Conformation Isomerism of Nonagermanide Ions. Crystal Structures of Brown and Red $[\mathrm{K}\text{-}([2.2.2]\mathrm{crypt})]_6\mathrm{Ge}_9\mathrm{Ge}_9\cdot(\mathrm{ethylenediamine})_x$ ($x = 0.5, 1.5$)

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Received September 28, 1998

A brown and a red form of the $[\mathrm{K}\text{-}([2.2.2]\text{-crypt})]^+$ salts of naked polyhedral nonagermanide anions were isolated by dissolving the alloy $\mathrm{K_4Ge_9}$ in ethylenediamine. The compounds $[\mathrm{K}\text{-}([2.2.2]\mathrm{crypt})]_6\mathrm{Ge_9Ge_9}\cdot(\mathrm{ethylenediamine})_x$ with $x = 0.5$ (**2a**, brown) and 1.5 (**2b**, red) crystallize in the $P\bar{1}$ space group with two independent cluster anions and six $[\mathrm{K}\text{-}([2.2.2]\text{-crypt})]^+$ units. The structures are almost isotypic, but differ by their cell parameters at 233 K (**2a**, $a = 14.397(1)$ Å, $b = 19.765(2)$ Å, $c = 28.898(2)$ Å, $\alpha = 87.485(9)°$, $\beta = 79.168(9)°$, $\gamma = 85.415(8)°$; **2a**, $a = 14.503(1)$ Å, $b = 19.924(2)$ Å, $c = 28.935(3)$ Å, $\alpha = 87.43(1)°$, $\beta = 80.85(1)°$, $\gamma = 85.92(1)°$) and atomic parameters. The differences arise with two additional ethylenediamine molecules in the case of red **2b**. These solvent molecules were refined at 50% occupancy. The solvent molecules have a significant influence on the color of the crystals and the conformation of the deltahedral anions. The structures of the clusters correspond to C_{2v} distorted polyhedra that lie between the D_{3h} tricapped trigonal prism and the C_{4v} monocapped square antiprism. A geometrically deduced charge allocation $\mathrm{Ge_9}^{2-}$ and $\mathrm{Ge_9}^{4-}$ in an earlier study of a red compound with $x = 2.5$ and a less accurate structure refinement are not supported by the structures of the anions. EPR measurements on a single crystal of **2a** reveal paramagnetic properties and presumably equal 3− charges for each of the two independent anions.

Introduction

The existence of nonagermanide clusters in solution has been known for a long time.[1] The anions form by reduction of the element germanium with alkali metals similar to synthetic procedures developed for lead and tin anions.[2−7] The most successful approach to crystalline products containing nine-atom germanium clusters is the extraction of A−Ge alloys (A = Na, K) with ethylenediamine (en) and addition of the sequestering agent [2.2.2]crypt to the solutions.[8−10] Using this method three compounds containing nine atom clusters of germanium have been characterized by single-crystal analyses: $[\mathrm{K}\text{-}([2.2.2]\text{-}\mathrm{crypt})]_6\mathrm{Ge_9Ge_9}\cdot2.5\mathrm{en}$ (**2c**),[11] $[\mathrm{K}\text{-}([2.2.2]\mathrm{crypt})]_3\mathrm{Ge_9}\cdot0.5\mathrm{en}$ (**1a**),[12] and $[\mathrm{K}\text{-}([2.2.2]\mathrm{crypt})]_3\mathrm{Ge_9}\cdot\mathrm{P(C_6H_5)_3}$ (**1b**).[13] The structure of the ten-atom anion $\mathrm{Ge_{10}}^{2-}$ with a bicapped square-antiprismatic structure was resolved from a $^1/_3$:$^2/_3$ disorder of the anions.[13] And just recently, a five-atom closo cluster known already in the case of tin and lead[14] was established for germanium.[15] An octahedral closo cluster synthesized by a different route was found in $[\mathrm{Ge_6\{Cr(CO)_5\}_6}]^{2-}$.[16]

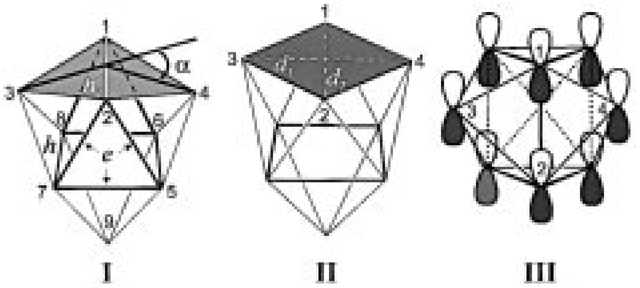

Figure 1. Conformations and frontier orbital of nine-vertex polyhedra. (**I**) Tricapped trigonal prism with C_{3v} symmetry (closo cluster). (**II**) Monocapped square antiprism with C_{4v} symmetry (nido cluster). (**III**) LUMO of cluster type **I** for 22 skeletal electrons. For explanations and values of the marked parameters see text and Table 3.

The single-crystal structure determination of **2c** containing nonagermanide clusters was solved more than 20 years ago and is still exceptional.[11] **2c** was the first example of a structure containing two kinds of cluster anions with different shapes and six $[\mathrm{K}\text{-}([2.2.2]\mathrm{crypt})]^+$ counterions. Although the quality of the X-ray data refinement of **2c** was not great ($R_1 = 0.149$), the structures of the two cluster ions were well resolved. The structure of one anion (**A**) was described as a tricapped trigonal prism **I** with one prism edge h elongated and thus between the boundary structures **I** and a monocapped square antiprism **II** (cf. Figure 1) The second anion (**B**) adapts structure type **II** almost perfectly. On the basis of structural arguments and applying Wade rules, a disproportionation into closo $\mathrm{Ge_9}^{2-}$ (20

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10.1021/ic981157j CCC: $18.00

skeletal electrons) and nido Ge_9^{4-} (22 skeletal electrons) rather than two Ge_9^{3-} units (21 skeletal electrons) was proposed.[11]

Because of the uniqueness of the nine-atom homoatomic closo structure, "Ge_9^{2-}" is cited in many textbooks,[17-19] despite the strong distortion of the Ge_9^{2-} anion, the uncertainty of the charge allocation to the individual clusters, and regardless of the observation that the structure is close to similarly distorted anions in **1a** and **1b**, synthesized and characterized over a decade later. Both compounds **1a** and **1b** contain paramagnetic Ge_9^{3-} cluster anions as shown by EPR measurement.[12,13,20]

There are two more findings that furthered the controversy about conformations of nonagermanide ions. On one hand, we found two independent cluster anions from single-crystal analyses of two isotypic monoclinic crystals [K-([2.2.2]-crypt)]$_6$E$_9$E$_9$•2.5en (E = Sn, Pb). The structure of one cluster (**A**) refined to an almost D_{3h} species **I**, and the second one (**B**) seemed to have perfect C_{4v} symmetry at the beginning of structure refinement. However, the analysis of the anisotropic displacement vectors showed, that in both cases the latter cluster **B** can be better described with a split model for some E atoms, leading to a superposition of two distorted units (rotated by 90°) with structures between **I** and **II**. We have further examined a single crystal of the tin compound by EPR and found a well-resolved anisotropic signal, showing the presence of paramagnetic E_9^{3-} clusters.[20,21] On the other hand, the recent discovery of nine-atom clusters in the diamagnetic binary phase Cs_4Ge_9 (**3**) shows that Ge_9^{4-} clusters possess C_{4v} symmetry with the topology of **II**. From there it was concluded again that cluster **B** in **2c** must be a 22-electron species and that thus **2c** contains the mixed valent cluster anions Ge_9^{4-} and Ge_9^{2-}.[22]

Following the experimental procedure for paramagnetic ions in **1a** described earlier,[12] we have now isolated two further single crystals with triclinic symmetry and the composition [K-([2.2.2]-crypt)]$_6$Ge$_9$Ge$_9$•0.5en (**2a**) and [K-([2.2.2]crypt)]$_6$Ge$_9$Ge$_9$•1.5en (**2b**). Even though the structures of the two crystals are almost isotypic, the crystals differ in color (deep brown and red, respectively) and the number of cocrystallized en molecules. Single-crystal structure refinements show two independent anions with different structures. All four cluster anions in **2a** and **2b** are well ordered and show significant distortions from D_{3h} and C_{4v} symmetry.

Experimental Section

Synthesis. The preparations of the alloys K_4Ge_9 and the extraction procedures were already described before[12] and are summarized here only briefly. After extraction of the alloy with ethylenediamine, the filtrate is added to solid [2.2.2]crypt and finally layered with toluene. Brick-shaped brown crystals of **2a** are formed within 1 week. For the crystallization of red **2a** approximately 50% of ethylenediamine is removed under vacuum after the extraction process. After addition of toluene clumps of red crystals of **2b** form at the bottom of the Schlenk tube.

Table 1. Crystallographic Data of {[K-(crypt)]$_3$Ge$_9$}$_n$(en)$_x$

compound	**1a**[12]	**2a**	**2b**	**2c**[a]
formula unit, n	1	2	2	2
number of en molecules, x	0.5	0.5	1.5	2.5
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	14.398(7)	14.397(1)	14.503(1)	14.546(2)
b [Å]	15.241(9)	19.765(2)	19.924(2)	20.037(2)
c [Å]	20.57(2)	28.898(2)	28.935(3)	28.984(2)
α [deg]	90.46(2)	87.485(9)	87.43(1)	87.60(1)
β [deg]	96.71(6)	79.168(9)	80.85(1)	80.644(8)
γ [deg]	114.09(4)	85.415(8)	85.92(1)	85.923(8)
V [Å^3]	4084(5)	8047(1)	8229(1)	8313(1)
Z	2	2	2	2
T [K]	193	233	233	293
	red needle	deep brown cube	deep red cube	deep red rod
R_1	0.102	0.075	0.088	0.149
R_w[b]	0.240	0.173	0.233	0.169[c]
μ [mm^{-2}]	3.48	3.53	3.45	3.6
ρ [g cm^{-3}]	1.57	1.58	1.53	

[a] After transformation of $a = 20.037(2)$ Å, $b = 28.944(2)$ Å, $c = 14.546(2)$ Å; $\alpha = 99.356(8)°$, $\beta = 94.077(8)°$, $\gamma = 87.60(1)°$ [11] to standard cell choice. [b] $R_w = \sqrt{\Sigma w(F_o^2 - F_c^2)^2/(\Sigma wF)}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$. [c] $R_w = \sqrt{\Sigma w(F_o - F_c)^2/(\Sigma wF_o^2)}$, $w = 1/[\sigma^2(F_o^2)]$.

X-ray Data Collection. Crystals were mounted in glass capillaries under the microscope in a drybox and checked on a Stoe IPDS diffractometer. The unit cell parameters (Table 1) were determined using 5000 reflections. The cell parameters of **2a** and **2b** are similar; however, the volume of **2b** is significantly larger. There are also significant differences in the cell parameters of **2c**, which were reported earlier using a different cell choice. Diffraction data of crystals of **2a** and **2b** were collected on a Stoe IPDS diffractometer with Mo Kα radiation and imaging plate detector at 80 mm and equipped with Oxford Cryosystem.

Structure Solution and Refinement. The structures were solved by direct methods (SHELXS-86), indicating the presence of two independent clusters. Difference Fourier analysis and least-squares cycles based on F^2 (SHELXTL) allowed the location of two well separated cluster units each consisting of nine Ge atoms and six (K-[2.2.2]crypt) units. The coordination of the potassium atoms were found to be very similar to the ones found earlier.[10] In **2a** six [-CH$_2$-CH$_2$-] groups and three O atoms of two (K-[2.2.2]crypt) units, and in **2b** two [-CH$_2$-CH$_2$-] groups were disordered and described with 50% split positions for the heavy atoms. The disordered parts of the cryptand molecules were refined with fixed C−C, C−N, and C−O bond lengths. Other heavy atoms beside the solvent molecules were refined anisotropically. The position of the hydrogen atoms of ordered C atoms were geometrically calculated and refined using a riding model with fixed bond lengths and temperature factors coupled to the attached heavy atoms. In **2a** one en molecule is symmetrically located around the inversion center leading to the final composition ([2.2.2]crypt)]$_6$Ge$_9$-Ge$_9$•0.5en. Further electron density maxima of 1 electron/Å^3 found in the final difference Fourier map are located close to Ge atoms. In **2b** the difference electron density toward the end of the refinement clearly indicates two further en molecules which could be refined at 50% occupancy rising in the total formula [K-([2.2.2]crypt)]$_6$Ge$_9$Ge$_9$•1.5en.

The structures of **2a** and **2b** are almost isotypic with **2c** after transforming the cell parameters of **2c** and shifting the origin of **2c** by the vector (0.5, 0, 0.5). The crystal quality does not depend on the number of en molecules. The best refinement of the three crystals was achieved for **2a**, which contains only 0.5 en molecules (located around the origin) per formula unit. The positions of the en molecules match approximately with the solvent molecules in the solvent richest compound **2c**. In an earlier study of **2c**, two en molecules were refined at full occupancy, however leading to very large displacement vectors and long C−C distances.

EPR Spectra. Spectra were recorded on a Varian E−12 EPR spectrometer. A single crystal of the brown crystal fraction **2a** with unknown orientation showed at room temperature an isotropic signal at $g = 2.04$. The lattice parameters were checked before on a Stoe IPDS imaging plate diffractometer.

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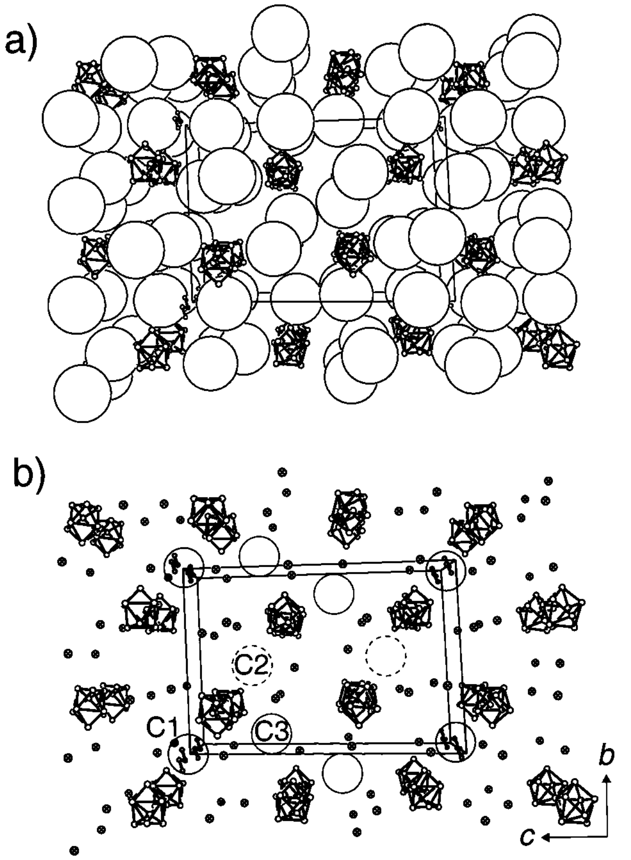

Figure 2. Unit cell of [K-([2.2.2]crypt)]$_6$Ge$_9$Ge$_9$(en)$_x$ viewed down the *a* axis. (a) Large circles represent the packing of the [K-([2.2.2]-crypt)]$^+$ units. (b) Small crosshatched circles indicate the K positions. Circle C1 includes the position of the en molecule in **2a**. The circles C2 and C3 indicate the cavities around the two additional en molecules in **2b** and **2c**.

Results

Crystal Packing. Crystal packing in **2a** and **2b** are similar to the one in **2c** reported earlier (after cell and origin transformations, see Experimental Section). The packing of the cationic [K$^+$-crypt] units creates channels in which the anionic clusters are located (Figure 2). Despite differences in crystal symmetry, such channels are found also in other crystal structures with the composition [K-crypt]$_3$E$_9$ (E = Ge, Sn, Pb; leaving cocrystallized solvent molecules out of consideration). The orientation of the clusters in these channels can differ.[23] Due to the irregularity of the anions and cations no dense packing is possible. There are three larger cavities with their centers approximately at the positions C1 (0.5, 0.0, 0.0), C2 (0.73, 0.53, 0.30), and C3 (0.93, 0.91, 0.32) as indicated in Figure 2. The colors of the compounds correlate with the number of solvent molecules. **2a** has a deep-brown color and contains only one en molecules centered around the inversion center C1. **2b** and **2c** are deep red and contain further en molecules in the cavities C2 and C3. In **2b** the two additional en molecules refine to 50% occupancy, in **2c** they were refined at full occupancy, however with large displacement vectors.

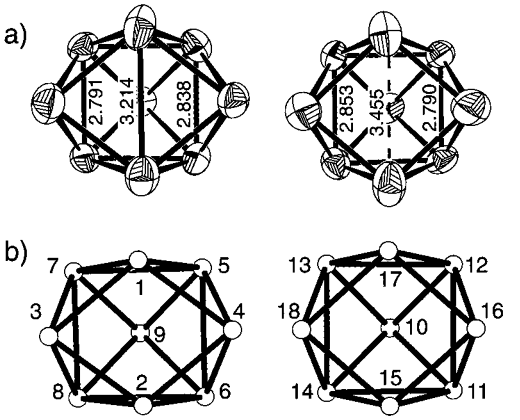

Figure 3. View of the $\mathrm{Ge_9}^{3-}$ anions in **2a**. (a) Cluster **A** (left) and **B** (right) with thermal ellipsoids shown at 50% probability level, atom labels see (b). (b) The same clusters shown as parallel projection emphasizing the different shapes of the two polyhedra.

Table 2. Significant Intercluster Distances (Å) in the Anions of the Compounds **2a** and **2b**

	2a	**2b**		**2a**	**2b**
Ge1−Ge4	2.573(2)	2.613(2)	Ge10−Ge11	2.562(2)	2.573(3)
−Ge3	2.587(2)	2.620(2)	−Ge13	2.580(1)	2.576(2)
−Ge5	2.614(2)	2.596(2)	−Ge12	2.585(2)	2.585(2)
−Ge7	2.627(2)	2.590(2)	−Ge14	2.598(2)	2.588(2)
−Ge2	3.214(2)	3.284(2)	Ge11−Ge16	2.608(2)	2.580(2)
Ge2−Ge4	2.574(2)	2.527(2)	−Ge15	2.631(1)	2.611(2)
−Ge3	2.577(2)	2.540(2)	−Ge12	2.790(2)	2.719(2)
−Ge6	2.599(2)	2.584(2)	−Ge14	2.792(2)	2.904(2)
−Ge8	2.643(9)	2.600(2)	−Ge13	3.951(2)	3.957(2)
Ge3−Ge8	2.611(2)	2.645(2)	Ge12−Ge17	2.622(2)	2.601(2)
−Ge7	2.623(2)	2.590(2)	−Ge16	2.624(2)	2.647(2)
−Ge4	4.028(2)	3.965(2)	−Ge13	2.796(2)	2.829(2)
Ge4−Ge5	2.594(2)	2.589(2)	−Ge14	3.990(2)	3.983(2)
−Ge6	2.640(2)	2.653(2)	Ge13−Ge17	2.588(2)	2.581(2)
Ge5−Ge9	2.572(2)	2.558(2)	−Ge18	2.628(2)	2.652(2)
−Ge7	2.817(2)	2.837(2)	−Ge14	2.853(2)	2.775(2)
−Ge6	2.838(2)	2.784(2)	Ge14−Ge18	2.591(2)	2.583(2)
−Ge8	3.961(2)	3.964(2)	−Ge15	2.614(2)	2.595(2)
Ge6−Ge9	2.597(2)	2.581(2)	Ge15−Ge16	2.576(2)	2.590(2)
−Ge8	2.783(2)	2.807(2)	−Ge18	2.592(2)	2.614(3)
−Ge7	3.979(2)	3.971(2)	−Ge17	3.455(2)	3.551(3)
Ge7−Ge9	2.586(2)	2.572(2)	Ge16−Ge17	2.595(2)	2.562(2)
−Ge8	2.791(2)	2.794(2)	−Ge18	3.858(2)	3.762(3)
Ge8−Ge9	2.594(2)	2.584(2)	Ge17−Ge18	2.598(2)	2.582(3)

Structures of Nonagermanide Anions. Besides the differences in crystal quality and data refinement there are unambiguous differences between the structures of the clusters. Each of the compounds **2a** and **2b** contains two crystallographically distinguishable clusters (Figure 3) which are denoted with **A** (Ge1 to Ge9) and **B** (Ge10 to Ge18). In both cases the two nine-atom clusters have structures between the boundary types **I** and **II** (Figure 1). The structures of the pair of clusters in **2a** are shown in Figure 3. Important distances are given in Table 2.

To assign the clusters to D_{3h} polyhedra **I**, C_{4v} polyhedra **II**, or C_{2v} or C_s intermediates, the following geometrical parameter are used (Figure 1, Table 3): The central unit in **I** is a trigonal prism which is characterized by the three prism edges h and basal edges e. Elongation or compression of the prism is expressed by the h/e ratio. Distortions from 3-fold symmetry become easily evident by differences in prism heights h_1 to h_3 or $d(1-2)$, $d(5-6)$, $d(7-8)$. For comparison reasons they are referred in Table 3 to the shortest one in **1a** (2.868 Å). As a result of different prism heights, opposed triangular prism faces deviate from coplanarity ($\gamma \neq 0$). The position of the capping atoms 3, 4, and 9 in **I** (Figure 1) can be described by cap-to-cap folds about each prism edge h (e.g. 1−2−3/1−2−4) or the dihedral angles α_1 to α_3 (180°−cap-to-cap fold angle). All 3-fold angles are equal if **I** possesses ideal D_{3h} point group symmetry.

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Table 3. Geometrical Parameters of Nine-Atom Clusters (cp. Figure 1)

				prism edges^{c,d}					dihedral cap to cap fold angle about h				
		a	e^b	h_1	h_2	h_3	γ^d	h/e^d	$\alpha_1{}^e$	α_2	α_3	$d_1/d_2{}^f$	
1a	$[Ge_9]^{3-}$		21	1.16	1.10	1^c	10	1.17	16	18	31	1.25	$\sim C_s$ [12]
1b	$[Ge_9]^{3-}$		21	1.14	1.12	0.98	10	1.17	14	17	32	1.17	$\sim C_s$ [13]
2a	$[Ge_9Ge_9]^{6-}$	**A**	21	1.12	0.99	0.97	10	1.10	5	23	24	1.25	$\sim C_{2v}$
	(brown)	**B**	21	1.21	0.97	1.00	17, 28	1.13	3	27	25	1.12	$\sim C_{2v}$
2b	$[Ge_9Ge_9]^{6-}$	**A**	21	1.15	0.97	0.97	13, 18	1.11	1	26	26	1.21	$\sim C_{2v}$
	(red)	**B**	21	1.24	0.97	0.95	20, 22	1.12	3	28	31	1.06	$\sim C_{2v}$
2c	$[Ge_9Ge_9]^{6-}$	**A**	20^g	1.12	0.99	0.98	9	1.11	8	23	25	1.26	$\sim C_{2v}$ [11]
	(red)	**B**	22^g	1.21	0.97	1.00	18, 24	1.21	5	24	32	1.02	$\sim C_{4v}$
3	$[Ge_9]^{4-}$	**A**	22	1.27	1.00	0.99	20, 25		4	26	30	1.02	$\sim C_{4v}$ [22]
		B	22	1.25	1.05	0.98	18, 25		7	25	33	1.04	$\sim C_{4v}$
		C	22	1.19	1.05	1.00	13, 31		11	23	27	1.12	$\sim C_{2v}$
		D	22	1.24	1.04	0.98	17, 29		6	24	27	1.07	$\sim C_{4v}$

[a] **A**, **B**, **C**, and **D** denote different cluster isomers E_9. [b] Electron count. [c] Relative prism heights, scaled to the value 2.868 Å. [d] The best trigonal prism is chosen. [e] Dihedral angle α with respect to the long prism height in **I** and the short diagonal in **II**, respectively. [f] The best monocapped square antiprism is chosen. [g] In $[K\text{-}(crypt)]_6Ge_9Ge_9\cdot 2.5en$ (**2c**) charge allocation for the clusters was based on structural arguments.[11]

For **II** with ideal C_{4v} point group symmetry, two angles are equal and the third is 0°. The angle α in Figure 1 and Table 3 also characterizes the deviation from planarity of the open square 1−2−3−4 if the cluster is regarded as a monocapped quadratic antiprism **II**. Starting with the description from boundary structure **II**, deviations from C_{4v} symmetry also show up in different diagonal lengths $d_1 = d(3-4)$ and $d_2 = d(1-2)$ of the open square 1−3−2−4 (Figure 1). To classify the distortions of **II** toward **I** the short diagonal is chosen as the third prism edge. The parameters describing the distortions for all known nonagermanide clusters are summarized in Table 3.

Inspection of the relative prism heights reveal that one cluster (denoted **A**) of the pairs in **2a**−**2c** is similarly or even more distorted from D_{3h} symmetry than those in **1a** and **1b**. The cluster in **1a** has three different heights, thus C_s symmetry results. In **1b** the anion has one short and two longer prism heights, whereas all clusters **A** in compounds **2** have two short and one longer height. In **1a** and **1b** three [K-crypt] units are present per one nine-atom anion and thus the clusters are paramagnetic. The 21 skeletal electron clusters in **1a** and **1b** show deviations in prism height of about 16%, clusters **A** in **2a**−**2c** between 14% and 18%. In summary, distortions with respect to different prism heights are in the range of 14−18% or expressed by the angle γ (deviation from coplanarity) from 9° to 13° and thus indicate strongly distorted prisms. The cap-to-cap fold angles about the prism heights h_1 to h_3 show that in the paramagnetic compounds **1** two angles are similar (14° to 18°) and one is significantly larger (>30°) implying approximately C_{2v} symmetry. In the compounds where more than one cluster is present (**2a**−**2c**) all clusters have an open rectangle of Ge atoms which is almost planar ($a = 1-8°$). The corresponding fold angle is about the longest edge h_1 of an assumed best trigonal prism.

Regarding the clusters as type-**II** polyhedra, h_1 becomes the short diagonal d_2. The corresponding diagonal distances of the open rectangle in clusters the first cluster species (**A**) of compounds **2** show large deviations as it is expressed by the ratio d_1/d_2 (21−26%). These clusters are therefore best described as monocapped square antiprisms which are compressed with respect to a mirror plane through two opposed atoms of the open square and the capping atom of the second square of the antiprism (atom number 9 in Figure 1). With exception of **2a**, the second cluster species (**B**) are close to C_{4v} symmetric polyhedra **II**: α_1 is close to 0 and the ratio d_1/d_2 is close to 1. In **2a**, which represents the best refined structure, the largest deviation in diagonal lengths is found (12% for the second cluster **B**). Remarkable is the fact that one cluster in Cs_4Ge_9 (**3**) has also a large deviation from C_{4v} symmetry (**C**, Table 3), even though all clusters in this binary phase clearly possess 22 skeletal electrons due to the number of K atoms.

An ideal trigonal prism consisting of six atoms of the same type might have equal bond lengths and thus the ratio of prism heights h and edges of the triangular faces e should be equal to 1. For the classic closo borane $B_9H_9{}^{2-}$ all rectangular faces of the trigonal prism of six B−H units are capped with B−H groups and h/e is 0.96. It was pointed out by Lohr[24] that the lowest unoccupied molecular orbital **III** (Figure 1) of such a 38-electron system (20 skeletal electrons + 18 electrons for nine external B−H bonds) is antibonding along the prism heights. Filling this orbital with one or two electrons should lead to an elongation of prism heights and to an distortion of the D_{3h} polyhedra. Substituting the external B−H bonds by nonbonding electron pairs leads to the isosteric homoatomic clusters E_9 under study. Extended-Hückel calculations for Ge_9 clusters with D_{3h} symmetry showed the same nodal properties of the highest occupied molecular orbitals.[25] For the 21-skeletal-electron clusters in **1a** and **1b** one additional electron is present and consequently the h/e ratio is larger (1.17). Adding two electrons, the prism heights could be further elongated and together with small rearrangements of the other atoms a C_{4v}-symmetric monocapped square antiprism of type **II** can result. Choosing the best trigonal prism in nine germanium atom polyhedra (the shortest diagonal of the open rectangle in **II** is chosen as third prism height) a maximal h/e ratio of 1.21 in compound **2c** results. This is about the value for an ideal C_{4v} polyhedron and represents the trend predicted from simple molecular orbital considerations. All clusters **A** in compounds **2** which might be considered as 20-skeletal-electron clusters show significantly larger h/e ratios than expected for closo compounds (1.0) but are smaller than the ones observed for 21-skeletal-electron clusters. As pointed out for **1a** and **1b** these clusters are C_{2v}-symmetric with one elongated prism height, in contrast to the 21-electron clusters of compound type **1** with three different prism heights.

The homoatomic clusters show the expected bond length trends in dependency of their number of skeletal electrons.

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(24) Lohr, L. L. *Inorg. Chem.* **1981**, *20*, 4229. See also: O'Neill, M. E.; Wade, K. *Inorg. Chem.* **1982**, *21*, 461

(25) Fässler, T. F. Unpublished results.

(26) Fässler, T. F.; Hoffmann, R. *Angew. Chem., Int. Ed.* **1998**, *38*, 543; 18-crown-6 = 1,7,10,13,16-hexaoxacyclooctadecane.

However, no clear distinction between 21- and 22-electron clusters is possible based on geometrical arguments.

Summary and Discussion

In summary, the two single-crystal X-ray structure investigations show that nonagermanide clusters do not have a strong correlation between observed structures and electron counts with respect to Wade rules. A similar observation was made recently for Sn_9^{4-} cluster anions. In $[K_4Sn_9(18\text{-crown-}6)_3]\cdot 1.0en$ and $[K\text{-}(18\text{-crown-}6)]_4Sn_9$, significant distortions of the clusters from the expexted C_{4v} symmetry are also observed.[26] ^{119}Sn NMR studies in solution reveal the fluctional behavior of Sn_9^{4-} and $Sn_{9-x}Pb_x^{4-}$ anions ($x = 0-9$).[27] Species generated from a AGeSn alloy (A = Na, K) which are probably $Sn_{9-x}Ge_x^{4-}$ ions ($x = 0-9$) show a similar behavior at room temperature.[28] In consequence we do not expect rigid structures in the solid state. Crystal packing and even influences by disordered solvent molecules have a significant influence on the arrangement of the atoms and eventually on the electronic properties as it is indicated by the brown and red color of **2a** and **2b**, respectively.

EPR measurements on a single crystal of **2a** show paramagnetic properties, thus fully disproportionation into Ge_9^{2-} and Ge_9^{4-} is unlikely. Since the structures of the anions in **2a** are similar to those in **2b**, small changes in cluster shapes might be responsible for the different colors of the compounds. The possibility of protonation of the solvent molecules as assumed in other cases[29] cannot be excluded but is unlikely because of strongly reducing conditions during the synthesis. Protonation of an en molecule would introduce an additional positive charge and the possibility of partial presence of Ge_9^{3-} anions beside Ge_9^{4-} anions.

Ge_9^{2-} is a nice textbook example for applying Wade electron counting rules also to naked homoatomic closo clusters. However, the results here show that an unambiguous prove for the existence of such an anion and its D_{3h}-closo structure is still a challenge.

Acknowledgment. This work was funded by a grant from the Eidgenössische Technische Hochschule Zürich (ETHZ).

Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determinations of **2a** and **2b** is available free of charge via the Internet at http://pubs.acs.org.

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(27) Pons, B. S.; Santure, D. J.; Taylor, R. C.; Rudolph, R. W. *Electrochim. Acta* **1981**, *26*, 365.

(28) Rudolph, R. W.; Wilson, W. L.; Taylor, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 2480.

(29) The presence of $[en\text{-}H]^+$ counterions was introduced for charge balance of $[Ge_2Se_6]^{2-}$ anions. However, there is no unambiguous proof for the presence of this unit. Park, C.-W.; Pell, M. A.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 4555.