# On the Oxidation of [Ge$_9$]$^{4-}$ – Crystal Structures and Raman Spectroscopic Investigation of Linked Ge$_9$ Clusters

Kerstin Mayer,[a] Wilhelm Klein,[a] Sebastian Geier,[a] and Thomas F. Fässler*[a]

*Dedicated to Professor Thomas Klapötke on the Occasion of his 60$^{th}$ Birthday*

Oxidation of Ge$_9$ Zintl clusters can afford condensed cluster species in the form of dimers, oligomers and polymers. In this work, we present a new route for the synthesis of Ge$_9$ tetramers present in the compound [K(18-crown-6)]$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·4 pyr. The reaction of a pyridine solution of K$_4$Ge$_9$ with 18-crown-6 first leads to the formation of green needles of yet unknown composition, which convert into the reported tetramer over time. In this reaction pyridine acts as oxidation reagent. Raman studies on the green needles as well as on tetrameric and polymeric Ge$_9$ feature complex vibrational patterns. Furthermore, we present the crystal structure of a new type of Ge$_9$ dimer in the compound K$_4$[K(2.2.2-crypt)]$_2$[Ge$_9$–Ge$_9$]·4 en·2 thf, which represents an intermediate between the two established conformers.

## Introduction

The Zintl phases $A_4$Ge$_9$ and $A_{12}$Ge$_{17}$ ($A$ = alkali metal) feature ready-made Ge$_9$ cluster anions embedded in an alkali metal counter ion matrix.[1] Several review articles cover the various reaction possibilities of these Zintl anions. In solution the nine-atomic clusters appear as differently charged species [Ge$_9$]$^{x-}$ ($x$ = 2, 3, 4), which all can be obtained and studied as solvates.[2] This structural diversity has also been observed for the homologous [Sn$_9$]$^{x-}$ ($x$ = 2, 3, 4), for which quantum chemical investigations have shown that the energy difference between the structures of differently charged species is only marginal.[3] As predicted by *Wade's* rules, different oxidation states lead to different cluster structures.[4] According to these rules, [Ge$_9$]$^{4-}$ is a 22 e$^-$ *nido* cluster with $C_{4v}$ symmetry, whereas the 20 e$^-$ *closo* cluster [Ge$_9$]$^{2-}$ possesses $D_{3h}$ symmetry. The symmetry of the radical [Ge$_9$]$^{3-}$ with 21 e$^-$ is not predictable by *Wade's* rules, and it takes either $C_{2v}$ or $C_s$ symmetry. By addition of mild oxidation agents, the Ge$_9$ clusters can combine to one dimensional dimers,[5,6] trimers,[7] tetramers,[8] and polymers.[9] However, the formation of such condensed species is still unclear, and besides the lack of any mechanistic explanation sometimes even the oxidizing agent cannot be determined exactly. The [Ge$_9$–Ge$_9$]$^{6-}$ dimers comprise two covalently bonded [Ge$_9$]$^{3-}$ clusters, with the connecting bond between two vertices of the square planes. The Ge$_9$ clusters of the oligomers and polymers are twofold negatively charged. In the polymer $_\infty^1$[Ge$_9$]$^{2-}$ the connection mode is comparable to that of the dimer. Trimeric [Ge$_9$=Ge$_9$=Ge$_9$]$^{6-}$ and tetrameric [Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]$^{8-}$ exhibit non-classical bonds with the formation of Ge$_4$ rectangles between two neighboring atoms forming edges of opposite trigonal cluster faces. For Ge$_9$ dimers, also substituted species, such as the bis-vinylated anion [(CH$_2$=CH)–Ge$_9$–Ge$_9$–(CH=CH$_2$)]$^{2-}$ and [Ph$_3$Sn–Ge$_9$–Ge$_9$–SnPh$_3$]$^{2-}$, are known.[6] The only other covalently connected [$E_9$] species is [Sn$_9$–Sn$_9$]$^{6-}$ as a chelating unit at an Ag$^+$ ion.[10] Further oxidation of Zintl clusters leads to the formation of clathrate framework structures,[11] and mesoporous Ge forms are likewise available via this route.[12] However, quantum chemical calculations revealed a certain stability of novel Si and Ge elemental allotropes as well as nanoparticles built-up solely by $E_9$ clusters. They show two-, one- and zero-dimensional structures with promising opto-electronic properties.[13]

In this work, we report on a synthetic route with proper yields for a new solvate structure of tetrameric Ge$_9$ by oxidation *via* pyridine. Additionally, we present Raman spectra of differently condensed cluster systems and the formation of a new [Ge$_9$–Ge$_9$]$^{6-}$ dimer.

## Results and Discussion

The bare tetrel cluster anions are soluble in certain amines and other solvents with Lewis base character, such as liquid ammonia, ethylenediamine (en), or dimethylformamide (dmf),[5b,14] under formation of deeply colored solutions. Mere K$_4$Ge$_9$ is insoluble in pyridine, however, the addition of sequestering agents such as 2.2.2-crypt and 18-crown-6 enhances the solubility. Layering of the deep brownish pyridine solution of K$_4$Ge$_9$ and 2.2.2-crypt with toluene leads to the crystallization of the established solvate [K(2.2.2-crypt)]$_2$Ge$_9$ (**1**), which contains [Ge$_9$]$^{2-}$ clusters that are also obtained from ethylenediamine solution.[15] Pyridine is known for its ability to oxidize Zintl ions under formation of bipyridine radicals,

[a] Dr. K. Mayer, Dr. W. Klein, Dr. S. Geier, Prof. Dr. T. F. Fässler
    Department Chemie, Technische Universität München
    Lichtenbergstraße 4, 85747 Garching, Germany
    E-mail: thomas.faessler@lrz.tum.de

accompanied by a blue coloration of the solution,[16] which is also observed in our experiment. A similar procedure, but with 18-crown-6 instead of cryptand, leads to a brownish solution that turns green overnight. From this solution dark green needles (**2**) crystallize, which are unfortunately too small for single crystal structure determination. However, after several weeks, these needles had completely disappeared and were replaced by brown block shaped crystals, which were suitable for single crystal diffraction. They have the composition [K(18-crown-6)]$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·4 pyr (**3**), which represents the fourth compound with a Ge$_9$ tetramer, and the first one not obtained from ethylenediamine solution. *Sevov et al.* obtained the two very similar compounds [Rb(18-crown-6)]$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·2 en (**4**) and [Rb(18-crown-6)]$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·6 en (**5**) from an ethylenediamine solution of Rb$_4$Ge$_9$ in the presence of 18-crown-6 and layering with thf or toluene,[8a] and *Fässler et al.* received another tetramer, [K(18-crown-6)]$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·8 en (**6**), by the reaction of K$_4$Ge$_9$ with a solution of GeI$_2$ and K in ethylenediamine, after addition of 18-crown-6 and layering with toluene.[8b] The tetramer in compound **3** not only differs in its containing solvent molecules, but also in the slightly different anion structure, and it shows a very different crystal packing. The anion contains two crystallographically independent Ge$_9$ clusters, A and B, with distorted $D_{3h}$ symmetry, which build – through an inversion center – the tetramer. The clusters are connected *via* two bonds of two neighboring atoms with

average bond lengths for the terminal *exo* bonds of 2.679 Å and for the central *exo* bonds of 2.557 Å (Figure 1). The symmetry of the single clusters and the bond lengths are similar to that in the tetramers of **4**–**6**. In Table 1 some important Ge–Ge distances of the different tetramers are summarized for comparison. The orientation of the clusters in the tetramer is slightly different in all compounds, and the outer cluster is tilted with respect to the inner cluster. In compound **3** the angle between the two planes through the atoms Ge1–Ge6–Ge8 (Cluster A) and Ge10–Ge15–Ge17 (Cluster B) is 6.2°, whereas these angles range between 7.2° and 17.4° in the other compounds, thus compound **3** contains the least tilted tetramer.

As in the other tetrameric Ge$_9$ cluster compounds, all eight K counter ions in **3** are sequestered by 18-crown-6 molecules. However, the packing of the [A(18-crown-6)]$^+$ (A = K, Rb) cations and the [Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]$^{8-}$ anions is completely different in the respective tetramers. In the two closely related tetramers **4** and **5**, all eight [Rb(18-crown-6)]$^+$ counter ions coordinate to the tetramer and thereby form a positive shielding layer around the negatively charged ion.[8a] In compound **6**, only four [K(18-crown-6)]$^+$ counter ions coordinate directly to the tetramer, two of them to the terminal trigonal faces of the tetramer and the other two to the pseudo square plane of the central clusters.[8b] In compound **3** again only four [K(18-crown-6)]$^+$ counter ions coordinate to the clusters, but in a different mode than that in **6**, since each of them coordinates to a square plane
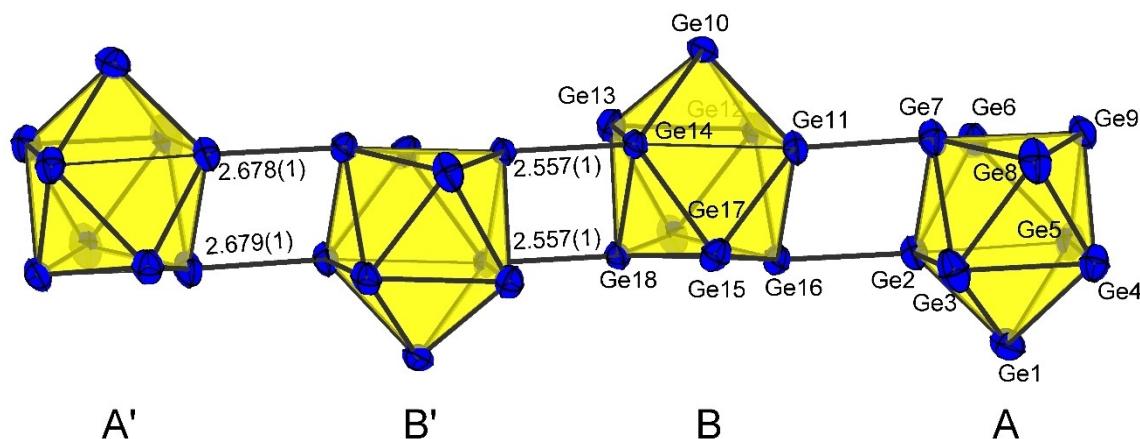


**Figure 1.** Structural details of the anion in [K(18-crown-6)]$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·4 pyr (**3**). Ellipsoids for all atoms are shown at a probability level of 70%. Ge atoms are blue, polyhedra are yellow.

**Table 1.** Selected bond lenghts and other structural details of [K(18-crown-6)]$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·4 pyr (**3**) and of Rb(18-crown-6)]$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·2 en (**4**), Rb(18-crown-6)]$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·6 en (**5**) and [K(18-crown-6)]$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·8 en (**6**).

| | **3** (this work) | **4**[8a] | **5**[8a] | **6**[8b] |
|---|---|---|---|---|
| Mean d(Ge–Ge)/Å | 2.628 | 2.636 | 2.606 | 2.638 |
| Central *exo* bond d(Ge14–Ge18)/Å | 2.557 | 2.546 | 2.532 | 2.554 |
| Terminal *exo* bond | | | | |
| d(Ge2–Ge16)/Å | 2.678 | 2.673 | 2.619 | 2.595 |
| d(Ge7–Ge11)/Å | 2.679 | 2.634 | 2.636 | 2.752 |
| Cluster symmetry | ~$D_{3h}$ | ~$D_{3h}$ | ~$D_{3h}$ | ~$D_{3h}$ |
| Angle between Ge1–Ge6–Ge8 and Ge10–Ge15–Ge17/deg | 6.2 | 7.2 | 8.9 | 17.4 |

of one cluster. The different coordination modes are shown in Figure 2.

Powder X-ray diffraction measurements on the bulk material reveal compound **3** as the only crystalline component in the sample. Also on the basis of powder X-ray diffraction studies it can be excluded that the initially formed green needles (**2**) are identical to compound **3** (Figure 3a and b). To gain insights into the composition of these green needles, we used Raman spectroscopy: $Ge_9$ clusters are Raman sensitive and exhibit strong characteristic Raman bands, however, the pattern of freestanding clusters is limited to three major bands at roughly 145, 163 and 220 $cm^{-1}$.[1b] The green needles (**2**) reveal a significantly more complex spectrum. For comparison, we measured a Raman spectrum of the known polymer $_\infty^1[-(Ge_9{}^{2-})-]$ (**7**).[9] Since **2** and **7** are similar in appearance, and their synthesis followed an analogous routine and differ only by using ethylenediamine instead of pyridine, we assumed

that both compounds could be related, but the likewise very complex spectrum of the polymer **7** exhibits no similarity to the one of the green needles **2**.

However, the Raman spectrum of the tetramer **3** and the spectrum of the green needles show some similarities which thus indicates a relation between these two compounds. Similarities occur between the bands at 136/140, 166/170, 185/185 and 210/205 $cm^{-1}$ (green needles **2**/tetramer **3**). However, the strongest Raman band of the green needles at 107 $cm^{-1}$ has completely disappeared, and instead the band at 243 $cm^{-1}$ has increased upon conversion into the tetramer (Figure 3c).

While in the former example the oxidation works with pyridine as most probable oxidant by forming the bipyridyl radical anion, several examples are known without a clearly identifiable oxidant. For instance, oxidation also occurs in a solution of $K_4Ge_9$ in ethylenediamine, layered with $Zn(CH_3COO)_2$
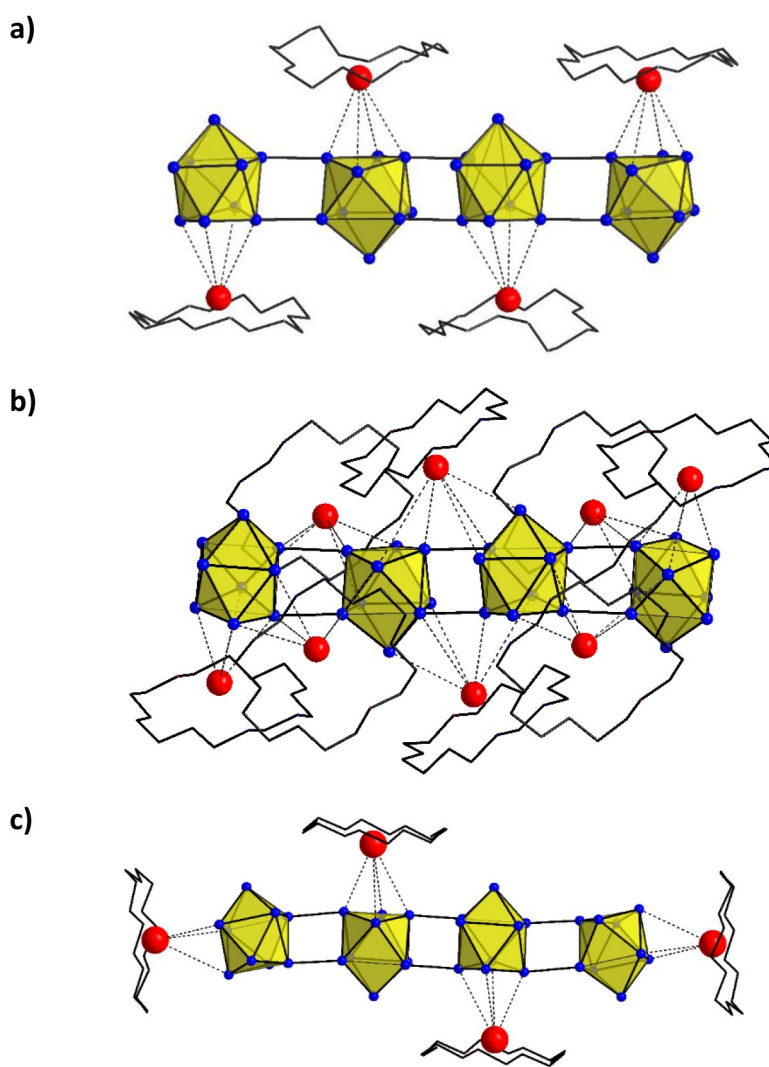


**Figure 2.** The different coordination spheres of the $Ge_9$ tetramers: a) [K(18-crown-6)]$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·4 pyr (**3**), b) Rb(18-crown-6)]$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·2 en (**4**, the coordination in compound **5** is similar),[8a] and c) [K(18-crown-6)]$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·8 en (**6**).[8b] Ge atoms are blue, alkali metal atoms (K and Rb) red; polyhedra are yellow. 18-Crown-6 is drawn schematically.
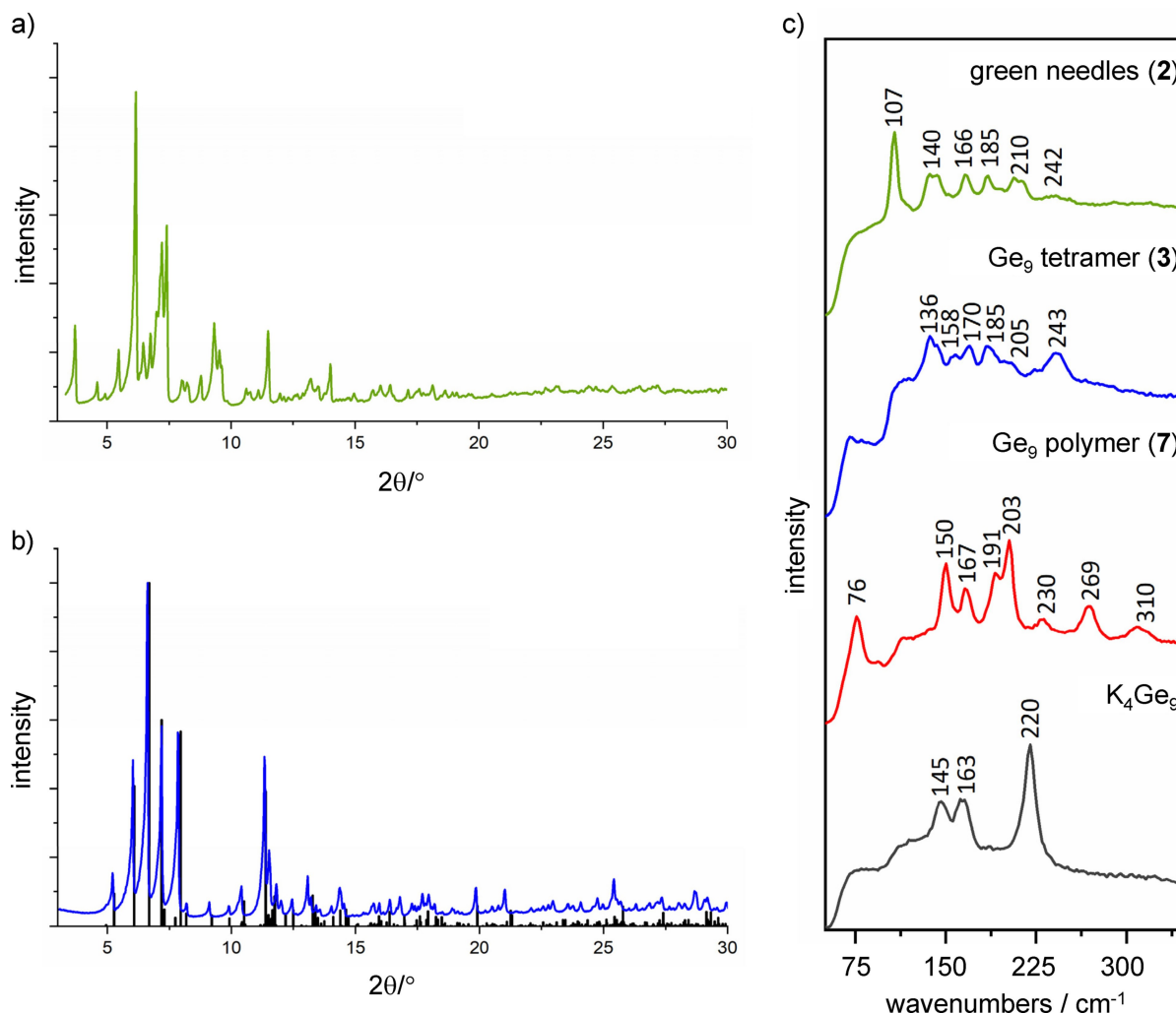
**Figure 3.** a) Powder XRD of the green needles (**2**, green) with unknown composition, measurement time 14 h; b) powder XRD of [K(18-crown-6)]$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·4 pyr (**3**, blue) with its calculated reference diffractogram (black), measurement time 14 h; c) Raman spectra of the green needles (**2**, green) with unknown composition, tetrameric [Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]$^{8-}$ (**3**, blue), polymeric $_\infty^1$[−(Ge$_9$$^{2-}$)−](**7**, red), and K$_4$Ge$_9$ (black).

and 2.2.2-crypt in thf. We obtained K$_4$[K(2.2.2-crypt)]$_2$[Ge$_9$−Ge$_9$]·4 en·2 thf (**8**) with a dimeric [Ge$_9$−Ge$_9$]$^{6-}$ ion although no obvious oxidizing agent is present. Solutions of K$_4$Ge$_9$ in the respective solvents or solvent mixtures are usually stable over long periods, and also the Zn acetate should not be oxidizable by Ge$_9$ cluster compounds. However, we found compound **8** as a minor byproduct besides **1**, and an equilibrium including different Ge cluster-containing compounds seems to be possible.

The dimer in compound **8** consists of one crystallographically independent cluster, which is duplicated by symmetry to give the dimeric anion with a bridging Ge−Ge distance of 2.462(2) Å. The cluster adopts a distorted $C_{4v}$ symmetry (h$_1$ = 3.88 Å, h$_2$ = 2.92 Å, h$_3$ = 2.83 Å; d$_1$/d$_2$ = 1.13; α$_1$ = 2.2°), where the Ge−Ge−Ge angle at the exo-bond bearing atom is significantly widened compared to a right angle (100.24(5)°). This shape is well known for clusters that carry one ligand, e.g. another cluster, connected through a covalent exo-cluster bond.

Four of the six K counter ions in compound **8** coordinate to the [Ge$_9$−Ge$_9$]$^{6-}$ dimer and are arranged around the bridging Ge−Ge bond (Figure 4a). The solvent molecules ethylenediamine and thf coordinate to these K cations. The remaining two K counter ions are sequestered by 2.2.2-crypt, and layers of {K$_4$(en)$_4$(thf)$_2$[Ge$_9$−Ge$_9$]}$^{2-}$ alternate with layers of [K(2.2.2-crypt)]$^+$ in direction of the crystallographic *c* axis (Figure 4b).

Very interestingly, the dimer appears in a new conformation. All so far known dimers occur as two different conformers: The more common shape is a dimer of two distorted $C_{4v}$ symmetric clusters with a rhombohedrally distorted square plane. The clusters are connected via corners of the square cluster faces, and the polyhedra are turned in a transoid manner, with the antiprism caps pointing in opposite directions. The *exo* bond is collinear to the shorter diagonal of the square planes (conformer "A", see Figure 4c).[5] The other conformer ("B") consists of two connected clusters with distorted $C_{2v}$ symmetry. Here the *exo* bond points toward the cluster centers
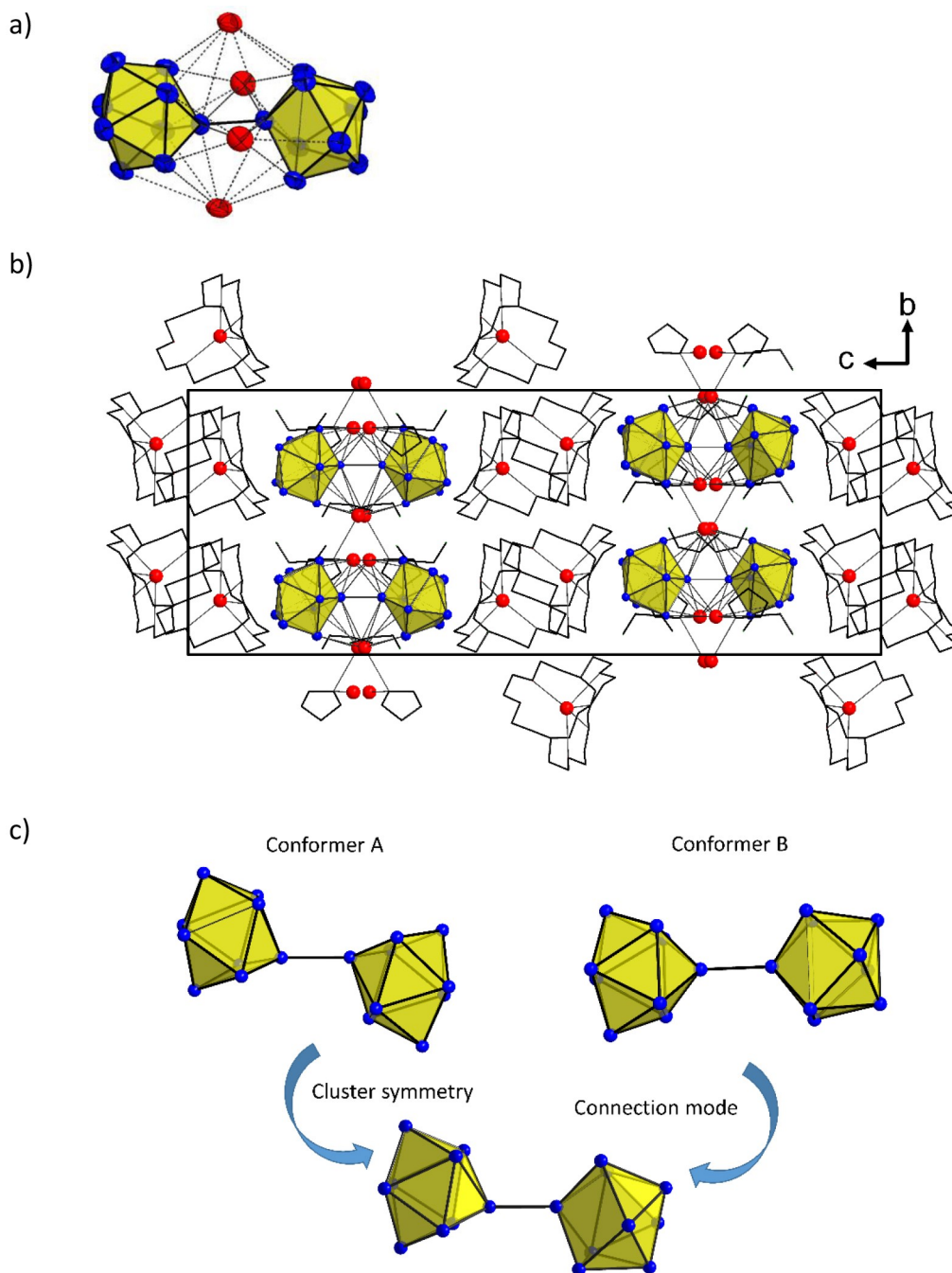
**Figure 4.** a) Structural details of the anion of $K_4[K(2.2.2\text{-crypt})]_2[Ge_9\!-\!Ge_9]\cdot 4$ en $\cdot 2$ thf (**8**) with coordinated K cations. Ellipsoids for all atoms are shown at a probability level of 70%; b) ion packing in crystals of **8**; c) structural relationship of the three different dimer conformations. Ge atoms are blue, K atoms red, polyhedra are yellow.

and is not collinear to the diagonals, the clusters are connected not in a transoid but perpendicular manner.[5b] The new conformer found in **8** represents a mixture of both: the shape of each single $Ge_9$ cluster is of distorted $C_{4v}$ symmetry which is significantly related to conformer A, while the perpendicular connection mode is reminiscent to conformer B (Figure 4c). We assume that packing effects are responsible for the appearance of isomers. For instance, the coordination by cations will affect

the relative orientation and the shape of the clusters. While the new conformer in **8** all coordinating $K^+$ ions are solely arranged around the bridging Ge atoms, in the related $K_4[K(2.2.2\text{-crypt})]_2[Ge_9\!-\!Ge_9]\cdot 7$ en[5c] the anion is coordinated by two more $K^+$ ions and is realizing the A conformer. The additionally coordinating cations should have a directing effect, and the lack of those in **8** might promote the new orientation found here. Finally, the only known example for conformer B was

found as a mixed Cs/K salt, where four $Cs^+$ ions coordinate the bridging atoms of the cluster dimer.

## Conclusion

During our investigations, two new compounds with condensed [$Ge_9$] clusters were found: a tetramer in [K(18-crown-6)]$_8$[$Ge_9$=$Ge_9$=$Ge_9$=$Ge_9$]·4 pyr (**3**) and a dimer in K$_4$[K(2.2.2-crypt)]$_2$[$Ge_9$—$Ge_9$]·4 en·2 thf (**8**). The structure of the tetrameric unit is reminiscent of the established tetramers; however, it exhibits a completely different coordination sphere of 18-crown-6-sequestered K cations and consequently has a different crystal packing. In a first step of the synthesis green needles (**2**) are formed, the Raman spectra of which reveal a complex vibrational pattern, and a comparison with the spectra of other condensed compounds shows similarities with the tetramer. The structure of the dimeric anion in **8** constitutes a mixture of the two known conformers: it possesses the cluster symmetry of conformer A, but the coordination mode of conformer B.

## Experimental

**General**. All reactions and manipulations were performed under a purified argon atmosphere using standard Schlenk and glove box techniques. The Zintl compound of nominal composition K$_4$Ge$_9$ was synthesized by heating (2 K/min) a stoichiometric mixture of the elements K (Merck, ≥ 98 %) and Ge (99.999 % Chempur) at 650 °C in a stainless-steel autoclave for 46 h and slow cooling (1 K/min) to room temperature. Toluene and pyridine were dried over molecular sieve (4 Å), thf over a special drying material in a solvent purification system. Ethylenediamine was dried over NaH and freshly distilled before use. 18-Crown-6 (Merck) was sublimated, 2.2.2-crypt (Merck) was dried for 8 h *in vacuo*, and Zn(CH$_3$COO)$_2$ (Merck) was used without further purification.

**Synthesis of [K(2.2.2-crypt)]$_2$Ge$_9$ (1)**. K$_4$Ge$_9$ (49 mg, 60 µmol, 1 eq.) and 2.2.2-crypt (90 mg, 240 µmol, 4 eq.) were weighed out into a Schlenk tube and dissolved in 3 mL pyridine, resulting in a dark reddish-brown suspension. After filtration, the solution was layered with toluene. After several days, the solution turned blue, and brownish red block shaped crystals (approx. 60 %), suitable for single crystal X-ray diffraction, were obtained. $a = b = 11.92$ Å, $c = 22.35$ Å; $\alpha = \beta = 90°$, $\gamma = 120°$; $V = 2748$ Å$^3$.[15]

**Synthesis of (2) and [K(18-crown-6)]$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·4 pyr (3)**. K$_4$Ge$_9$ (49 mg, 60 µmol, 1 eq.) and 18-crown-6 (63 mg, 240 µmol, 4 eq.) were weighed out into a Schlenk tube and dissolved in 3 mL pyridine, resulting in a dark brown suspension. After filtration, the solution was layered with toluene. The color of the solution changed from brown to green, and dark green needles (**2**) appeared after several days. During the next approx. 4 months, the green needles disappeared, and brownish block-shaped crystals (37 %) of compound **3**, suitable for single crystal X-ray diffraction, emerged. EDX measurements confirmed the presence of K and Ge.

**Synthesis of [K(18-crown-6)]$_2$[Ge$_9$]·en (7)**. K$_4$Ge$_9$ (97 mg, 119 µmol, 1 eq.) and 18-crown-6 (127 mg, 484 µmol, 4 eq.) were weighed out into a Schlenk tube and dissolved in 3 mL ethylenediamine. The resulting yellow greenish suspension was stirred for 4 days, filtered and layered with toluene. After several weeks, dark green needles suitable for single crystal X-ray diffraction, were obtained. $a = 11.27$ Å, $b = 14.70$ Å, $c = 27.83$ Å; $\alpha = \beta = \gamma = 90°$; $V = 4611$ Å$^3$.[9] Pow-

der XRD of the bulk species revealed compound **7** as the only crystalline component (Figure S1).

**Synthesis of K$_4$[K(2.2.2-crypt)]$_2$[Ge$_9$—Ge$_9$]·4 en·2 thf (8)**. K$_4$Ge$_9$ (122 mg, 150 µmol, 2.5 eq.) was dissolved in 3 mL ethylenediamine. After filtration of the orange solution, it was layered with Zn(CH$_3$COO)$_2$ (11 mg, 60 µmol, 1 eq.) and 2.2.2-crypt (61 mg, 230 µmol, 3.8 eq.) in 4 mL thf. The solution changed color from orange to green. After four months, dark brown block-shaped crystals of compound **8** suitable for single crystal X-ray diffraction were obtained (yield < 5 %). Besides compound **8**, also crystals of compound **1** were formed (yield approx. 50 %).[15] EDX of **8**: K 27.5 % (calc. 25.0 %), Ge 72.5 % (calc. 75.0 %).

**Energy Dispersive X-Ray (EDX) Analysis**. Single crystals of compounds **3** and **8** were analyzed with a scanning electron microscope equipped with an energy dispersive X-ray analyzer (Hitachi TM-1000 Tabletop microscope).

**Single-Crystal Structure Determination**. Single crystals were fixed on a glass fibre with perfluorinated ether and positioned in a 120 K or 253 K cold N$_2$ stream. For single crystal X-ray diffraction data collection, an Oxford-Diffraction Xcalibur3 diffractometer (Mo $K_\alpha$ radiation) and a Bruker FR591 APEX-II diffractometer (Mo $K_\alpha$ radiation) were used. The structures were solved by Direct Methods and refined by full-matrix least-squares calculations against $F^2$ using SHELX-2014.[17] Non-hydrogen atoms were, if possible, treated with anisotropic displacement parameters. Pictures of the crystal structures were created with the program Diamond.[18] Several C and N atoms had to be treated with the ISOR command. A relatively high residual electron density is found around the Ge$_9$ clusters of compound **8**; refinement as minor component of a disordered structure was not possible. Table 2 contains selected crystallographic data and refinement details, Tables 3 and 4 selected bond lengths of compounds **3** and **8**. CCDC 2040102 (**3**) and CCDC-2040103 (**8**) contain the supplementary crystallographic data for

**Table 2.** Selected crystallographic data of the crystal structures of **3** and **8**.

| Compound | 3 | 8 |
|---|---|---|
| Formula | C$_{58}$H$_{106}$Ge$_{18}$K$_4$N$_2$O$_{24}$ | C$_{26}$H$_{60}$Ge$_9$K$_3$N$_6$O$_7$ |
| fw (g mol$^{-1}$) | 2678.46 | 1339.41 |
| Space group (no.) | $P\bar{1}$ (2) | $C2/c$ (15) |
| $a$ (Å) | 15.3088(3) | 16.0178(8) |
| $b$ (Å) | 17.6444(4) | 15.1180(7) |
| $c$ (Å) | 17.8346(3) | 39.7394(19) |
| $\alpha$ (deg) | 88.546(2) | 90 |
| $\beta$ (deg) | 88.0100(10) | 93.345(3) |
| $\gamma$ (deg) | 71.697(2) | 90 |
| $V$ (Å$^3$) | 4570.38(16) | 9606.8(8) |
| $Z$ | 2 | 8 |
| T (K) | 120(2) | 253(2) |
| $\lambda$ (Å) | 0.71073 | 0.71073 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.946 | 1.852 |
| $\mu$ (mm$^{-1}$) | 6.065 | 5.850 |
| Collected reflections | 72256 | 70281 |
| Independent reflections | 17927 | 8924 |
| $R_{int}$ | 0.0572 | 0.0635 |
| Parameters/restraints | 963/12 | 474/24 |
| $R_1$ [$I > 2\,\sigma(I)$/all data] | 0.0302/0.0684 | 0.0775/0.0903 |
| w$R_2$ [$I > 2\,\sigma(I)$/all data] | 0.0497/0.0537 | 0.2303/0.2451 |
| Goodness of fit | 0.779 | 1.078 |
| Max./min. diff. el. density/ e·Å$^{-3}$ | 0.686/−0.812 | 2.595/−2.063 |
| Depository no. | CCDC-2040102 | CCDC-2040103 |

**Table 3.** Selected bond lengths (Å) in **3**.

$[K(18\text{-}crown\text{-}6)]_8[Ge_9{=}Ge_9{=}Ge_9{=}Ge_9]\cdot 4\,pyr$

| Cluster A | | Cluster B | |
|---|---|---|---|
| Ge1—Ge2 | 2.5261(7) | Ge10—Ge11 | 2.6178(6) |
| Ge1—Ge3 | 2.6157(7) | Ge10—Ge12 | 2.5862(7) |
| Ge1—Ge4 | 2.5606(7) | Ge10—Ge13 | 2.6149(7) |
| Ge1—Ge5 | 2.6245(7) | Ge10—Ge14 | 2.5324(6) |
| Ge2—Ge3 | 2.7353(8) | Ge11—Ge12 | 2.7255(7) |
| Ge2—Ge6 | 2.5573(6) | Ge11—Ge15 | 2.6538(6) |
| Ge2—Ge7 | 2.6530(7) | Ge11—Ge16 | 2.5883(7) |
| Ge3—Ge4 | 2.7604(7) | Ge12—Ge13 | 2.7576(6) |
| Ge3—Ge7 | 2.6981(7) | Ge12—Ge16 | 2.7032(7) |
| Ge3—Ge8 | 2.6302(7) | Ge12—Ge17 | 2.6163(7) |
| Ge4—Ge5 | 2.7155(7) | Ge13—Ge14 | 2.7062(7) |
| Ge4—Ge8 | 2.5518(7) | Ge13—Ge17 | 2.6137(7) |
| Ge4—Ge9 | 2.6675(7) | Ge13—Ge18 | 2.7218(6) |
| Ge5—Ge6 | 2.6251(7) | Ge14—Ge15 | 2.5602(6) |
| Ge5—Ge9 | 2.5369(7) | Ge14—Ge18 | 2.6059(6) |
| Ge6—Ge7 | 2.5641(7) | Ge15—Ge16 | 2.6710(7) |
| Ge6—Ge9 | 2.6497(7) | Ge15—Ge18 | 2.5891(6) |
| Ge7—Ge8 | 2.5274(7) | Ge16—Ge17 | 2.6204(7) |
| Ge8—Ge9 | 2.6421(7) | Ge17—Ge18 | 2.5451(7) |
| Ge7—Ge11 | 2.6793(6) | Ge14—Ge18′ | 2.5565(6) |
| Ge2—Ge16 | 2.6776(6) | Ge18—Ge14′ | 2.5565(6) |

**Table 4.** Selected bond lengths (Å) in **8**.

$K_4[K(2.2.2\text{-}crypt)]_2[Ge_9{-}Ge_9]\cdot 4\,en\cdot 2\,thf$

| | | | |
|---|---|---|---|
| Ge1—Ge2 | 2.5140(13) | Ge4—Ge8 | 2.5794(15) |
| Ge2—Ge3 | 2.6386(14) | Ge4—Ge5 | 2.6552(13) |
| Ge3—Ge4 | 2.6514(14) | Ge5—Ge6 | 2.9162(13) |
| Ge4—Ge1 | 2.5354(13) | Ge6—Ge7 | 2.7518(14) |
| Ge1—Ge5 | 2.5782(13) | Ge7—Ge8 | 2.8276(14) |
| Ge1—Ge6 | 2.5703(13) | Ge8—Ge5 | 2.7813(14) |
| Ge2—Ge6 | 2.6500(13) | Ge5—Ge9 | 2.5757(15) |
| Ge2—Ge7 | 2.5803(15) | Ge6—Ge9 | 2.5694(15) |
| Ge3—Ge7 | 2.6118(13) | Ge7—Ge9 | 2.6003(15) |
| Ge3—Ge8 | 2.6037(14) | Ge8—Ge9 | 2.5946(14) |
| Ge1—Ge1′ | 2.4624(19) | | |

this paper and are available free of charge via https://www.ccdc.cam.ac.uk/structures.

**Raman Spectroscopy.** Raman spectroscopy was performed using a Renishaw inVia Raman microscope equipped with a CCD detector and four different lasers (266 nm, 532 nm, 633 nm, and 785 nm) with a maximum power of 500 mW. The software WiRE 4.2 (build 5037, Renishaw 2002) was used for operating the device. All samples were measured in quartz capillaries (MARK-Kapillaren, *Müller & Müller OHG*).

**Powder X-Ray Diffraction.** Phase analyses of bulk products were performed using a Stoe STADIP diffractometer [Ge(111) monochromator; Cu $K_{\alpha1}$ radiation] with a linear position-sensitive detector (Mythen). The compounds were pestled, sealed in glass capillaries and measured in Debye-Scherrer geometry. Data evaluation was done using the Stoe WinXPOW[19] software package by comparing the measured diffractogram with the calculated reflections obtained from single crystal analyses.

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