Synthesis and Structure of [K$^+$-(2,2)diaza-[18]-crown-6][K_3Ge_9]·2Ethylenediamine: Stabilization of the Two-Dimensional Layer $^2_\infty[K_3Ge_9{}^{1-}]$

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Large bright-red, transparent crystalline plates of [K-(2,2)diaza-[18]-crown-6]K_3Ge_9·2*en* are obtained, in high-yield, from a reaction of (2,2)diaza-[18]-crown-6 in toluene with a solution of K_4Ge_9/potassium metal (K) in ethylenediamine (*en*). The compound crystallizes in the monoclinic space group $P2_1/m$ (a = 10.740(1) Å, b = 15.812(1) Å, c = 12.326(1) Å, β = 114.74°; Z = 2). The crystal structure of [K-(2,2)diaza-[18]-crown-6]K_3Ge_9·2*en* features two-dimensional [K_3Ge_9] layers formed by uncomplexed K^+ cations and $Ge_9{}^{4-}$ anions. The "not-so-bare" cluster compound features a unique $Ge_9{}^{4-}$ cluster that exhibits a slightly distorted C_{2v} geometry that is closer to D_{3h} than the expected C_{4v}. Use of noncryptand sequestering agents in the isolation of Ge cluster anions from *en* solutions opens new avenues in understanding important cation−anion interactions in the stability and reactivity of Zintl ions, as well as a viable route to isolating Zintl anions with higher charges per atom.

Introduction

The question of how properties of semiconductors evolve as dimensions approach interatomic distances is currently a topic of great scientific interest and technological implications.[1−5] Zintl anions of group 14 elements (Ge, Sn, Pb), in particular the germanium nine-atom clusters, offer a unique class of "naked" elemental cluster ions that represent a bridge between small clusters and their corresponding nanocrystalline bulk semiconductors.[6] The relevance of $Ge_9{}^{n-}$ anions was recently emphasized by the results of an unbiased global search for the ground-state structures of Si and Ge clusters.[2,7] Using molecular geometry optimization calculations, it was shown that the structures of medium-sized Si and Ge clusters are based on tricapped trigonal prism Si_9 and Ge_9 units.[2,5,7] Recently we have reported the synthesis of a novel polymeric $[Ge_9]^{2-}$ chain composed of *nido*-Ge_9 clusters linked through their vertexes.[8] Moreover, the preparation of similar $Ge_{18}{}^{6-}$ dimer anions lends support to the oxidative coupling of *nido*-Ge_9 clusters. The existence of the polymeric $[Ge_9]^{2-}$ cluster chain and the dimeric $[Ge_{18}]^{6-}$ anions provides support to the theoretical cluster models associated with larger Ge clusters based on tricapped trigonal prism units.[8,9] Thus, oxidative coupling of Ge cluster anions represents a viable chemical route to the controlled growth of larger Ge clusters and nanocrystals. Likewise, this has significant implications to the cluster chemistry of silicon.[7]

A number of homopolyatomic germanium Zintl cluster anions have been previously isolated from basic solution.[8−14] The general route to their isolation from ethylenediamine solution has been the use of strong sequestering agents for alkali metal ions, as in [2.2.2]cryptand. Recent investigations on the nature of $Ge_9{}^{n-}$ clusters in ethylenediamine (*en*) have addressed the validity of charge allocation assignments among $Ge_9{}^{n-}$ (n = 2−4).[10−12,15] These investigations posed questions on the existence of *closo*-$Ge_9{}^{2-}$ and the geometry of *nido*-$Ge_9{}^{4-}$. Thus, it became important to unambiguously isolate the *closo*-$Ge_9{}^{2-}$ and *nido*-$Ge_9{}^{4-}$ anions from appropriate alloy-*en* solutions. Previous investigations show that *en* solutions of K_4Ge_9 and alloys with similar nominal compositions yield only solid products with a ratio K:Ge = 3:9, when "extracted" with [2.2.2]-cryptand.[6] It is also important to note that *nido*-$Ge_9{}^{4-}$ clusters prepared via the solid state as "neat" binary salts exhibit essentially C_{4v} geometry.[16] To date, the only evidence of an isolated $Ge_9{}^{4-}$ cluster drawn from solution was observed in Rb_4Ge_9·*en*.[17] However, the crystallographic studies were not

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conclusive with several germanium atoms exhibiting "nonpositive definite" thermal parameters.[17] Thus, the ability to isolate the Ge_9^{4-} anion from ethylenediamine−alloy solutions without the use of sequestering agents was deemed promising. Considering the above observations, our attempts to isolate higher charged Ge_9^{4-} anion from K/Ge alloy−*en* solutions exploited trends in stability constants of the alkali metal complexes. In this work, it was presumed that the use of sequestering agents that result in alkali metal complexes with lower stability constants in *en* would allow the isolation of higher charged "not-so-naked" cluster anions with direct cation−anion interactions. These interactions would lower the net charge of the cation−anion "complex", and presumably promote the stabilization of anions with high formal charges per atom, as in $Ge_9^{4-} = Ge^{(-4/9)}$. The necessary prerequisites were fulfilled by the use of diaza-crown ethers whose alkali metal complexes exhibit significantly weaker stability constants in *en* than cryptands.[18] Herein we report the synthesis and structure of [K-(2,2)diaza-[18]-crown-6]K_3Ge_9·2*en* which features two-dimensional layers of $[K_3Ge_9^{1-}]$ and a "not-so-naked" Ge_9^{4-} anion with a C_{2v} distorted polyhedra that lies intermediate between a D_{3h} tricapped trigonal prism and a C_{4v} monocapped square antiprism.

Experimental Section

Synthesis. The compound [K-(2,2)diaza-[18]-crown-6]K_3Ge_9·2*en* (**1**) was obtained from the reaction of (2,2)diaza-[18]-crown-6 (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane) with potassium metal and a binary alloy with a nominal composition "K_4Ge_9" in "neat" *en*. All experimental handling and manipulations were carried out under an inert argon atmosphere within a glovebox with moisture levels < 0.1 ppm. All solvents were degassed, distilled, and dried accordingly. The (2,2)-diaza-[18]crown-6 (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane) was purchased from Aldrich and further oven- and vacuum-dried before use.

A binary alloy of composition K_4Ge_9 was prepared by high-temperature reactions of the pure elements within sealed Nb tubing. A 0.104 g sample of the precursor "K_4Ge_9" alloy was dissolved in "neat" ethylenediamine (3 mL) resulting in a brown-red solution. Subsequent addition and dissolution of 0.023 g (0.59 mmol) of potassium metal turned the opaque brown-red alloy−*en* solution to transparent and bright red. Identical results can be observed by the addition of a saturated (gold-colored) K−*en* solution to the brown-red alloy−*en* solution.

A separate solution of 0.067 g (0.255 mmol) of (2,2)diaza-[18]-crown-6 was prepared in 4 mL of "neat" toluene. Subsequently, aliquot portions (0.3 mL) of each K-alloy/*en* solution were slowly layered with (0.3 mL) portions of the diaza-crown/toluene solution. The formation of large transparent bright-red platelike crystals of **1** was observed within 24 h at room temperature. Consequently, compound **1** was obtained in high yields (>75%).

Structure Determination. Single-crystal X-ray analyses were performed on high-quality crystals of compound **1** formed from slow diffusion reactions. The single crystals were extremely air, moisture, and heat sensitive and were hence preserved in a mother liquor. Single crystals of **1** were subsequently isolated under mineral oil and Ar and mounted on glass fibers protected under Ar gas. The mounted crystal was then quickly mounted on a goniometer under the diffractometer cold stream (liquid N_2).

Diffraction intensities were measured, at −50 °C, on a Siemens SMART platform diffractometer with a 1K CCD area detector using Mo Kα radiation. A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 30 s/frame. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability, and the maximum correction on I was <1%. The data were integrated using the Siemens SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption and absorption due to variation in the path length through the detector faceplate. Empirical absorption correction was applied on the hemisphere of data and redundant reflections averaged. The space group was shown to be $P2_1/m$ with the following final cell constants $a = 10.7398(9)$ Å; $b = 15.812(1)$ Å; $c = 12.3259(10)$ Å, $\beta = 114.738(1)°$; $V = 1901.1(3)$ Å^3. Relevant data collection and structural refinement information are listed in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares calculations and refined to final R indices of $[I > 2\sigma(I)]$: R1 = 0.0318, wR2 = 0.0842; [all data]: R1 = 0.0410, wR2 = 0.0898, GOF = 1.024. Hydrogen atoms were located from a Fourier difference map and refined isotropically using a riding model ($d = 0.9$ Å). The final Fourier difference map was essentially featureless. The refinement also indicated that one *en* molecule is disordered 50:50 over two slightly shifted orientations. The list of relevant bond distances and angles is given in Table 2.

Table 1. Crystallographic Parameters for [K-(2,2)diaza-[18]-crown-6]K_3Ge_9·2*en*[a]

empirical formula	$K_4Ge_9C_{16}H_{22}N_6O_4$
formula weight	1192.27
temp (K)	223(2)
space group	$P2_1/m$
a (Å)	10.7398(9)
b (Å)	15.8121(13)
c (Å)	12.3259(10)
β (deg)	114.7380(10)
vol (Å^3)	1901.1(3)
Z	2
λ (Å)	0.710 73
ρ_{calc}	2.083 mg/m^3
μ (mm^{-1})	7.478
goodness-of-fit (GOF)	1.024
final R indices $[I > 2\sigma(I)]$	R1 = 0.0318; wR2 = 0.0842
R indices (all data)	R1 = 0.0410; wR2 = 0.0898
largest diff. peak and hole	0.880 and −0.648 e Å^3

[a] GOF = $[\Sigma(w(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$. R1 = $(\Sigma||F_o| - |F_c||)/(\Sigma|F_o|)$. wR2 = $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Results and Discussion

In our synthetic work, attempts to isolate Ge_9^{4-} anion clusters with [2.2.2]cryptand from brown-red and bright-red alloy solutions yielded only crystalline salts containing Ge_9^{3-} and $[K_4Ge_{18}]^{2-}$ clusters.[19] Moreover, the yields of the cluster anions were observed to be lower for reactions involving the potassium-richer bright-red alloy solutions.

Dissolution of "less-reduced" alloys with germanium-richer compositions (e.g., "KGe_4") in *en* resulted in dark green alloy−*en* solutions. Isolation of Ge_9 clusters from the green alloy solutions, using [2.2.2]cryptand, produced predominantly Ge_9^{2-} anions, as well as very low yields of isolated Ge_9^{3-} and dimeric $[K_4Ge_{18}]^{2-}$ anions. The reaction of [18]crown-6 with the dark green alloy−*en* solutions affords the $[Ge_9]^{2-}$ polymer anions.[8]

Consequently, the seemingly reversible color changes (green-to-brown-to-red) of the alloy *en* solutions can be induced by the addition of appropriate amounts of potassium metal. These observations strongly imply that the color of alloy−*en* solutions and the seemingly reversible changes they exhibit are useful indicators of the degree of reduction (bright red) or oxidation (forest green) of the germanium anion clusters in *en*. Further electrochemical and spectroscopic studies are currently in progress to elucidate the solution chemistry of the Ge_9 anions.

The title compound [K-(2,2)diaza-[18]-crown-6]K_3Ge_9·2*en* (**1**) crystallizes in the monoclinic space group $P2_1/m$. X-ray

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Table 2. Selected Bond Lengths [Å] and Angles [deg] for [K(2,2) diaza-[18]-crown-6}K_3Ge_9•2*en*

Ge(1)−Ge(3) (2×)	2.5720(6)	Ge(1)−Ge(2) (2×)	2.5964(7)
Ge(2)−Ge(4) (2×)	2.6046(7)	Ge(2)−Ge(5)	2.6267(6)
Ge(2)−Ge(3)	2.7197(6)	Ge(2)−Ge(2)	2.9087(9)
Ge(3)−Ge(6) (2×)	2.5740(6)	Ge(3)−Ge(5)	2.6136(6)
Ge(4)−Ge(5) (2×)	2.5731(6)	Ge(5)−Ge(6) (2×)	2.5858(6)
K(1)−Ge(6)	3.434(1)	K(1)−Ge(5)	3.959(1)
K(2)−Ge(6)	3.3998(8)	K(2)−Ge(2)	3.6941(9)
K(2)−Ge(3)	3.5977(9)	K(2)−Ge(5)	3.5019(9)
K(2)−Ge(5)	3.5224(9)	K(3)−Ge(4)	3.568(2)
K(2)−Ge(3)	3.6117(9)	K(3)−Ge(6)	3.492(2)
K(1)−K(2)	4.422(1)	K(1)−K(2)	4.422(1)
K(3)−K(2)	4.2808(13)	K(2)−K(2)	4.108(2)
K(2)−K(3)	4.2808(13)	K(1)−N(2)	2.793(5)
K(1)−N(1)	2.882(4)	K(1)−O(1)	2.923(3)
K(1)−O(2)	2.938(3)	K(2)−O(1)	2.912(3)
K(2)−N(3)	3.032(5)	K(2)−C(2)	3.535(5)
K(3)−N(4′)	2.699(11)	K(3)−N(4)	2.888(9)
K(3)−N(3)	3.411(6)	K(3)−C(8′)	3.482(14)
Ge(6)−K(1)−Ge(5)	40.16(2)	Ge(5)−K(1)−Ge(5)	50.37(2)
Ge(6)−K(2)−Ge(5)	43.97(1)	Ge(6)−K(2)−Ge(5)	136.31(3)
Ge(5)−K(2)−Ge(5)	108.41(2)	Ge(6)−K(2)−Ge(3)	137.94(3)
Ge(5)−K(2)−Ge(3)	93.96(2)	Ge(5)−K(2)−Ge(3)	43.06(1)
Ge(6)−K(2)−Ge(3)	42.94(1)	Ge(5)−K(2)−Ge(3)	43.08(1)
Ge(5)−K(2)−Ge(3)	93.37(2)	Ge(3)−K(2)−Ge(3)	110.52(2)
Ge(6)−K(2)−Ge(2)	177.38(3)	Ge(5)−K(2)−Ge(2)	137.64(3)
Ge(5)−K(2)−Ge(2)	42.61(1)	Ge(3)−K(2)−Ge(2)	43.77(1)
Ge(3)−K(2)−Ge(2)	135.88(3)	Ge(6)−K(3)−Ge(4)	159.34(5)
Ge(3)−Ge(1)−Ge(3)	71.31(2)	Ge(3)−Ge(1)−Ge(2)	63.50(2)
Ge(3)−Ge(1)−Ge(2)	101.93(2)	Ge(3)−Ge(1)−Ge(2)	101.93(2)
Ge(3)−Ge(1)−Ge(2)	63.50(2)	Ge(2)−Ge(1)−Ge(2)	68.13(3)
Ge(1)−Ge(2)−Ge(4)	107.89(2)	Ge(1)−Ge(2)−Ge(5)	107.37(2)
Ge(4)−Ge(2)−Ge(5)	58.93(2)	Ge(1)−Ge(2)−Ge(3)	57.81(2)
Ge(4)−Ge(2)−Ge(3)	103.19(2)	Ge(5)−Ge(2)−Ge(3)	58.50(1)
Ge(1)−Ge(2)−Ge(2)	55.93(1)	Ge(4)−Ge(2)−Ge(2)	56.06(1)
Ge(5)−Ge(2)−Ge(2)	95.04(1)	Ge(3)−Ge(2)−Ge(2)	90.94(1)
Ge(1)−Ge(3)−Ge(6)	105.76(2)	Ge(1)−Ge(3)−Ge(5)	108.51(2)
Ge(6)−Ge(3)−Ge(5)	59.79(2)	Ge(1)−Ge(3)−Ge(2)	58.69(2)
Ge(6)−Ge(3)−Ge(2)	102.87(2)	Ge(5)−Ge(3)−Ge(2)	58.97(2)
Ge(5)−Ge(4)−Ge(5)	81.81(2)	Ge(5)−Ge(4)−Ge(2)	60.96(2)
Ge(5)−Ge(4)−Ge(2)	104.24(2)	Ge(5)−Ge(4)−Ge(2)	104.24(2)
Ge(5)−Ge(4)−Ge(2)	60.96(2)	Ge(2)−Ge(4)−Ge(2)	67.89(3)
Ge(4)−Ge(5)−Ge(6)	97.84(2)	Ge(4)−Ge(5)−Ge(3)	107.13(2)
Ge(6)−Ge(5)−Ge(3)	59.34(2)	Ge(4)−Ge(5)−Ge(2)	60.11(2)
Ge(6)−Ge(5)−Ge(2)	105.17(2)	Ge(3)−Ge(5)−Ge(2)	62.53(2)
Ge(3)−Ge(6)−Ge(3)	71.25(2)	Ge(3)−Ge(6)−Ge(5)	105.79(2)
Ge(3)−Ge(6)−Ge(5)	60.87(2)	Ge(3)−Ge(6)−Ge(5)	60.87(2)
Ge(3)−Ge(6)−Ge(5)	105.79(2)	Ge(5)−Ge(6)−Ge(5)	81.32(2)

single-crystal structure determination confirms that **1** contains four potassium ions for one unique Ge_9 cluster and agrees with a negative charge of 4 for the polyatomic anion. The crystal structure, as shown in Figure 1, features a layered structure consisting of salt-like intermetallic slabs of [$K_3Ge_9$$^{1-}$] alternately stacked with and isolated by "organic" layers of "cluster-capping" K$^+$-(2,2)diaza-[18]-crown-6 complex cations (K1) and *en* molecules. The layered [$K_3Ge_9$$^{1-}$] structure can be described in terms of nominal "ion-pair" [K_2Ge_9] chains, running along *b*, as building units. The "ion-pair" [K_2Ge_9] chains are illustrated in Figure 2. The "not-so-naked" Ge_9^{4-} clusters in the chain are linked through a pair of potassium ions (K2) that cap triangular faces of neighboring clusters. The bridging role of the K2 atoms in the "ion-pair" [K_2Ge_9]$^{2-}$ chain is also observed for Cs atoms that "link" [Cs_4Ge_{18}]$^{2-}$ clusters in [K-[2.2.2]crypt]$_2$[Cs_4Ge_{18}]•6*en*.[9]

Connecting parallel neighboring "ion-pair" [K_2Ge_9]$^{2-}$ chains along the *a* axis results in the layered structure of **1**, as shown in Figure 3. The "ion-pair" chains are connected in two ways: (a) through potassium atoms (K3) that join adjacent Ge_9 clusters of neighboring chains and (b) through *en* solvent molecules that coordinate adjacent K2 ions of neighboring [K_2Ge_9]$^{2-}$ chains. A second *en* molecule, disordered over two slightly shifted ("rocking") orientations, coordinates every chain-linking K3 cation in a bidentate manner. The coordination of K3 by *en* effectively fills-in the gaps between linked "ion-paired" chains. Each complex cation [K$^+$-(2,2)diaza-[18]-crown-6] caps the "exposed" open base of the Ge_9^{4-} clusters. Thus, the bidentate *en* molecules and the complex cation practically sheath and isolate the [$K_3Ge_9$$^{1-}$] slabs. Additional stabilization of the layered anion formation comes from the interaction between the oxygen atoms of the sequestering agent and face-bridging potassium (K2) manifested by the short O−K distances.

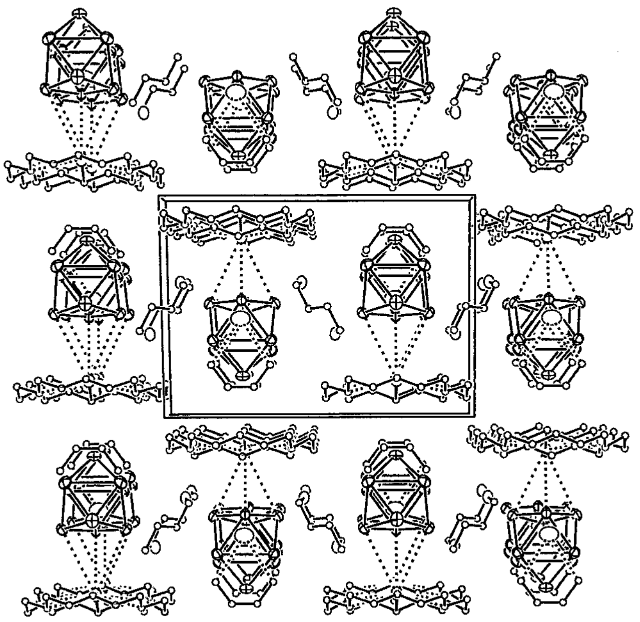

Figure 1. A [100] view of the unit cell of **1**. Ge and K atoms are represented as crosshatched and open ellipsoids, respectively. Lighter atoms (C, N, O) are represented as small circles. Ellipsoids are drawn at 60% probability. For clarity, only one orientation of the disordered *en* solvent molecule is drawn.

The important feature of **1** is the Ge_9^{4-} anion, shown in Figure 4. The excellent structural refinement of **1**, with low standard deviations, allows for a definitive geometric description of the Ge_9^{4-} anion. The crystal structure reveals that the Ge_9^{4-} anion exhibits C_s symmetry. Inspection of the bond distances, dihedral angles, and diagonal distances leads to the conclusion that the 22-electron cluster is approximately C_{2v} and close to D_{3h}, contrary to Wade's rules.[20] When compared with known *nido*-Ge_9 clusters, the anion in **1** is significantly distorted from C_{4v}.[8−10,16,17] A list of known distances and Ge_9 cluster dimensions is given in Table 4 for comparison. The calculated height (*h*)/edge (*e*) ratio of 1.17, prism heights (2.909(1) Å, 2.998(1) Å, and 3.370(1) Å), and dihedral angles for the nominal tricapped trigonal prism (11°, 23°, and 26°) illustrate the significant deviations of the Ge_9^{4-} anion in **1** from C_{4v} symmetry. Furthermore, the diagonal distances in the nominal "square base" for a monocapped square antiprism in **1** are significantly unsymmetrical (d_1/d_2 ratio = 1.16). Thus, the geometry of the Ge_9^{4-} cluster compares well with that of known Ge_9^{3-} anions, found in Ge cluster compounds with crystallographically unique cluster units, which are essentially closer to being tricapped trigonal prism (D_{3h}).[10−12] The possibility of having a Ge_9^{3-} anion is discounted by the presence of one unique cluster and confirmed by magnetic susceptibility measurements which indicate that compound **1** is diamagnetic.

The observed deviations from ideal C_{4v} values may be manifestations of the layered nature of the crystal structure and

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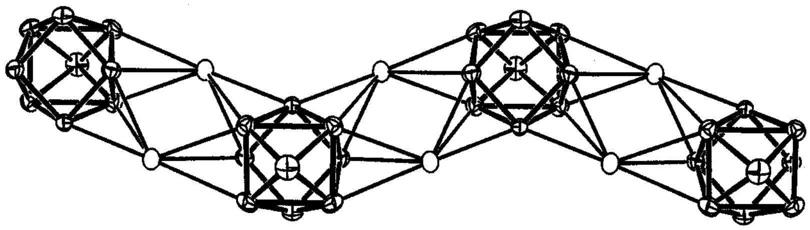

Figure 2. ORTEP representation of the "ion-paired" $[K_2Ge_9]^{2-}$ chain in **1**. Ge and K2 atoms are represented as crosshatched and open ellipsoids, respectively. Distances between K2 and Ge that range from 3.400(1) to 3.694(1) Å are drawn for clarity. Ellipsoids are drawn at 90% probability.

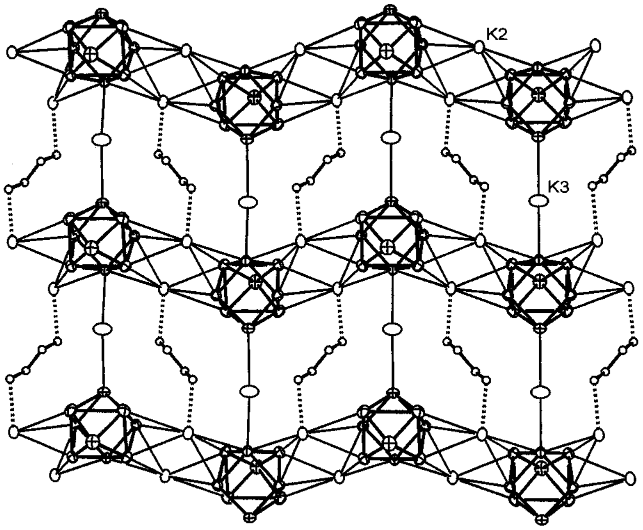

Figure 3. ORTEP representation of the $[K_3Ge_9]^{1-}$ slab in **1**. Ge and K atoms are represented as crosshatched and open ellipsoids, respectively. Lighter atoms (C and N) are represented as small circles. Distances between Ge and K atoms are drawn as thin solid lines. Coordination of K2 by *en* is drawn as dashed lines for clarity. Ellipsoids are drawn at 60% probability.

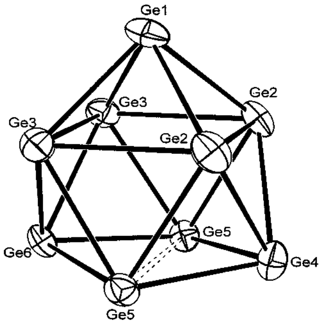

Figure 4. ORTEP representation of the unique Ge_9^{4-} cluster in **1**. Ellipsoids are drawn at 50% probability. Bond lengths [Å] within the cluster: Ge1−Ge2 2.5964(7), Ge1−Ge3 2.5720(6), Ge2−Ge2 2.9087(9), Ge2−Ge3 2.7197(6), Ge2−Ge4 2.6046(7), Ge2−Ge5 2.6267(6), Ge3−Ge3 2.9980(7), Ge3−Ge5 2.6136(6), Ge3−Ge6 2.5740(6), Ge4−Ge5 2.5731(6), Ge5−Ge6 2.5858(6). The distance Ge5−Ge5, represented by a dashed line, is 3.3702(6) Å.

Table 3. Relevant Geometrical Parameters in Some Isolated Ge_9^{n-} Clusters and Related Nine-Atom Clusters

		prism heights					
cluster	symmetry	h1	h2	h3	*h*/*e*	α1[a]	ref
Ge_9^{4-}	C_s ($\sim D_{3h}$)	2.90	3.00	3.37	1.17	11	this work
Ge_9^{4-}	$\sim C_{4v}$	2.83	2.88	3.62		4	24b
Ge_9^{4-}	$\sim C_{4v}$	2.80	2.99	3.54		6	24b
Ge_9^{4-}	$\sim C_{4v}$	2.81	3.00	3.58		7	24b
Ge_9^{4-}	$\sim C_{2v}$	2.87	3.01	3.41	1.17	11	24b
Ge_9^{4-}	$\sim C_{4v}$	2.78	2.87	3.47		5	10
Ge_9^{2-}	C_{2v} ($\sim D_{3h}$)	2.81	2.84	3.21	1.11	8	10
Ge_9^{3-}	C_s ($\sim D_{3h}$)	2.81	3.21	3.27	1.17	14	11a
Ge_9^{3-}	C_s ($\sim D_{3h}$)	2.87	3.15	3.33	1.17	16	11b
Bi_9^{5+}	D_{3h}	3.74	3.74	3.74	1.15	22	21a
Bi_9^{5+}	$\sim D_{3h}$	3.70	3.70	3.98	1.19	16	21b
Sn_9^{4-}	$\sim C_{2v}$ ($\sim D_{3h}$)	3.32	3.45	3.54	1.14	15	22
Sn_9^{4-}	$\sim C_{2v}$ ($\sim D_{3h}$)	3.35	3.38	3.74	1.15	13	22
Pb_9^{4-}	C_{2v} ($\sim D_{3h}$)	3.45	3.90	3.90	1.16	17	23
Si_9^{4-}	$\sim D_{3h}$	2.67	2.94	3.08	1.16	19	24a

[a] Angle α1 is the smallest "cap-to-cap" dihedral (waist) angle.

can be attributed to the direct cation−anion interactions of the "not-so-naked" cluster compound and to the "softness" of the Ge_9^{4-} anion. Moreover, the crystal packing effects of non-spherical complex cations and co-crystallized solvent molecules may play significant roles in the local symmetry of the anionic Ge_9 clusters in the solid state. However, a *nido*-E_9^{4-} that exhibits nearly D_{3h} geometry can also be rationalized in terms of electronic effects analogous with those observed for the Bi_9^{5+} cation and Sn_9^{4-} anions in $[K_4Sn_9([18]\text{-crown-6})_3]$ and $[K_4Sn_9([18]\text{-crown-6})_4]$.[6a,21−22] Furthermore, inspection of cluster geometry parameters in the solid-state compounds K_4Pb_9, Cs_4Ge_9, and $Rb_{12}Si_{17}$ indicate that at least one type of Pb_9^{4-}, Ge_9^{4-}, or Si_9^{4-} cluster anion in each compound, respectively, exhibits significant distortion toward D_{3h} symmetry.[6a,23−24] These ions form a separate group of nine-atom *22-electron* clusters that mainly exhibit elongated trigonal prisms and larger height-to-edge (*h/e*) ratios that correlate with the stabilization of the *a″* orbital (HOMO for 22-electrons) of a D_{3h} (E_9)-cluster.[6a,22−24] The relevant molecular orbital is found to be antibonding with respect to the trigonal prism lengths and bonding with respect to the triangular faces of the trigonal prism. Comparisons of geometric ratios indicate close similarities between the unique anion in **1** with non-Wade's rule clusters Bi_9^{5+}, Sn_9^{4-}, Ge_9^{4-} (1 of 4 clusters in Cs_4Ge_9), and Pb_9^{4-} (1 of 2 clusters in K_4Pb_9).[21−23] Hence, the Ge_9^{4-} anion in **1** may be considered a representative of this group of non-Wade's rule clusters. Thus, the findings of this work prove that assigning charge allocation to Ge_9^{n-} anions solely based on geometric parameters is insufficient.

Our findings support earlier proposals that the first steps of "alloy" solvation in *en* does not involve the immediate breaking of the intimate close contact between cations and the distinct anionic clusters.[17] Our results suggest that the solvation process is an "exfoliation" of the alloy structure into lower-dimensional derivative "ion-pair" structures of "not-so-naked" anions with lower net negative charges.

Of course, the isolation and crystallization of large unligated anion clusters depend on several rather complex and subtle factors (e.g., ionic sizes, cation−cation and anion−anion

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interactions, anion−cation interactions, nature of the solvent, solute−solvent effects). However, the successful use of noncryptands (e.g., [18]-crown-6 and (2,2)diaza-[18]-crown-6) with weaker sequestering abilities, in addition to controlled concentration, significantly add new synthetic handles for investigating the important chemistry of polyanionic clusters in ethylenediamine and in similar basic solvents.

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Supporting Information Available: X-ray crystallographic file in CIF format for the structure determination of [K-(2,2)diaza-[18]-crown-6]K_3Ge_9·2*en*. This material is available free of charge via the Internet at http://pubs.acs.org.

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