Inorg. Chem. **2004**, *43*, 1992–1997

Inorganic Chemistry
Article

The Role of Sequestering Agents in the Formation and Structure of Germanium Anion Cluster Polymers

Craig Downie, Jiang-Gao Mao, Hiten Parmar, and Arnold M. Guloy*

Department of Chemistry and the Center for Materials Chemistry, University of Houston, Houston, Texas 77204-5003

Received June 20, 2003

Large blue-green, transparent crystalline needles of [K-(2,2)diaza-[18]-crown-6]KGe_9•3en are prepared, in high yield, from the reaction of (2,2)diaza[18]-crown-6 in toluene with a solution of “KGe_4” in ethylenediamine (en). The compound crystallizes in the orthorhombic space group *Pnma* ($a = 10.9763(12)$ Å, $b = 27.265(3)$ Å, $c = 13.880(1)$ Å; $Z = 4$). The crystal structure of [K-(2,2)diaza-[18]-crown-6]KGe_9•2en features one-dimensional $[KGe_9]^-$ bare intermetallic chains formed from the linking, via *exo*-bonds, of *nido*-Ge_9^{2-} clusters. Uncomplexed K atoms effectively cap the square bases of the monocapped square antiprismatic $[Ge_9]^{2-}$ clusters. The optical band gap of the title compound is 1.25 eV. The use of weaker sequestering agents in the isolation of Ge cluster anions from en solutions provides an additional handle in a controlled molecular route to preparing new low-dimensional Zintl phases.

Introduction

Renewed interest on polyhedral Zintl anion clusters is motivated by interesting problems of significant scientific interest and technological implications. Some of these scientific problems pertain to how properties of bulk semiconductors evolve as their dimensions approach interatomic distances.[1−5] The polyhedral anions of group 14 elements (Ge, Sn, Pb), in particular the germanium 9-atom clusters, offer a unique family of bare elemental clusters that represents a direct link between small molecular clusters and their corresponding nanophase and solid-state semiconductors.[6] Furthermore, the chemical analogy of Zintl polyhedral cluster anions with novel fullerenes is too obvious to ignore.[7]

The relevance of Ge_9^{n-} anions to the structures of nanoscale semiconductors was recently emphasized by results of theoretical studies on the ground state structures of Si and Ge clusters.[2,8] Using geometry optimization calculations, Ho and co-workers showed that the structures of medium-sized Si and Ge clusters are based on tricapped-trigonal prismatic Si_9 and Ge_9 units.[2,5,8] We have reported the synthesis of a polymeric $[Ge_9]^{2-}$ chain in [K-18-crown-6]$_2$$Ge_9$.[9] The novel polymer anion of vertex linked *nido*-Ge_9 clusters provides credence to the theoretical model that large Ge and Si clusters are based on tricapped trigonal prismatic units. Moreover, Sevov’s preparation of related oligomers, Ge_{18}^{6-} [10] and Ge_{27},$^{6-}$[11] as well as the recently reported functionalized cluster anion, $Ph_2Bi{-}Ge_9{-}BiPh_2$,[12] lends support to the oxidative coupling and reactivity of these anionic clusters. These results further suggest that oxidative coupling of Zintl anion clusters offers viable low-temperature routes to the controlled growth of larger clusters and metastable Ge phases.

Our attempts to isolate Ge_9^{n-} anion clusters and polymers from K/Ge alloy−en solutions exploited trends in stability constants of the alkali metal complexes. The possibility of

---

* To whom correspondence should be addressed. E-mail: aguloy@uh.edu.

(1) (a) Brus, L. E.; Szajowski, P. F.; Wilson, W. L.; Harris, T. D.; Schuppler, S.; Citrin, P. H. *J. Am. Chem. Soc.* **1995**, *117*, 2915. (b) Heath, J. R. *Science* **1992**, *258*, 1131. (c) Jarrold, M. F.; Honea, E. C. *J. Phys. Chem.* **1991**, *95*, 9181. (d) Bley, R. A.; Kauzlarich, S. M. *J. Am. Chem. Soc.* **1996**, *118*, 12461.

(2) Ho, K. M.; Shvartsbyrg, A. A.; Pan, B.; Lu, Z.-Y.; Wang, C.-Z.; Wacker, J. G.; Fye, J. L.; Jarrold, M. F. *Nature* **1998**, *392*, 582.

(3) (a) Vasiliev, I.; Ögut, S.; Chelikowsky, J. R. *Phys. Rev. Lett.* **1997**, *78*, 4805. (b) Ögüt, S.; Chelikowsky, J. R. *Phys. Rev.* **1997**, *B55*, R4914.

(4) Hunter, J. M.; Fye, J. L.; Jarrold, M. F. *Phys. Rev. Lett.* **1994**, *73*, 2063.

(5) Lu, Z.-Y.; Wang, C.-Z.; Ho, K.-M. *Phys. Rev.* **2000**, *B61*, 2329.

(6) (a) Corbett, J. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 671. (b) Corbett, J. D. *Struct. Bonding* **1997**, *87*, 157. (c) von Schnering, H.-G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 33.

(7) Faessler, T. F. *Angew. Chem., Int. Ed. Engl.* **2001**, *113*, 4289.

(8) (a) Shvartsburg, A. A.; Jarrold, M. F.; Liu, B.; Lu, Z.-Y.; Wang, C.-Z.; Ho, K.-M. *Phys. Rev. Lett.*, **1998**, *81*, 4616. (b) Shvartsburg, A. A.; Liu, B.; Lu, Z.-Y.; Wang, C.-Z.; Jarrold, M. F.; Ho, K.-M. *Phys. Rev. Lett.* **1999**, *83*, 2167. (c) Liu, B.; Lu, Z.-Y.; Wang, C.-Z.; Ho, K.-M.; Shvartsburg, A. A.; Jarrold, M. F. *J. Chem. Phys.* **1998**, *109*, 9401.

(9) Downie, C. D.; Tang, Z.; Guloy, A. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 338.

(10) Xu, L.; Sevov, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 9245.

(11) Ungrinov, A.; Sevov, S. C. *J. Am. Chem. Soc.* **2002**, *124*, 10990.

(12) Ungrinov, A.; Sevov, S. C. *J. Am. Chem. Soc*. **2002**, *124*, 2442.

10.1021/ic034704w CCC: $27.50

using sequestering agents other than cryptands was first shown in the case of Sn_9^{4-} that was isolated using crown ethers.[13] Use of alkali metal sequestering agents with different molecular shapes and varying degrees of stability constants of their alkali metal complexes in en would allow the isolation of germanium cluster anions with direct alkali metal−anion interactions.[14,15] Herein we report the synthesis, structure, and properties of [K-(2,2)diaza-[18]-crown-6]-KGe_9·3en that features a new Zintl anion polymer, $_{1\infty}[KGe_9]^-$.

Table 1. Crystallographic Data for **1**

fw	1174.17
cryst color	blue-green
cryst dimensions	0.44 × 0.14 × 0.08 mm^3
T (K)	223(2)
cryst syst	orthorhombic
space group	*Pnma*
a (Å)	10.9763(12)
b (Å)	27.265(3)
c (Å)	13.880(2)
V (Å^3)	4153.9(8)
Z	4
λ (Å)	0.71073
ρ_{calcd}	1.878 Mg/m^3
μ (mm^{-1})	6.649
θ range for data collection (deg)	1.65−24.17
reflns collected	18911
indep reflns	3381 [R(int) = 0.0980]
GOF on F^2	1.191
final R indices [$I > 2\sigma(I)$]	R1 = 0.0621; wR2 = 0.1627
R indices (all data)	R1 = 0.1077; wR2 = 0.2079
largest diff peak and hole	1.533 and −1.473 e·Å^3

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **1**[a]

	x	y	z	U(eq)
K1	−1.0148(3)	0.2500	0.4784(3)	0.0781(14)
K2	−1.5000	0.5000	0.5000	0.0730(12)
Ge1	−0.93903(11)	0.2500	0.21236(12)	0.0444(5)
Ge2	−0.71388(12)	0.2500	0.23244(12)	0.0452(5)
Ge3	−1.07485(10)	0.32470(5)	0.23665(10)	0.0550(5)
Ge4	−0.99877(10)	0.30143(6)	0.06103(10)	0.0644(5)
Ge5	−0.73993(9)	0.30204(5)	0.39020(10)	0.0579(5)
Ge6	−1.15536(18)	0.2500	−0.03147(14)	0.0844(8)
N1	−1.3140(12)	0.5664(6)	0.5543(11)	0.111(5)
N2	−1.3269(16)	0.4210(7)	0.460(2)	0.186(11)
N3	−1.1739(13)	0.3295(7)	0.5133(12)	0.118(5)
N4	−0.973(6)	0.2500	0.686(5)	0.38(3)
N5	−0.834(6)	0.2500	0.807(5)	0.40(4)
O1	−1.3848(15)	0.5567(6)	0.3564(10)	0.119(5)
O2	−1.3919(13)	0.4892(6)	0.6844(10)	0.122(5)
C1	−1.463(3)	0.5720(16)	0.2802(19)	0.23(2)
C2	−1.318(3)	0.5976(10)	0.392(2)	0.192(18)
C3	−1.2398(19)	0.5793(8)	0.470(2)	0.160(14)
C4	−1.245(2)	0.5477(9)	0.638(2)	0.167(15)
C5	−1.325(2)	0.5318(9)	0.7185(18)	0.175(17)
C6	−1.477(3)	0.4704(14)	0.7570(16)	0.23(3)
C7	−1.2095(19)	0.4186(8)	0.5008(19)	0.137(8)
C8	−1.1267(15)	0.3770(8)	0.5095(15)	0.116(7)
C9	−0.922(6)	0.2995(19)	0.687(4)	0.25(4)
C10	−0.859(4)	0.3027(11)	0.783(3)	0.144(17)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor. Only non-hydrogen atoms are listed.

Experimental Section

Synthesis. The title compound, [K-(2,2)diaza-[18]crown-6]KGe_9·3en (**1**), was obtained from the reaction of (2,2)diaza-[18]crown-6 (1,4,10,13 tetraoxa-7,16 diazacyclo-octadecane) with a binary alloy, with a nominal composition "KGe_4", in neat en. The binary alloy of nominal composition, KGe_4, was prepared via high-temperature reactions between pure elements (Aldrich) at 1000 °C, within sealed Nb tubes enclosed in quartz jackets. All manipulations and reactions were carried out under an Ar atmosphere. All solvents were degassed, distilled, and dried accordingly. Crown ethers were oven- and vacuum-dried before use. A sample (0.120 g) of the binary alloy, "KGe_4", was dissolved in neat en (5 mL) immediately forming a dark green solution. A separate solution of [2.2]diaza-(18) crown-6 (1,4,10,13 tetraoxa-7,16 diaza-cyclooctadecane) was prepared by dissolving 0.065 g (0.551 mmol) of the crown ether in neat toluene (4 mL). The crown ether solution was slowly added and layered on the green alloy solution, as 0.3 mL aliquot portions of each. Formation of translucent light green-blue, flat, needlelike crystals was observed after two weeks. Using a slight excess of the [2.2]diaza-(18) crown-6 also resulted in the formation of the title compound. The extremely moisture and heat sensitive crystals, preserved in the mother liquor, were found to be of compound **1** (yield of 20−30% based on the crown ether).

Structure Determination. Single crystals of **1** were selected for X-ray diffraction analyses. The single crystals were kept under dry hydrocarbon-based grease inside an argon-atmosphere glovebox, with total moisture and O_2 content of <0.01 ppm. Single crystals mounted on glass fibers were quickly placed on a goniometer under a cold nitrogen stream (−50°C), and data were collected using a Siemens SMART diffractometer, equipped with a 1K CCD detector. A hemisphere of data was collected at −50 °C, with an exposure time at 30 s/ frame. The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability.

Diffraction data were integrated using the Siemens SAINT program and corrected for Lorentz factor and polarization. Redundant reflections were averaged, and empirical absorption corrections were applied to the hemisphere of data. The space group *Pnma*, chosen on the basis of Laue symmetry and systematic absences, was subsequently confirmed by the results of least-squares refinement. The final cell constants were $a = 10.9763(12)$ Å; $b = 27.265(3)$ Å; $c = 13.880(2)$ Å; $V = 4153.9(8)$ Å^3. A total of 18911 reflections were collected of which 3381 were independent.

The structure was solved by direct methods and refined by full-matrix least-squares calculations. Final refinement converged and led to satisfactory final R indices [$I > 2\sigma$] of R1 = 0.0621, wR2 = 0.1627; for all data, R1 = 0.1077, wR2 = 0.2079. All non-hydrogen atoms were refined anisotropically resulting in well-behaved thermal parameters for Ge, K, and two ethylenediamine molecules (C and N). One ethylenediamine molecule was found to exhibit rotational disorder as manifested by the partial occupancies (50%) over two sites of the carbon positions. The nitrogen atoms of the disordered en molecule were reasonably ordered. Hydrogen atoms were assigned to ideal positions and refined isotropically using a riding model ($d = 0.9$ Å). Relevant crystallographic data, atomic coordinates, distances and angles for compound **1** are listed in Tables 1, 2, and 3, respectively.

UV−Vis−NIR Spectroscopy and Magnetic Properties. Optical diffuse reflectance spectra were collected at room temperature using a CARY-500 Scan UV−vis−NIR spectrophotometer. A white standard of poly(tetrafluoroethylene) was used as a reference. Absorption spectra were calculated from the reflectance data using the Kubelka−Munk function:[16]

---

(13) Fässler, T. F.; Hoffmann, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 543.

(14) Downie, C. Ph.D. Thesis, University of Houston, 2002.

(15) Downie, C.; Mao, J.-G.; Guloy, A. M. *Inorg. Chem.* **2001**, *40*, 4721.

(16) Kotiim, G. *Reflectance Spectroscopy*; Springer-Verlag: New York, 1969.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for **1**

Ge1	Ge2	2.487(2)		K1	Ge2	3.653(5)	
Ge1	Ge2	3.113(2)		K1	Ge1	3.786(5)	
Ge1	Ge3	2.5466(15)	(2×)	K1	Ge3	3.981(4)	(2×)
Ge1	Ge4	2.6093(18)	(2×)	K1	N3	2.826(15)	
Ge2	Ge3	2.5810(15)	(2×)	K1	N3	2.826(15)	
Ge2	Ge5	2.6248(19)	(2×)	K1	N4	2.92(6)	
Ge3	Ge5	2.6009(17)		K2	O1	2.822(14)	
Ge3	Ge4	2.654(2)		K2	O1	2.822(14)	
Ge3	Ge3	4.074(2)		K2	N1	2.830(14)	
Ge4	Ge6	2.563(2)	(2×)	K2	N1	2.830(14)	
Ge4	Ge5	2.7322(15)		K2	O2	2.836(12)	
Ge4	Ge4	2.804(3)		K2	O2	2.836(12)	
Ge5	Ge6	2.592(2)	(2×)	K2	N2	2.92(2)	
Ge5	Ge5	2.838(3)		K2	N2	2.92(2)	
K1	Ge5	3.552(4)	(2×)				

Ge5	K1	Ge5	47.09(7)	Ge2	K1	Ge3	39.23(5)
Ge5	K1	Ge2	103.41(11)	Ge1	K1	Ge3	38.18(5)
Ge5	K1	Ge1	58.47(7)	Ge5	K1	Ge3	69.24(7)
Ge2	K1	Ge1	49.43(7)	Ge2	K1	Ge3	39.23(5)
Ge5	K1	Ge3	93.11(10)	Ge3	K1	Ge3	61.55(8)
Ge5	K1	Ge3	69.24(7)	Ge2	Ge1	Ge3	124.54(4)
Ge3	Ge1	Ge3	106.23(7)	Ge4	Ge1	Ge4	65.01(8)
Ge2	Ge1	Ge4	109.87(6)	Ge1	Ge2	Ge3	127.31(4)
Ge3	Ge1	Ge4	61.94(5)	Ge3	Ge2	Ge3	104.21(7)
Ge3	Ge1	Ge4	112.91(6)	Ge3	Ge2	Ge5	110.63(7)
Ge1	Ge2	Ge5	89.15(6)	Ge3	Ge4	Ge4	103.84(4)
Ge3	Ge2	Ge5	59.94(5)	Ge5	Ge4	Ge4	90.35(4)
Ge5	Ge2	Ge5	65.44(8)	Ge6	Ge5	Ge3	113.12(6)
Ge1	Ge3	Ge2	74.75(5)	Ge6	Ge5	Ge2	107.23(6)
Ge1	Ge3	Ge5	97.36(6)	Ge3	Ge5	Ge2	59.19(5)
Ge2	Ge3	Ge5	60.87(5)	Ge6	Ge5	Ge4	57.48(6)
Ge1	Ge3	Ge4	60.19(5)	Ge3	Ge5	Ge4	59.62(5)
Ge2	Ge3	Ge4	98.63(6)	Ge2	Ge5	Ge4	95.62(5)
Ge5	Ge3	Ge4	62.65(5)	Ge6	Ge5	Ge5	56.81(4)
Ge6	Ge4	Ge1	106.13(6)	Ge3	Ge5	Ge5	103.74(4)
Ge6	Ge4	Ge3	112.33(7)	Ge2	Ge5	Ge5	57.28(4)
Ge1	Ge4	Ge3	57.87(5)	Ge4	Ge5	Ge5	89.65(4)
Ge6	Ge4	Ge5	58.52(6)	Ge4	Ge6	Ge4	66.34(8)
Ge1	Ge4	Ge5	92.71(5)	Ge4	Ge6	Ge5	64.01(5)
Ge3	Ge4	Ge5	57.73(5)	Ge4	Ge6	Ge5	99.25(8)
Ge6	Ge4	Ge4	56.83(4)	Ge5	Ge6	Ge5	66.37(8)
Ge1	Ge4	Ge4	57.49(4)				

$$\alpha/S = (1 - R)^2/2R$$

R is the reflectance at a given wavelength ($\lambda = 200-2000$ nm), α is the absorption coefficient, and S is the scattering factor.

Magnetic susceptibility measurements were performed using an Oxford Instruments Maglab 9 T vibrating sample magnetometer (VSM). The magnetic susceptibilities were measured under applied fields of 1 and 3 T, and over a temperature range 10−300 K.

Results and Discussion

Homopolyatomic germanium cluster anions have been isolated from ethylenediamine solution using the general route of strong sequestering agents for alkali metal ions, as in [2.2.2]cryptand.[17,18] This technique arguably takes advantage of lattice energy effects afforded by large cation complexes to crystallize the unligated anions. Later investigations showed that *nido*-E_9^{4-} (E = Ge, Sn, Pb) clusters can also be prepared via the solid state as "neat" binary salts.[19] More recently, E_9^{4-} anions were also crystallized from solution as crown ether salts and as solvates (e.g., $\text{Rb}_4\text{Ge}_9\cdot$en).[20] In these novel salts, direct alkali metal-cluster interactions remain, and thus, a direct relationship between the solution-based Zintl anions and solid-state Zintl phases was established. Consequently, the isolation and crystallization of Zintl anions from ethylenediamine−alloy solutions without the use of sequestering agents can be viewed as a promising soft-chemical approach to new complex Zintl polar intermetallic phases.

Diaza-crown ethers form alkali metal complexes with significantly weaker stability constants in en than cryptands and corresponding crown ethers.[21,22] Use of diaza-crown ethers was recently applied to the preparation of [K-(2,2)-diaza-[18]-crown-6]$\text{K}_3\text{Ge}_9\cdot$2en.[15] The compound features an intermetallic $[\text{K}_3\text{Ge}_9]^{1-}$ slab with direct interactions between K and the Ge_9^{4-} cluster. The successful use of cryptands and noncryptands (e.g., [18]-crown-6 and (2,2)diaza-[18]-crown-6) with varying degrees of binding alkali metals significantly adds a useful handle for the isolation of unusual polyanionic Zintl intermetallic clusters, with direct metal−cluster interactions, from ethylenediamine.

The title compound crystallizes in the space group *Pnma*, $Z = 4$. The asymmetric unit consists of one [K-[2.2]diaza-(18)crown-6]$^+$ complex, one uncomplexed K atom, one $[\text{Ge}_9]^{2-}$ unit, and three en molecules. The crystal structure, as shown in Figure 1, features parallel anionic chains of $_{1\infty}[\text{KGe}_9]^{1-}$ that extend along the *a* axis. Adjacent chains form nominal $[\text{KGe}_9]^{1-}\cdot$en layers, with en molecules as chain "spacers", along the *a*−*c* plane. The spacer en molecules within the nominal slab exhibit rotational disorder of the carbon positions, and effectively separate the parallel $[\text{KGe}_9]^{1-}$ chains. The $[\text{KGe}_9]^{1-}\cdot$en layers are alternately stacked, along the *b* axis, with cationic layers of [K-[2.2]diaza(18)crown-6]$^+\cdot$2en. The two remaining types of en molecules coordinate the open sides of K$^+$-complex and serve as spacers that effectively separate the cationic and anionic slabs.

The unique $_{1\infty}[\text{KGe}_9]^{1-}$ polymer of **1**, as shown in Figure 2, can be described as a "buckled" up−down *trans* chain of *nido*-Ge_9 clusters capped by K atoms. The polymer is defined by intercluster *exo*-bonds that link the basal vertices of neighboring clusters. The intercluster *exo*-bond distance in $[\text{KGe}_9]^-$ of 2.487(1) Å is comparable to known Ge−Ge single bonds and reflects the polyhedral cluster linkage of the $[\text{Ge}_9]^{2-}$ polymer in $[\text{K[18]-crown-6}]_2\text{Ge}_9\cdot$en. The buckling or bending of the polymeric chain in the title compound with respect to the Ge_9^{2-} polymer in $[\text{K-(18-crown-6)}]_2\text{Ge}_9\cdot$en is manifested by the resulting angle (28.5°) formed by the exo-bond and the rhomboidal basal plane of the cluster. This is significantly larger than the analogous angle (6°) exhibited by the Ge_9^{2-} polymer in $[\text{K-(18-crown-6)}]_2\text{Ge}_9\cdot$en.

The Ge_9 cluster unit of the $[\text{KGe}_9]^-$ polymer resembles a slightly distorted monocapped square antiprism with C_{2v}

---

(17) Corbett, J. D. *Chem. Rev.* **1985**, *85*, 383.

(18) Corbett, J. D. *Struct. Bonding* **1997**, *87*, 157.

(19) (a) Queneau, V.; Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1754. (b) Queneau, V.; Sevov, S. C. *Inorg. Chem.* **1998**, *37*, 1358. (c) von Schnering, H. G.; Baitinger, M.; Bolle, U.; Carrillo-Cabrera, W.; Curda, J.; Grin, Y.; Heinemann, F.; Llanos, J.; Peters, K.; Schmeding, A.; Somer, M. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1037.

(20) Somer, M.; Carillo-Cabrera, W.; Peters, E. M.; Peters, K.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1915.

(21) Burgess, J. *Ions in Solution*: *Basic Principles of Chemical Interactions*; Ellis Horwood Ltd.: Chichester, U.K., 1998; pp 74−92.

(22) Lehn, J. M. *Tetrahedron Lett.* **1980**, *21*, 1323.

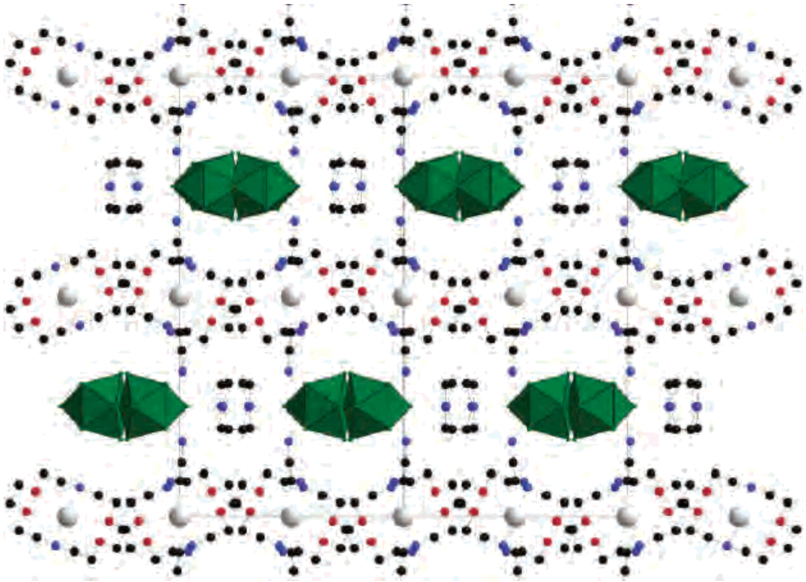


Figure 1. A [100] view of the unit cell of **1**: Ge_9 as polyhedra; K atoms as large spheres; C, N, and O as black, blue, and red spheres, respectively. Hydrogen atoms are not shown.

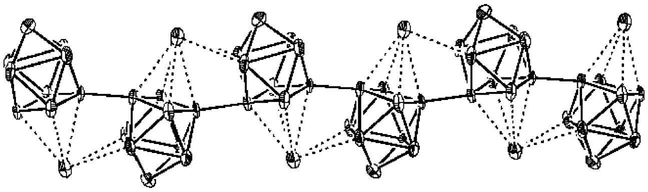


Figure 2. An ORTEP representation of the $[\mathrm{KGe}_9]^{1-}$ chain in **1**. Distances between K1 and Ge atoms that range from 3.552(1) to 3.981(1)Å are drawn as dashed lines. Ellipsoids are drawn at 50% probability.

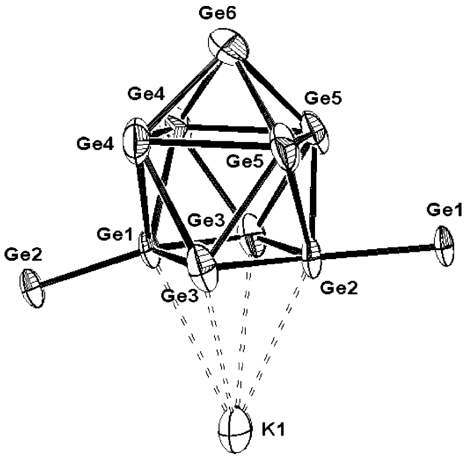


Figure 3. An ORTEP representation of the Ge−$[\mathrm{KGe}_9]$−Ge section of the $[\mathrm{KGe}_9]^{1-}$ polymer in **1**. Bond lengths [Å] within the cluster follow: Ge1−Ge2 2.487(1), Ge1−Ge3 2.547(1), Ge2−Ge3 2.581(1), Ge2−Ge5 2.625(1), Ge1−Ge4 2.609(1), Ge3−Ge5 2.601(1), Ge3−Ge4 2.654(1), Ge4−Ge4 2.805(1), Ge4−Ge5 2.2.732(1), Ge5−Ge5 2.838(1), Ge4−Ge6 2.563(1), Ge5−Ge6 2.592(1). Distances between K and Ge9 cluster are the following: K1−Ge1 3.786(5), K1−Ge2 3.653(5), K1−Ge3 3.981(4). Ellipsoids are drawn at 50% probability.

symmetry, as shown in Figure 3. The observed Ge−Ge cluster distances range from 2.547(1) to 2.838(1) Å and are consistent with the distances found in isolated *nido*-Ge_9^{4-} and in the $[\mathrm{Ge}_9]^{2-}$ polymer. The longest cluster edges are located at the trapezoidal "waist". A distinctive angular distortion from ideal C_{4v} symmetry of the monocapped square antiprismatic cluster is observed at the basal planes. This is manifested as a rhomboidal distortion and compression of the cluster basal planes along the polymer axis, resulting in basal angles of 106° and 75° at the *exo*-bonded and nonbonded vertices, respectively. The basal distortion also leads to a significantly larger anisotropy of the base diagonals ($d1/d2$ = 4.074 Å/3.113 Å = 1.31). Moreover, a slight "butterfly" distortion is observed around the long diagonal of the base (dihedral angle = 3.1°) that could be attributed to close approach of the uncomplexed K atom. The structure and bonding description of the *nido*-Ge_9 cluster polymer can be rationalized by Wade's rule.[23] The intermetallic polymer can be formulated as $-[\mathrm{KGe}_9{}^-]-[\mathrm{KGe}_9{}^-]-$ with covalent (single) bonds between *exo* Ge atoms of neighboring clusters. The formal charge on the cluster, assuming an ionic picture, is $\mathrm{Ge}_9{}^{2-}$, with each cluster anion having 40 electrons, appropriate for an isolated *closo*-Ge_9 cluster. However, the apparent electron deficiency for a *nido*-Ge_9 count is nicely satisfied by the formation of 2 intercluster Ge *exo*-bonds per cluster unit.

The uncomplexed K atoms lie between two adjacent Ge_9 clusters of the polymer. The coordination of the K atoms with respect to its two nearest neighboring Ge_9 clusters can be described as edge-bridging (η^2) on the first cluster, and square base capping (η^4) on the second Ge_9 cluster. The resulting skeletal structure of the Ge_9 chain in $[\mathrm{KGe}_9]^-$ is significantly distorted (bending) with respect to the regular $\mathrm{Ge}_9{}^{2-}$ polymer in $[\mathrm{K}\text{-(18-crown-6)}]_2\mathrm{Ge}_9{\cdot}\mathrm{en}$.[9] Despite the severe conformational distortion of the polymer, the Ge−Ge *exo*-bond length remains seemingly unaffected and suggests an angular flexibility of the intercluster bond.

The "solvation" role of alkali metal atoms in the neat binary cluster compounds is usually displayed by how the metal environment of the cluster is formed.[24] The metal coordination of the cluster consists of alkali metal ions that cap cluster faces, bridge edges, and terminate (outward from)

---

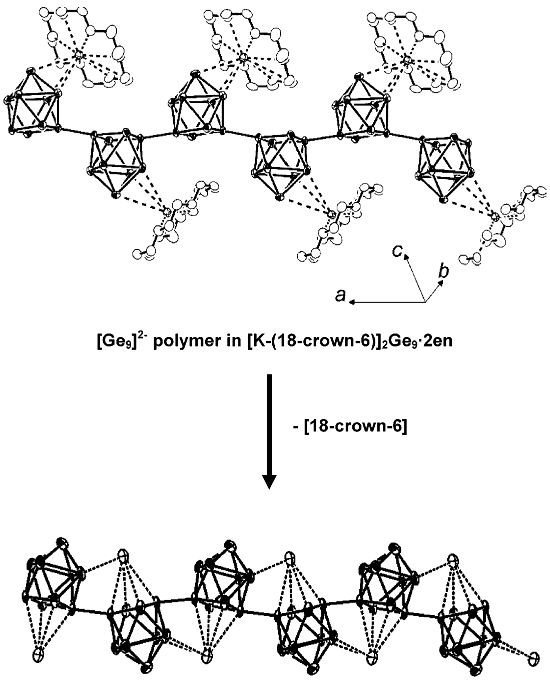
(23) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.
(24) Corbett, J. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 670.

vertices. Since post-transition metal clusters are polarizable, some covalent character between the alkali metals and the cluster is expected to arise. However, it is presumed that the electrostatic portion of these direct interactions is dominant, with the strongest interactions being attributed to the face-capping positions. Direct cation interactions with two or more clusters commonly serve as bridges to keep the cluster anions apart. The nonbridging role of the K atom in the $[KGe_9]^-$ polymer contrasts the common intercluster bridging (face-capping) role of the alkali metals in the one-dimensional chain structures of $[KSn_9]^{3-}$ and $[KPb_9]^{3-}$.[13,25−26] The unusual square base capping of the alkali metal has previously been observed in K(18-crown-6)$_4$Pb$_9$.[27] However, this is in contrast to the capping of the square base of the Ge_9^{4-} anion by [K-(2,2)diaza-[18]-crown-6] complex in [K-(2,2)diaza-[18]-crown-6]K_3Ge_9•2en.[15] In [K-(2,2)diaza-[18]-crown-6]K_3Ge_9•2en, the square base of the Ge_9^{4-} anion is distorted resulting in a cation face-capping that is essentially triangular.

The common face-capping coordination of alkali metals around E_9 clusters is through a triangular face. Interestingly, the unusual η^4 coordination of the uncomplexed K atom of the $[KGe_9]^-$ cluster unit in the novel polymer mirrors the role of Tl in the *closo*-$[TlSn_9]^{3-}$ Zintl polyanion,[28] and that of transition metal complexes in $[Cr(CO)_3E_9]^{4-}$ (E = Sn, Pb).[29,30] However, a naked *closo*-ME$_9$ cluster must have lone pairs at each vertex, and K atoms cannot provide the necessary electrons [20(lone pairs) + 22(skeletal) = 42; $[KGe_9]^-$ = 40]. Moreover, the highly acute Ge−K−Ge angles preclude 4-center−3-electron bonding. The observed structural behavior can be rationalized by the fact that the frontier orbitals in *nido*-E$_9$ polyhedral clusters show significant electron densities at the open square base of the 9-atom *nido*-clusters.[27,29] Thus, the observed square base-capping location of K in **1** can be considered to be electrostatically driven, while the triangular face-capping behavior of the K-(18-crown-6) complex in [K-(18-crown-6)]$_2$Ge$_9$•en is sterically directed. This structural relationship is summarized and illustrated in Scheme 1.

The structural relationship between the two cluster polymers is also reflected in the notable increase in instability of **1** to air and moisture, and the difference in their optical band gaps, as measured by UV−vis diffuse reflectance. The optical band gap (E_g) of **1**, that contains the naked $[KGe_9]^-$ polymer, is 1.25 eV. The measured band gap is smaller than the corresponding optical band gap, $E_g = 1.31$ eV, of [K-(18-crown-6)]$_2$Ge$_9$•en. The decrease in the optical band gap of **1** with respect to [K-(18-crown-6)]$_2$Ge$_9$•en can be attributed to the increased alkali metal-cluster interactions in $[KGe_9]^-$ that broaden and stabilize the energy bands derived from the germanium atoms at the basal plane of the cluster. Moreover, preliminary band structure calculations on the skeletal Ge$_9$ chain structures of the $[KGe_9]^-$ and Ge_9^{2-} polymers show that the "buckling" of the Ge$_9$ chain in $[KGe_9]^-$ also results in a slightly narrower band gap.[14]

Scheme 1



$[Ge_9]^{2-}$ polymer in [K-(18-crown-6)]$_2$Ge$_9$·2en

- [18-crown-6]

$[KGe_9]^{1-}$ polymer in (1)

An important aspect of the structural chemistry of the Ge$_9$ anionic polymers is the need for crown ethers as sequestering agents. So far, the *nido*-Ge$_9$ polymers have only been prepared and isolated with crown ethers as sequestering agents.[9] Furthermore, this is indicated by unsuccessful attempts to synthesize and isolate $[Ge_9]^{2-}$ cluster polymers with alkali metal cryptates, and the straightforward formation of the cryptate salt of the isolated *closo*-Ge_9^{2-} anion.[14] The structure of the (K-2,2,2 crypt)$_2$Ge$_9$ features isolated *closo*-Ge$_9$ clusters that exhibit severe orientational disorder in the solid state.[14] Attempts to prepare the cryptate salts of the polymeric structures also resulted in the isolation of the Ge_{18}^{6-} anions.[14] The failure to prepare cryptate salts of the Ge_9^{2-} polymer can be attributed to the matrix effects of the large spherical cation complex. Alkali metal cryptate complex cations inhibit the close approach of the Ge$_9$ clusters necessary for the formation of extended intercluster *exo*-bonds. In contrast, the disk-shaped alkali metal crown ether complexes allow for the close approach between cluster units, at least along one dimension, that results in the formation of the *exo*-bonded $[Ge_9]^{2-}$ and $[KGe_9]^-$ naked cluster polymers. The robustness of both the *nido*-Ge$_9$ cluster unit of the polymer and the intercluster *exo*-bonds is further evidenced by the η^4 capping rather than the expected intercluster bridging role of the K atom in the $[KGe_9]^-$ chain. The formation of similar adducts in **1** and [K-(18-crown-6)]$_2$Ge$_9$•en reflect sequestering and templating roles of the disk-shaped complexes of K with the crown ethers, (2,2)-diaza[18]-crown-6 and [18]-crown-6. However, the different

---

(25) Burns, R. C.; Corbett, J. D. *Inorg. Chem.* **1985**, *24*, 1489.
(26) Campbell, J.; Dixon, D. A.; Mercier, H. P.; Schrobilgen, G. J. *Inorg. Chem.* **1995**, *34*, 5798.
(27) Fassler, T. M.; Hoffmann, R. *J. Chem. Soc., Dalton Trans.* **1999**, 3339.
(28) Burns, R. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 2804.
(29) (a) Eichhorn, B. W.; Haushalter, R. C.; Pennington, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 8704. (b) Kesanli, B.; Fettinger, J. C.; Gardner, D. R.; Eichhorn, B. W. *Chem. Eur. J.* **2001**, 5277.
(30) Campbell, J.; Mercier, H. P.; Holger, F.; Santry, D.; Dixon, D. A.; Schrobilgen, G. J. *Inorg. Chem.* **2002**, *41*, 86.

$[KGe_9]^-$ anionic chains exhibited by the 2 polymeric compounds, in terms of the nature of the complexed potassium, can be rationalized in terms of the stability constants of the alkali metal complexes. The K-(2,2)diaza-[18]-crown-6 complex has a significantly weaker stability constant than its corresponding [18]-crown-6 complex.[22] Thus, the formation of the naked $[KGe_9]$ polymer in **1** reflects the weaker complexing ability of the diaza-crown with respect to [18]-crown-6.

The recent report on a novel $[HgGe_9]^{2-}$ chain in (K[2.2.2]-crypt)$_2$[$HgGe_9$](en)$_2$ provides further insight into the structural behavior of the Ge_9 cluster polymers.[31] In the $[HgGe_9]^{2-}$chains, Hg atoms are directly involved as intercluster covalent links between *nido*-Ge_9 units via Hg−Ge *exo*-bonds of the clusters. This role also contrasts that of K in $[KGe_9]^-$. The unexpected formation of a $[HgGe_9]^{2-}$ polymer with potassium cryptates can be rationalized in terms of the need for "bridge linkers" between cluster units. In $[HgGe_9]^{2-}$, the close packing problems posed by the spherical cation complex (K[2.2.2]crypt) that inhibits direct intercluster bonds are solved by the insertion of Hg as covalent bridges between Ge_9 clusters. The different packing effects of the cryptates on the $[HgGe_9]^{2-}$ chains, and the crown ethers on $[KGe_9]^-$, are illustrated in Figure 4. The steric and geometrical restrictions imposed by the nature of the complex cations are critical in the design and synthesis of Ge_9 anions (isolated and polymeric). The possibility of covalent functional links between Ge_9 clusters to form novel polymers is thereby enhanced by using appropriately sized complex cations as spacers between polymers, as well as by allowing the useful insertion of covalent bridging ligands.

To assess the electronic structure of compound **1**, magnetic measurements were taken on an ~80 mg sample using an Oxford Instruments VSM. The magnetic susceptibilities (10−300 K), corrected for diamagnetic core corrections and sample holder diamagnetism, were found to be negative and essentially temperature-independent ($\sim -1.55 \times 10^{-4}$ to -1.71×10^{-4} emu/mol, for $H = 3$ T). This behavior is similar to that exhibited by $[K\text{-}(18\text{-crown-}6)]_2Ge_9\cdot en$ and consistent with a diamagnetic semiconductor.

Conclusion

The surprising formation of **1** was realized by exploiting the nature of the alkali metal sequestering agents in the isolation and crystallization of germanide cluster polymers. Use of sequestering agents with a wide range of cation complex stability constants provides a useful handle in modulating cluster anion−cation supramolecular interactions. An improved understanding of these interactions and the reactivity of the cluster anions allow for the design and preparation of new polymeric structures. Moreover, rational synthesis of new low-dimensional polar intermetallics and Zintl phases, from the redox reactions of molecular Zintl anion building blocks and unsequestered cations, will be quite feasible.

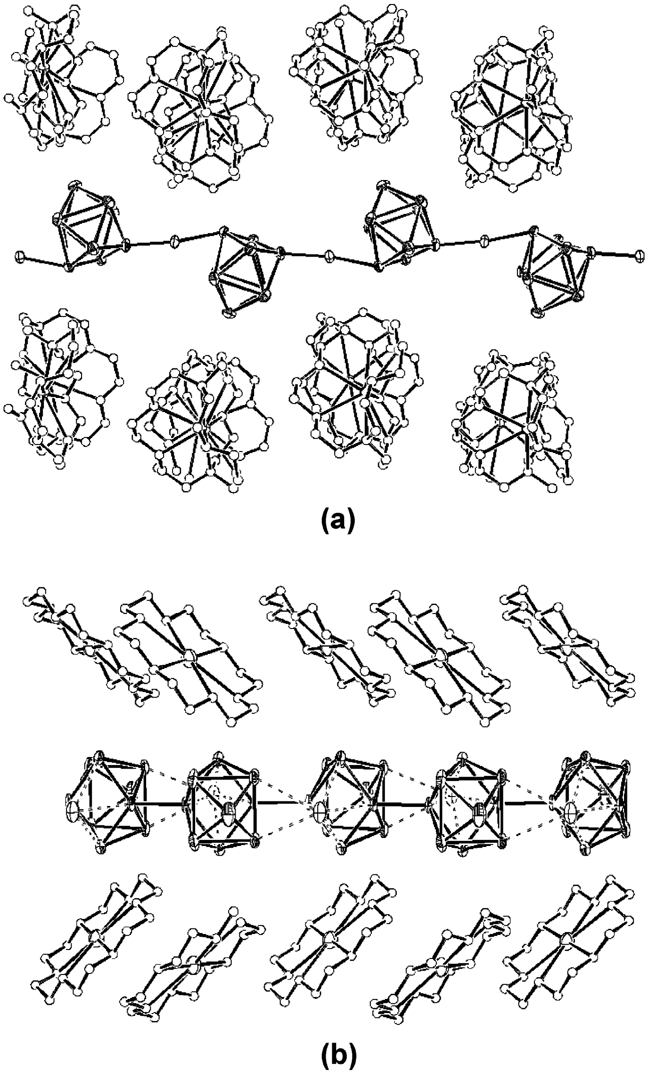


Figure 4. (a) The K-cryptate environment of $[HgGe_9]^{2-}$ in $[K(crypt)]_2[HgGe_9](en)_2$. (b) The K-diazacrown ether environment of $[KGe_9]^-$ in **1**.

Acknowledgment. Financial support from the Petroleum Research Fund, R. A. Welch Foundation, and the National Science Foundation (CAREER Award, DMR-9733587) is gratefully acknowledged. The Welch Scholars Summer Program provided support for H. Parmar. The work made use of MRSEC/TCSUH facilities at the University of Houston supported by the NSF (Grant DMR-9632667).

Supporting Information Available: Crystallographic data and structural information for compound **1** including positional parameters, thermal parameters, and bond distances and angles (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC034704W

---

[31] Nienhaus, A.; Hauptmann, R.; Faessler, T. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 3213.