We have provided strong evidence that the GGGX motif described for some lipases not only plays a role in stabilizing the tetrahedral intermediate during catalysis, but also governs activity towards TAs. With the exception of GCL, all tested esterases and lipases bearing the GGGX motif hydrolyzed the model acetates. In the case of GCL, we assume that this lipase will accept other TAEs.

The overall amino acid sequence similarity between these hydrolases originating from bacteria, yeast, and mammalian sources is rather low and only small regions around the GGGX motif and the active serine residue are conserved. This structure dissimilarity is also reflected by the large differences between the substrates normally accepted by these hydrolases,[15] which means, in turn, that knowledge about their usual biocatalytic activity would not suggest that these enzymes would have activity towards TAs in common.

Furthermore, our computer model also allows the prediction of mutants with enhanced or even inverse stereoselectivity in the resolution of the model acetates of TAs.[16]

### *Experimental Section*

All experimental details can be found in the Supporting Information.

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# $_{\infty}^{1}$[HgGe$_9$]$^{2-}$—A Polymer with Zintl Ions as Building Blocks Covalently Linked by Heteroatoms[**]

Anke Nienhaus, Ralf Hauptmann, and
Thomas F. Fässler[*]

*Dedicated to Professor Dr. Gottfried Huttner on the occasion of his 65th birthday*

Homoatomic-element polyhedra of the type $E_n^{x-}$ (E = Group 14 element) are promising candidates for the formation of complex structures with interesting electronic properties. The polyhedra $E_n$ are stable with different charges so they can be employed as electron reservoirs and suitable coupling of the clusters can lead to unexpected properties. The alkali-metal fulleride phases are a particularly impressive example of this. They contain $C_{60}^{3-}$ ions and become superconducting at relatively high critical temperatures.[1] The structural characterizations of the linear polymer anions with $C_{70}$[2] and $Ge_9$[3] as building blocks show new possibilities for obtaining complex structures by covalent linking of the polyhedra. Recently we have pointed out parallels between fullerides and homoatomic polyhedra of the heavier elements of Group 14, the latter are known as Zintl ions.[4] Such homoatomic Zintl ions have been known since 1891 when there formation by dissolving elementary tin or lead in a solution of sodium in liquid ammonia was reported,[5] however, there is still little known about their chemical reactivity.[6]

During our examinations of semiconductors and metal clusters as building blocks for ordered structures, we successfully coupled $Ge_9$ clusters with Hg atoms for the first time.[7] The compound $[K(crypt)]_2[HgGe_9](en)_2$ (**1**) can be prepared by the reaction of a solution of the binary alloy $K_4Ge_9$ in ethylenediamine (en) with elementary mercury in the presence of [2.2.2]cryptand (crypt).[8] As expected the Hg atoms appear as bridges between the $E_9$ clusters forming a linear polymer of the composition $_{\infty}^{1}[HgGe_9]$.

Single-crystal structure determination of **1** shows that the Hg atoms are connected to two Ge atoms situated opposite of the open rectangular face of the $Ge_9$ cluster.[9] The shortest Hg–Ge separations (Figure 1) are 2.543(1) Å (Hg−Ge3) and 2.606(1) Å (Hg−Ge4). There are significantly longer separations from the Hg atom to two more sets of Ge atoms 3.049(1) Å (Hg−Ge5) and 3.120(1) Å (Hg−Ge6) as well as 4.096(1) Å (Hg−Ge7) and 4.043(1) Å (Hg−Ge8). The shorter distances to the atoms Ge5 and Ge6 means that the $Ge_9$ cluster is tilted with respect to the Hg–Hg vector.

The bond angle Ge3-Hg-Ge4 is 172.2(3)° and points to a coordination number of two for the Hg atom and thus to a covalent interaction between Hg and the Ge atoms. The

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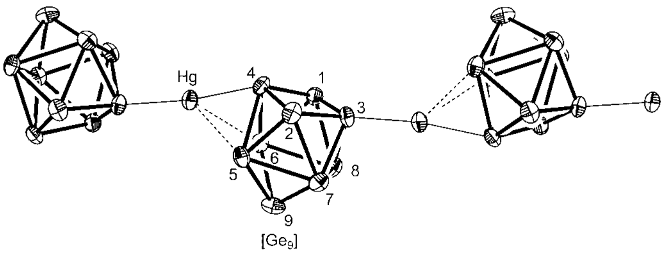

Figure 1. Section of the molecular structure of the linear polymer ${}^{1}_{\infty}[HgGe_9]$ in **1** (thermal ellipsoids set at 50 % probability). Interatomic distances [Å]: Ge1-Ge3 2.555(2), Ge1-Ge4 2.583(1), Ge1-Ge6 2.550(1), Ge1-Ge8 2.682(1), Ge2-Ge3 2.555(1), Ge2-Ge4 2.575(2), Ge2-Ge5 2.537(1), Ge2-Ge7 2.643(1), Ge3-Ge7 2.606(1), Ge3-Ge8 2.590(1), Ge4-Ge5 2.726(1), Ge4-Ge6 2.725(1), Ge5-Ge6 2.904(1), Ge5-Ge7 2.750(1), Ge5-Ge9 2.560(1), Ge6-Ge8 2.756(1), Ge6-Ge9 2.567(1), Ge7-Ge8 2.776(1), Ge7-Ge9 2.589(1), Ge8-Ge9 2.587(1), Hg-Ge3 2.543(1), Hg-Ge4 2.606(1).

shortest Ge–Hg separations are in the range of the sum of covalent radii which again indicate a covalent bond ($r_{Hg} = 1.30$ Å, $r_{Ge} = 1.22$ Å).[10] Comparable bond parameters are observed in the organometallic compound $Ph_3Ge$-Hg-$GePh_3$ with Ge–Hg separations of 2.543(1) and 2.514(2) Å and a Ge-Hg-Ge bond angle of 178.68°.[11]

There are two $[K(crypt)]^+$ ions for each $[HgGe_9]$ unit which leads to a charge of $-2$ for the monomer of the polymer chain (Figure 2). The Ge–Ge bond lengths range from 2.537(1) to 2.904(1) Å and are in accordance with those known in other $Ge_9$ clusters.[12] Here the longest bond, 2.904 Å, is between Ge5 and Ge6, which have weak interactions with the Hg atom. Depending on how the charges are allocated, the polymer can be formulated as -($[Ge_9]^{2-}$)-Hg-($[Ge_9]^{2-}$)-Hg- with covalent bonds between the Ge and Hg atoms, or with the formal charges of ($[Ge_9]^{4-}$)$Hg^{2+}$($[Ge_9]^{4-}$)$Hg^{2+}$. The clusters possess 22 skeletal electrons independent of charge allocation. From Wade rules a *nido* structure in form of a mono-capped square-antiprism with $C_{4v}$ symmetry is expected. The geometric bond parameters in **1** point to a $C_s$ symmetric body with a structure between the *nido* and *closo* (tri-capped trigonal-prism, $D_{3h}$ symmetry) type. The *closo* structure is expected for 20 skeletal electrons. The open rectangular face of the underlying $C_{4v}$ symmetric polyhedra in **1** is clearly a distorted rhombus with the shorter diagonal parallel to the polymer axis ($d$(Ge1···Ge2) = 4.049(2) Å, $d$(Ge3···Ge4) = 3.149(1) Å). Assuming a trigonal prism of the atoms Ge3 to Ge8, the prism edge (Ge3···Ge4) is extended by 14 % compared to the edges Ge5–Ge7 and Ge6–Ge8. The nearly $C_{2v}$ symmetric topology of clusters is common and observed in a large number of $Ge_9$ clusters with 22 and 21 skeletal electrons.[12]

The ${}^{1}_{\infty}[HgGe_9]$ chains in **1** are separated from each other by $[K(crypt)]^+$ ions and arranged parallel to the $c$ axis in the form of a distorted hexagonal-close packing of rods (Figure 3). There are no bonding interactions between the ${}^{1}_{\infty}[HgGe_9]$ chains and the cations. The distances between the centers of gravity of the clusters of neighboring chains are in the range from 14.736 to 16.242 Å. The en molecules occupy the space between the ${}^{1}_{\infty}[HgGe_9]$ chains showing no bonding interactions to the chains or to the cations (Figure 2).

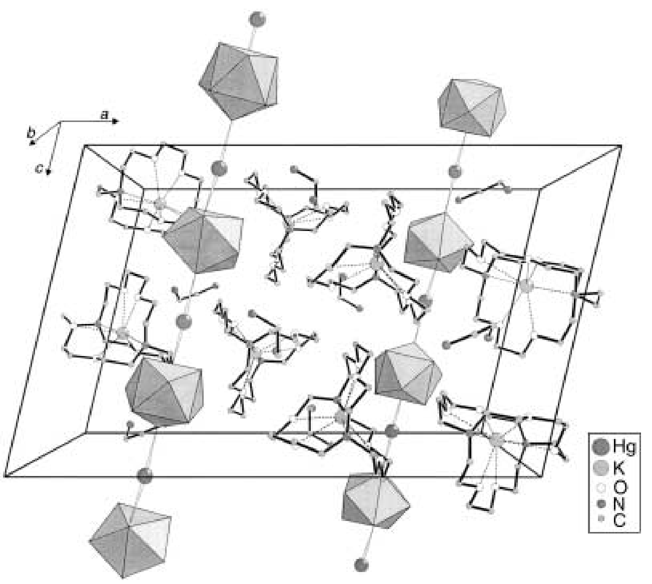

Figure 2. Unit cell of **1** with projection along the $b$ axis.

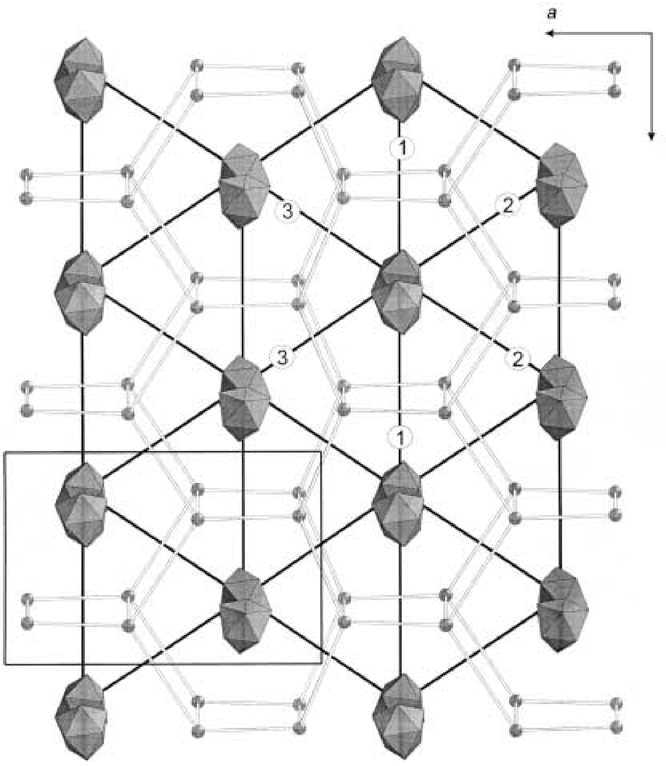

Figure 3. Crystal structure of **1** with projection along the $c$ axis. The polymer chains are ordered analogously to a hexagonal close-packing of rods. Distances between the centers of gravity of the clusters: ① 16.242, ② 15.084, and ③ 14.736 Å. The $[K(crypt)]^+$ ions form a strongly distorted lattice of hexagons. For the reason of clarity the $[K(crypt)]^+$ units are represented by the central K atoms alone.

Compound **1** is synthesized from $[Ge_9]^{4-}$ ions and $Hg^0$ without using an oxidant. The comparable formations of ${}^{1}_{\infty}[Ge_9]^{2-}$,[3] $[Ge_9\text{-}Ge_9]^{6-}$,[13] $[Ph_2Bi\text{-}Ge_9\text{-}BiPh_2]$,[14] and the paramagnetic ions $[Ge_9]^{3-}$[15–17] using $[Ge_9]^{4-}$ ions as precursors also proceed without oxidizing agents. For the present reaction which uses an excess of mercury, oxidation might occur through impurities, but also by the reduction of mercury.

Synthesis of compound **1** shows the possibility to use Zintl ions as building blocks to construct complex structures. In agreement with the structural results and charge allocation, crystals of **1** shows no signal in the EPR spectrum.[18] Partial oxidation or reduction of the polymer chain—which corresponds to an insertion of paramagnetic clusters into the chain—should lead to interesting magnetic properties. Each homoatomic cluster of the one-dimensional polymer in **1** has two more reactive sites. In principle, these sites hold the possibility to build two-dimensional polymers by repeated oxidative coupling in presence of atoms able to build bridges. In attempts to prepare analogues of **1**, syntheses using $Sn_9$ clusters instead of $Ge_9$, up to now, simply lead to the decomposition of the solution and formation of elementary tin. A comparable synthesis to link $Sn_9$ clusters with Te atoms leads to the break down of the cluster and formation of the heteroatomic ions $[Te_2Sn(\mu_2\text{-}Te)_2SnTe_2]^{4-}$ and $[Sn(\mu_2\text{-}Te)_3Sn]^{2-}$.[19]

## *Experimental Section*

The synthesis of compound **1** was carried out under argon atmosphere using a glove-box or Schlenk line. Toluene (Merck) and en (Merck) were dried over $CaH_2$ (Fluka), freshly distilled and degassed. The binary phase of the formal composition "$K_4Ge_9$" was prepared by high-temperature reaction (650 °C) from the elements K and Ge (Chempur) in the ratio 4:9.

$K_4Ge_9$ (200 mg, 0.25 mmol) was dissolved in en (3 mL) in a Schlenk tube and stirred for 5 min in an ultrasonic bath. The resulting dark green solution was filtered onto to Hg (300 mg, 1.5 mmol). Afterwards the reaction mixture was treated for 20 min in an ultrasonic bath, filtered, and added to [2.2.2]crypt (376 mg, 1 mmol). The resulting solution was layered with toluene (3 mL). After about three days compound **1** crystallized as red brown columnar crystals with a yield of 90 mg (20 % with respect to $K_4Ge_9$). Elemental analysis (%) calcd: C 26.61, H4.91, N 6.21; Found: C 26.82, H 4.95, N 6.04.

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# A Further Step towards Single-Molecule Sequencing: *Escherichia coli Exonuclease* III Degrades DNA that is Fluorescently Labeled at Each Base Pair**

Susanne Brakmann* and Sylvia Löbermann

The international race to sequence the human genome as well as the genomes of other model organisms encouraged efforts to realize "single-molecule sequencing"—an idea which nourishes the hope to simplify and speed up the task of sequencing DNA segments as long as 50000 base pairs (bp) and joining the sequence information of genome fragments.[1–5] The different strategies to realize single-molecule sequencing are based on that single fluorescent molecules can be identified within milliseconds,[6] and they combine sequential enzymatic hydrolysis of individual DNA molecules with subsequent identification of the released monomers by their

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