $d(\text{Ge3-Ge3}) = 2.684(1)$  Å in **1a** and  $d(\text{Ge4-Ge4}) = 2.713(1)$  Å and  $d(\text{Ge6-Ge6}) = 2.693(1)$  Å in **1b** are significantly longer than the Ge-Ge bonds of the non-coordinating Ge atoms (2.568(1) Å for Ge1-Ge2 and 2.580(1) Å for Ge2-Ge3 in **1a** and 2.564(1) Å for Ge4-Ge5 and 2.572(1) Å for Ge5-Ge6 in **1b**). In the Zn-

bridged molecule  $[(\eta^3\text{-Ge}_9\text{R}_3)\text{Zn}(\eta^3\text{-Ge}_9\text{R}_3)]$  in which the capping Ge atoms are bound to silyl groups ( $R = \text{Si}(\text{SiMe}_3)_3$ ) considerably longer Ge-Ge bonds of 2.868 Å 2.947 Å are observed within the coordinating  $\text{Ge}_3$  triangle. [21]

In Table 1 typical structural parameters of  $\text{Ge}_9$  cluster with almost perfect  $D_{3h}$  symmetry are compared. The 20 skeletal electron (SE) cluster  $[\text{Ge}_9]^{2-}$  in  $[\text{K}([2.2.2]\text{crypt})]_2[\text{Ge}_9]$  which according to Wade rules posses a  $D_{3h}$  symmetric tri-capped trigonal prismatic structure exhibits mean prism height ( $h_{\text{mean}}$ ) of 2.72 Å and coplanar opposite triangular faces of the trigonal prism ( $\gamma = 0^\circ$ ). [38] The 22 SE  $\text{Ge}_9$  clusters **1a** and **1b** posses also  $D_{3h}$  symmetric tri-capped trigonal prismatic structure however with larger values  $h_{\text{mean}} = 2.94$  and 2.93 Å, respectively. This is in agreement with the observation that the  $D_{3h}$  symmetric structure may appear instead of the expected  $C_{4v}$  symmetric mono-capped square anti prismatic nido-structure in which the LUMO - that is anti-bonding along the prism heights of the 20 SE cluster - is occupied. [39] [40-41] Interestingly compare the lengths of the base of trigonal prism  $e$  in **1a** und **1b** with coordination to Zn atoms well to the lengths in  $[\text{Ge}_9]^{2-}$ .

**Table 1.** Structural parameters of the  $\text{Ge}_9$  clusters **1a** and **1b** in compound **1** and of  $[\text{Ge}_9]^{2-}$  [38],  $h$ : height of the prism,  $e$ : length of the base of the trigonal prism,  $c$ : distance to the capping Ge atoms,  $\gamma$ : deviation from coplanarity of opposite triangular faces of the trigonal prism. [39]

Cluster	$h/\text{Å}$	$e/\text{Å}$	$c/\text{Å}$	$\gamma/\text{deg}$	$h/e$	$h/c$
<b>1a</b>	2.943(1)	2.684(1) 2.710(1)	2.568(1) 2.580(1)	0	1.09	1.14
<b>1b</b>	2.927(1)	2.693(1) 2.713(1)	2.564(1) 2.572(1)	0	1.08	1.14
$[\text{Ge}_9]^{2-}$ [38]	2.710(13) 2.733(14)	2.731(3) 2.759(3)	2.533(2) 2.588(5)	0.5	0.99	1.06

The Zn-Ge distances in compound **1** range from 2.704(1) Å (Ge1-Zn1) to 2.717(1) Å (Ge6-Zn2) and are slightly longer than the Zn-Ge contacts in  $[(\eta^3\text{-Ge}_4)\text{Zn}(\eta^3\text{-Ge}_4)]^{6-}$  and  $[(\eta^3\text{-Ge}_4)\text{Zn}(\eta^2\text{-Ge}_4)]^{6-}$  in  $\text{Cs}_6\text{Ge}_8\text{Zn}$  [42] and  $\text{K}_{14}\text{ZnGe}_{16}$  [43] with mean distances of 2.664 Å and 2.604 Å, respectively. The bond angles in the  $\text{Ge}_3\text{Zn}$  tetrahedra are close to  $60^\circ$ , which is reasonable due to the rather similar Ge-Ge and Zn-Ge bond lengths.

## Discussion

Reactions of deltahedral nine-atomic Zintl clusters with Zn(II) organyls  $ZnR_2$  ( $R = iPr, Ph, Mes$ ) lead to monomeric *closo*-clusters of the type  $[(\eta^4-Ge_9)-ZnR]^{3-}$ .<sup>[23, 25, 44]</sup> In contrast, the reaction of elemental mercury leads to the polymeric anion  ${}_{\infty}^1[Hg(Ge_9)]^{2-}$  with Hg linking the  $Ge_9$  clusters,<sup>[37, 45-46]</sup> and the reaction with  $HgPh_2$  yields oligomeric units  $[Hg_3(\eta^1:\eta^2-Ge_9)_4]^{10-}$ .<sup>[45]</sup> Remarkably, Hg- $Ge_9$  interactions in these complexes slightly differ. The Hg atoms in  $[K([2.2]crypt)]_2[Hg(\eta^1:\eta^1-Ge_9)](dmf)$  are linearly coordinated by two  $Ge_9$  cluster via one Ge atom.<sup>[46]</sup> In contrast, additional longer Hg-Ge bonds appear in the oligomer  $[Hg_3(\eta^1:\eta^2-Ge_9)_4]^{10-}$  as observed in  $[K([2.2.2]crypt)]_{10}[Hg_3(Ge_9)_4](en)_2(tol)_2$ <sup>[45]</sup> as well as in the polymer  ${}_{\infty}^1[Hg(\eta^1:\eta^3-Ge_9)]^{2-}$  as found in  $[K([2.2.2]crypt)]_2[Hg(Ge_9)](en)$ .<sup>[37]</sup> The coordination of the Hg atom to nearest Ge atoms deviate from linearity by forming additional bonds to other Ge atoms of a deltahedral cluster face, leading to slightly elongated Hg-Ge bonds.  $\eta^3$ -coordination is also favored when the threefold-substituted  $[Ge_9R_3]^-$  clusters with the bulky ligand  $R = Si(SiMe_3)_3$  are connected by bridging atoms  $M^+ = Cu, Ag, Au$  and  $M^{2+} = Zn, Cd, Hg$  as observed in compounds of the type  $[(\eta^3-Ge_9R_3)(M^{n+})(\eta^3-Ge_9R_3)]^{(2-n)-}$ .<sup>[19-21]</sup>

In contrast to the formation of Cd(I) complexes  $[(\eta^4-Pb_9)Cd-Cd(\eta^4-Pb_9)]^{6-}$  with a formal  $[Cd-Cd]^{2+}$  unit originating from the reduction of a Cd(II) organometallic compound<sup>[47]</sup>, we did not observe the formation of a corresponding Zintl ion complex with an analogous  $[Zn-Zn]^{2+}$  unit. Instead, the formation of a dark precipitate during the dissolution of  $Zn_2(Mesnacnac)_2$  in ethylenediamine hinted to a disproportionation of the  $[Zn-Zn]^{2+}$  unit of the starting material to  $Zn^0 / Zn^{2+}$ . The  $^1H$  NMR spectrum and the powder X-ray diffraction pattern of the solid residue of the reaction revealed the presence of undissolved  $Zn_2(Mesnacnac)_2$  (Supporting Information, Figure S3 and S4), whereas crystalline Zn powder could not be detected. In addition to the signals of  $Zn_2(Mesnacnac)_2$ , resonances of small amounts of  $MesnacnacH$  were found in the  $^1H$  NMR spectrum (Figure S4b) of the extract of the residue, clearly indicating that the Zn(I) complex was at least partially protonated. Reactions of  $Zn_2(Mesnacnac)_2$  with different H-acidic reagents showed that the first protonation reaction with formation of  $[Zn_2(Mesnacnac)]^+$  monocation, which unfortunately could not be isolated, to date, occurs relatively fast at temperatures as low as  $-30$  °C, whereas the second protonation reaction typically requires higher reaction temperatures and elongated reaction times.<sup>[55]</sup> Most likely, ethylenediamine acted as the proton donor which is already known from the vinylation reactions of  $E_9$  clusters ( $E = Ge, Sn$ ) with bis(trimethylsilyl)acetylene in ethylenediamine.<sup>[48-50]</sup> In strongly coordinating solvents such

as ethylenediamine MesnacnacH might leave the  $[\text{Zn-Zn}]^{2+}$  unit. The resulting monocation  $[\text{Zn}_2(\text{Mesnacnac})]^+$  may then cause the disproportionation of the  $[\text{Zn-Zn}]^{2+}$  unit at a rate that allows for the reaction of the formed  $\text{Zn}^{2+}$  ions with the  $[\text{Ge}_9]^{4-}$  clusters. Solutions of  $\text{Zn}_2(\text{Mesnacnac})_2$  in organic solvents such as hexane or  $\text{Et}_2\text{O}$  are stable towards disproportionation reaction even at elevated temperatures up to 60 °C. We therefore believe that the protonation of  $\text{Zn}_2(\text{Mesnacnac})_2$  in ethylenediamine with subsequent formation of the monocation  $[\text{Zn}_2(\text{Mesnacnac})]^+$  followed by a disproportionation to Zn(0) and Zn(II), is the rate limiting step for the formation of Zn(II) species. Since a control experiment under identical conditions using  $\text{ZnPh}_2$  led to the formation of  $[\text{PhZn}(\eta^4\text{-Ge}_9)]^{3-}$ , we assume that the  $\text{Zn}^{2+}$  concentration is the key point for a controlled reaction of  $[\text{Ge}_9]^{4-}$  with  $\text{Zn}^{2+}$  and the formation of compound **1**. In the case of  $\text{Zn}_2(\text{Mesnacnac})_2$  the ligand can easily be removed by protonation. In contrast, in  $\text{ZnPh}_2$  a reductive cleavage of  $\text{Ph}^-$  is necessary for the subsequent reaction with Zintl anions.  $^1\text{H}$  NMR studies of a mixture of  $\text{Zn}_2(\text{Mesnacnac})_2$  and ethylenediamine confirm the protonation of  $\text{Mesnacnac}^-$  to MesnacnacH and the deprotonation of ethylenediamine (see Supporting Information, Figure S5). In a further experiment the acidic character of ethylenediamine with respect to the ligand was confirmed by the formation of  $\text{Cp}^*\text{H}$  when  $\text{ZnCp}^*_2$  is treated with ethylenediamine (Figure S6). Additional experiments of Zn(I) complexes with the  $[\text{Ge}_9]^{4-}$  clusters will be performed using different Zn(I) complexes in order to clarify both the role of the Zn(I) species as well as the assumed protonation reaction of the organic substituent on the reaction rate.

**Table 3:** Selected crystallographic and refinement data for compound **1**.

<b>Compound:</b>	<b>1</b>
Empirical formula	C <sub>28</sub> H <sub>56</sub> Ge <sub>9</sub> K <sub>2</sub> N <sub>4</sub> O <sub>12</sub> Zn
Formula weight / g·mol <sup>-1</sup>	1437.65
Temperature / K	100(2)
Crystal size / mm <sup>3</sup>	0.1 × 0.1 × 0.1
Crystal system	trigonal
Space group	<i>P</i> 3 <sub>1</sub> <i>m</i>
Unit cell dimensions / Å	<i>a</i> = 24.3239(2) <i>c</i> = 7.3728(1)
Volume / Å <sup>3</sup> , <i>Z</i>	3777.72(7), 3
Calculated density / g·cm <sup>-3</sup>	1.90
Absorption coefficient / mm <sup>-1</sup>	6.0
<i>F</i> (000) / <i>e</i>	2112
Θ-range / deg	2.90 – 27.50
Measured reflections	131059
Independent reflections	6021 [ <i>R</i> <sub>int</sub> = 0.0876]
Completeness / %	99.8
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameter	6021 / 1 / 280
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.908
<i>R</i> -indices [ <i>I</i> > 2 σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0312, <i>wR</i> <sub>2</sub> = 0.0647
<i>R</i> -indices for all data	<i>R</i> <sub>1</sub> = 0.0430, <i>wR</i> <sub>2</sub> = 0.0662
Largest diff. peak and hole / e·Å <sup>3</sup>	0.91 / -0.64

## Conclusion

The reaction of the binary Zintl phase K<sub>4</sub>Ge<sub>9</sub> with the Zn(I) complex Zn<sub>2</sub>(Mesnacnac)<sub>2</sub> in ethylenediamine at ambient temperature and layering of the reaction mixture with a toluene/[18]crown-6 solution yielded brown crystals of the compound [K([18]crown-6)]<sub>2</sub>{Zn[*trans*-μ<sub>2</sub>(η<sup>3</sup>:η<sup>3</sup>-Ge<sub>9</sub>)]}(en) (**1**) which contains strands of  $\frac{1}{\infty}$  {Zn[*trans*-μ<sub>2</sub>(η<sup>3</sup>:η<sup>3</sup>-Ge<sub>9</sub>)]}<sup>2-</sup> units. Due to the poor solubility of Zn<sub>2</sub>(Mesnacnac)<sub>2</sub> in ethylenediamine the major amount of the precursor was found in the residual solid as confirmed by <sup>1</sup>H NMR spectroscopy and powder X-ray diffraction after filtration of the reaction suspension. <sup>1</sup>H NMR spectroscopy also indicated

the protonation of the Mesnacnac<sup>-</sup> ligand by the solvent ethylenediamine. The disproportionation of the [Zn-Zn]<sup>2+</sup> unit to Zn<sup>2+</sup> and Zn<sup>0</sup> in ethylenediamine most probably adjusts the Zn<sup>2+</sup> concentration for an optimal formation of the {Zn[*trans*-μ<sub>2</sub>(η<sup>3</sup>:η<sup>3</sup>-Ge<sub>9</sub>)]}<sup>2-</sup> polymer. In contrast, the reaction of [Ge<sub>9</sub>]<sup>4-</sup> with ZnPh<sub>2</sub> in ethylenediamine led to the monomeric complex [PhZn(η<sup>4</sup>-Ge<sub>9</sub>)]<sup>3-</sup>.<sup>[23]</sup>

## Experimental Section

**General:** All manipulations and reactions were performed under a purified argon atmosphere, using standard Schlenk line and glove box techniques. The Zintl compound of the nominal composition K<sub>4</sub>Ge<sub>9</sub> was synthesized by heating (2 °C/min) a stoichiometric mixture of the elements K and Ge at 650 °C for 20 h in a stainless-steel tube and slowly cooling to room temperature with a rate of 1 °C/min. ZnCp\*<sub>2</sub>, Zn<sub>2</sub>(Mesnacnac)<sub>2</sub> and ZnPh<sub>2</sub> were synthesized according to literature methods.<sup>[51,52]</sup> Ethylenediamine (Merck) was distilled from calcium hydride and used immediately after collection. [18]crown-6 (Merck) was sublimed *in vacuo* at 80 °C. Toluene was dried using an MBraun solvent purification system.

**[K([18]crown-6)]<sub>2</sub>{Zn[*trans*-μ<sub>2</sub>(η<sup>3</sup>:η<sup>3</sup>-Ge<sub>9</sub>)]}(en), 1:** A solution of 49 mg K<sub>4</sub>Ge<sub>9</sub> (60 μmol) in 2 mL ethylenediamine was added via a syringe to a suspension of 96 mg Zn<sub>2</sub>(Mesnacnac)<sub>2</sub> (120 μmol) in 1 mL ethylenediamine, and the mixture was stirred for 12 h at 25 °C. After filtration of the dark-green suspension through a cannula packed with glass wool the filtrate was layered with a solution of 60 mg [18]crown-6 (230 μmol) in 4 mL toluene. The remaining residue after filtration was dried, weighted back (60 mg) and identified via <sup>1</sup>H NMR spectroscopy and P-XRD as the non-dissolved precursor Zn<sub>2</sub>(Mesnacnac)<sub>2</sub>. After two months dark-brown block-shaped crystals were isolated from the filtrate and characterized by single crystal X-ray diffraction. Semi-quantitative energy dispersive X-ray analysis (EDX) of a crystal of compound **1** confirmed its composition.

**[K([2.2.2]crypt)]<sub>3</sub>[PhZn(η<sup>4</sup>-Ge<sub>9</sub>)](en)<sub>2</sub>(tol), 2:** The synthesis was performed according to the procedure described in the literature.<sup>[23]</sup> 102 mg K<sub>4</sub>Ge<sub>9</sub> (126 μmol) and 170 mg [2.2.2]crypt (450 μmol, 3.6 eq) were dissolved in 3 mL of ethylenediamine and stirred for 5 min. Then 64 mg ZnPh<sub>2</sub> (290 μmol, 2.3 eq.) was added to this solution, and the mixture was stirred for 2 h at room temperature. After filtration, the filtrate was layered with 3 mL of toluene. Crystals of compound **2** were obtained after 1 d, and the identity was confirmed by a fast single crystal X-ray diffraction experiment.

**Single crystal structure determination:** The air- and moisture-sensitive crystals of **1** were transferred from the mother liquor into perfluoropolyalkyl ether oil inside a glove box. A single crystal was fixed on a glass capillary and positioned in a 100 K cold N<sub>2</sub> stream. Data collection at 100(2) K: Oxford-Diffraction Xcalibur3 diffractometer (MoK $\alpha$  radiation). The structure was solved by Direct Methods and refined by full-matrix least-squares calculations against  $F^2$  (SHELXL-97).<sup>[53]</sup> CCDC-123456 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Structure Refinement:** Two datasets of two individual crystals of compound **1** were collected at 150 K with an Oxford-Diffraction Xcalibur3 diffractometer. Both structure refinements showed a translation-disorder of the strands of the  $\frac{1}{\infty}\{\text{Zn}[\textit{trans}\text{-}\mu_2(\eta^3:\eta^3\text{-Ge}_9)]\}^{2-}$  units built by the Zn atom at Wyckoff site  $1a$  and the Ge atoms at Wyckoff site  $3c$  along the crystallographic  $c$  axis. Refinement of the data set did not give acceptable results. The measurement of a third crystal which had been performed at 100 K appeared without disorder, and a refinement of the structure led to reliable results. Due to the lack of reliable data at 150 K a probable disorder-order transition between 150 and 100 K could not yet be verified. In the final structure refinement the methylene carbon atoms of the en molecules coordinating to K2 in the strands of  $\frac{1}{\infty}[\text{K}([\text{18}]\text{crown-6})(\eta^1:\eta^1\text{-en})]^+$  have to be refined using two split positions.

**X-ray powder diffraction:** Phase analyses of K<sub>4</sub>Ge<sub>9</sub> and Zn<sub>2</sub>(Mesnacnac)<sub>2</sub> were performed using a Stoe STADI P diffractometer (Ge(111) monochromator; CuK $\alpha_1$  radiation) equipped with a linear position-sensitive detector (Mythen), measured in Debye-Scherrer mode. Data analysis was carried out using the Stoe WinXPOW software package.<sup>[54]</sup>

**NMR Spectroscopy:** The spectra were recorded with a Bruker Ultrashield400 Spectrometer and a Bruker AvanceIII400 FT-System (400 MHz, 64 scans, 298(2) K). Deuterated benzene was used as solvent and internal standard.

**EDX:** A JEOL-SEM 5900LV electron microscope equipped with a tungsten cathode was used for energy dispersive X-ray analytic.

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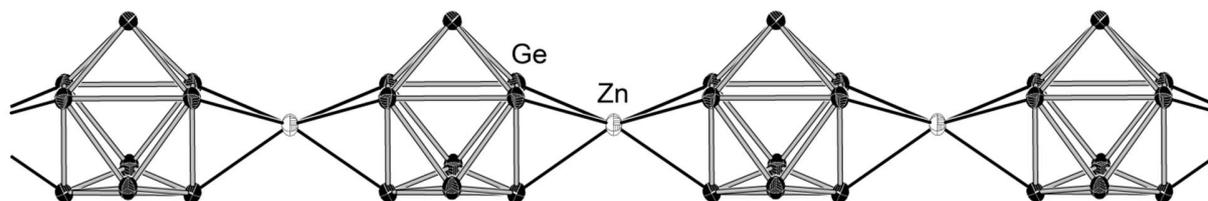
## Literature:

- [1] R. Hauptmann, T. F. Fässler, *Z. Kristallogr. NCS* **2003**, *218*, 461-463.
- [2] R. Hauptmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2266-2273.
- [3] A. Nienhaus, S. D. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1752-1758.
- [4] L. Xu, S. C. Sevov, *J. Am. Chem. Soc.* **1999**, *121*, 9245-9246.
- [5] L. Yong, S. D. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1149-1153.
- [6] A. Ugrinov, S. C. Sevov, *J. Am. Chem. Soc.* **2002**, *124*, 10990-10991.
- [7] L. Yong, S. D. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1977-1198.
- [8] A. Ugrinov, S. C. Sevov, *Inorg. Chem.* **2003**, *42*, 5789-5791.
- [9] C. Downie, J.-G. Mao, H. Parmar, A. M. Guloy, *Inorg. Chem.* **2004**, *43*, 1992-1997.
- [10] C. Downie, Z. Tang, A. M. Guloy, *Angew. Chem. Int. Ed.* **2000**, *39*, 337-340.
- [11] B. W. Eichhorn, R. C. Haushalter, W. T. Pennington, *J. Am. Chem. Soc.* **1988**, *110*, 8704-8706.
- [12] S. Scharfe, F. Kraus, S. Stegmaier, A. Schier, T. F. Fässler, *Angew. Chem. Int. Ed.* **2011**, *50*, 3630-3670.
- [13] S. Scharfe, T. F. Fässler, *Philosoph. Trans.* **2010**, *368*, 1265-1284.
- [14] J. D. Corbett, *Chem. Rev.* **1985**, *85*, 383-397.
- [15] S. C. Sevov, J. M. Goicoechea, *Organometallics* **2006**, *25*, 5678-5692.
- [16] T. F. Fässler (Ed.), *Zintl Phases: Principles and Recent Developments, Struct. Bond.* **2011**, *140*, Springer-Verlag, Heidelberg.
- [17] S. Scharfe, T. F. Fässler, *Eur. J. Inorg. Chem.* **2010**, 1207-1213.
- [18] A. Spiekermann, S. D. Hoffmann, F. Kraus, T. F. Fässler, *Angew. Chem. Int. Ed.* **2007**, *46*, 1638-1640.
- [19] C. Schenk, F. Henke, G. Santiso-Quinones, I. Krossing, A. Schnepf, *Dalton Trans.* **2008**, 4436-4441.
- [20] C. Schenk, A. Schnepf, *Angew. Chem. Int. Ed.* **2007**, *46*, 5314-5316.
- [21] F. Henke, C. Schenk, A. Schnepf, *Dalton Trans.* **2009**, 9141-9145.
- [22] A. Spiekermann, S. D. Hoffmann, T. F. Fässler, I. Krossing, U. Preiss, *Angew. Chem. Int. Ed.* **2007**, *46*, 5310-5313.
- [23] J. M. Goicoechea, S. C. Sevov, *Organometallics* **2006**, *25*, 4530-4536.
- [24] A. Ugrinov, S. C. Sevov, *J. Am. Chem. Soc.* **2003**, *125*, 14059-14064.
- [25] B. Zhou, M. S. Denning, C. Jones, J. M. Goicoechea, *Dalton Trans.* **2009**, 1571-1578.
- [26] A. Gorrane, I. Resa, A. Rodriguez, E. Carmona, E. Alvarez, E. Gutierrez-Puebla, A. Monge, A. Galindo, D. del Río, R. A. Andersen, *J. Am. Chem. Soc.* **2006**, *129*, 693-703.
- [27] Y. Wang, B. Quillian, P. Wei, H. Wang, X.-J. Yang, Y. Xie, R. B. King, P. v. R. Schleyer, H. F. Schaefer, G. H. Robinson, *J. Am. Chem. Soc.* **2005**, *127*, 11944-11945.
- [28] Z. Zhu, M. Brynda, R. J. Wright, R. C. Fischer, W. A. Merrill, E. Rivard, R. Wolf, J. C. Fettinger, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2007**, *129*, 10847-10857.
- [29] Z. Zhu, R. J. Wright, M. M. Olmstead, E. Rivard, M. Brynda, P. P. Power, *Angew. Chem. Int. Ed.* **2006**, *45*, 5807-5810.
- [30] I. L. Fedushkin, A. A. Skatova, S. Y. Ketkov, O. V. Eremenko, A. V. Piskunov, G. K. Fukin, *Angew. Chem. Int. Ed.* **2007**, *46*, 4302-4305.
- [31] X.-J. Yang, J. Yu, Y. Liu, Y. Xie, H. F. Schaefer, Y. Liang, B. Wu, *Chem. Commun.* **2007**, *0*, 2363-2365.
- [32] S. Schulz, D. Schuchmann, U. Westphal, M. Bolte, *Organometallics* **2009**, *28*, 1590-1592.

- [33] S. Schulz, S. Gondzik, D. Schuchmann, U. Westphal, L. Dobrzycki, R. Boese, S. Harder, *Chem. Commun.* **2010**, 46, 7757-7759.
- [34] S. Gondzik, D. Bläser, C. Wölper, S. Schulz, *Chem. Eur. J.* **2010**, 16, 13599-13602.
- [35] T. Li, S. Schulz, P. W. Roesky, *Chem. Soc. Rev.* **2012**, 41, 3759-3771.
- [36] I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Science* **2004**, 305, 1136-1138.
- [37] A. Nienhaus, R. Hauptmann, T. F. Fässler, *Angew. Chem.* **2002**, 114, 3352-3355.
- [38] J. Åkerstedt, S. Ponou, L. Kloo, S. Lidin, *Eur. J. Inorg. Chem.* **2011**, 3999-4005.
- [39] T. F. Fässler, *Coord. Chem. Rev.* **2001**, 215, 347-377.
- [40] K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, 18, 1-66.
- [41] K. Wade, *Inorg. Nucl. Chem. Lett.* **1972**, 8, 559-562.
- [42] V. Queneau, S. C. Sevov, *J. Am. Chem. Soc.* **1997**, 119, 8109-8110.
- [43] S. Stegmaier, M. Waibel, A. Henze, L.-A. Jantke, A. J. Karttunen, T. F. Fässler, *J. Am. Chem. Soc.* **2012**, 134, 14450-14460.
- [44] B. Zhou, M. S. Denning, T. A. D. Chapman, J. M. Goicoechea, *Inorg. Chem.* **2009**, 48, 2899-2907.
- [45] M. S. Denning, J. M. Goicoechea, *Dalton Trans.* **2008**, 5882-5885.
- [46] M. B. Boeddinghaus, S. D. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2007**, 633, 2338-2341.
- [47] B. Zhou, M. S. Denning, T. A. D. Chapman, J. E. McGrady, J. M. Goicoechea, *Chem. Commun.* **2009**, 7221-7223.
- [48] M. W. Hull, S. C. Sevov, *Inorg. Chem.* **2007**, 26, 10953-10955.
- [49] M. W. Hull, S. C. Sevov, *J. Am. Chem. Soc.* **2009**, 131, 9026-9037.
- [50] C. B. Benda, J. Q. Wang, B. Wahl, T. F. Fässler, *Eur. J. Inorg. Chem.* **2011**, 4262-4269.
- [51] S. Schulz, D. Schuchmann, U. Westphal, M. Bolte, *Organometallics* **2009**, 28, 1590-1592.
- [52] N. I. Sheverdina, K. A. Kocheshkov, N. A. Zaitseva, I. E. Paleeva, *Doklady Akademii Nauk Sssr* **1964**, 155, 623.
- [53] *SHELXTL, Bruker Analytical X-ray instruments: Madison, WI 1998.*
- [54] *STOE/WinXPow, Version 2.08, STOE & Cie GmbH, Darmstadt 2003*
- [55] S. Schulz, R. Schäper, S. Gondzik, *unpublished results.*

## Table of Contents:

By the reaction of the binary Zintl phase  $K_4Ge_9$  with  $Zn_2(Mesnacnac)_2$  in ethylenediamine (en) crystals of the compound  $[K([18]crown-6)]_2\{Zn[trans-\mu_2(\eta^3:\eta^3-Ge_9)]\}(en)$  were obtained containing strands of  ${}^\infty_1\{Zn[trans-\mu_2(\eta^3:\eta^3-Ge_9)]\}^{2-}$  units in which Zn atoms connect  $Ge_9$  clusters in a  $\eta^3$ -fashion.



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