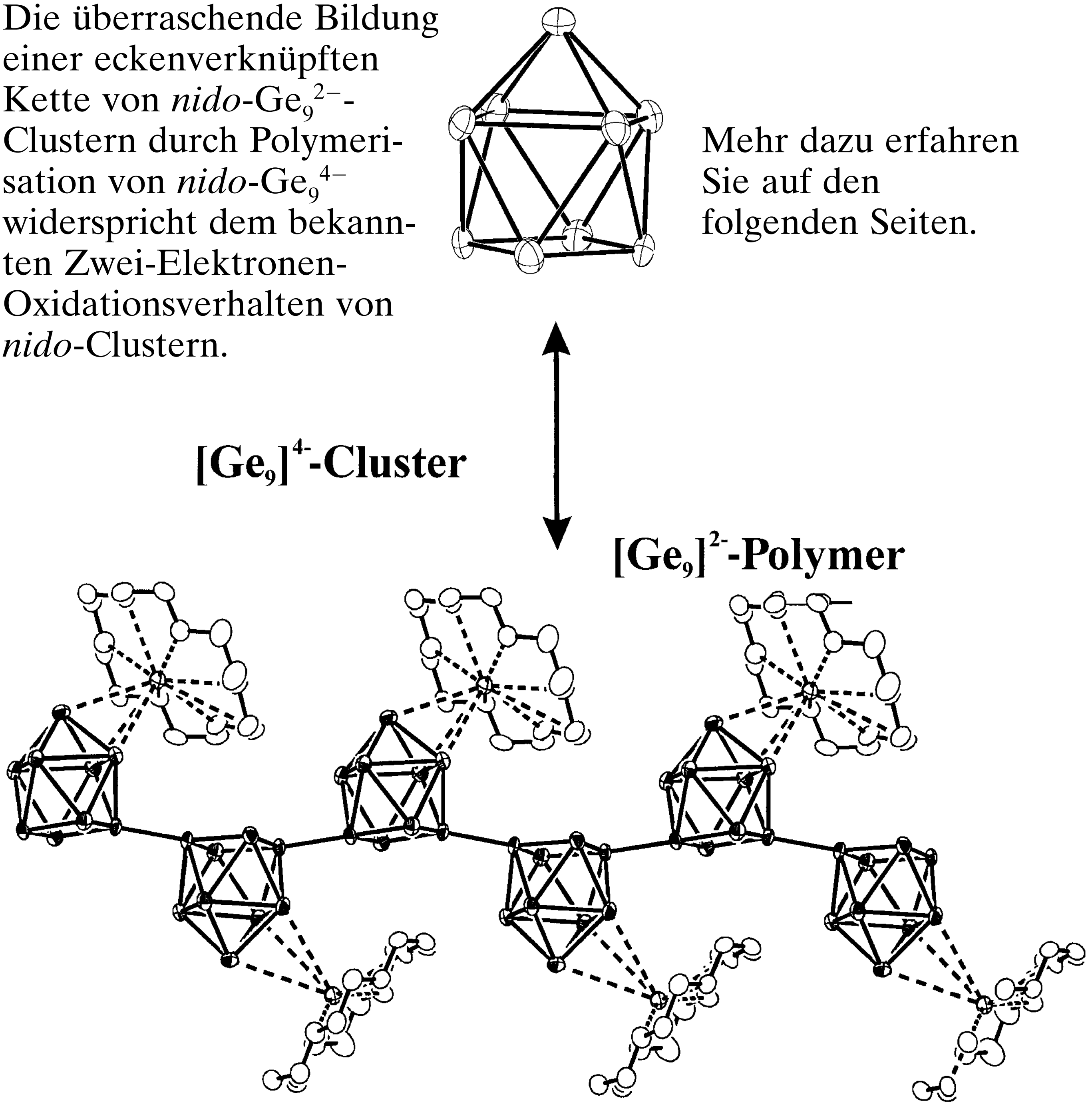
Die überraschende Bildung einer eckenverknüpften Kette von *nido*-Ge_9^{2-}-Clustern durch Polymerisation von *nido*-Ge_9^{4-} widerspricht dem bekannten Zwei-Elektronen-Oxidationsverhalten von *nido*-Clustern.



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An Unprecedented $_{1\infty}[\mathrm{Ge}_9]^{2-}$ Polymer: A Link between Molecular Zintl Clusters and Solid-State Phases**

Craig Downie, Zhongjia Tang, and Arnold M. Guloy*

Understanding relationships between the geometry, properties, and reactivity of small semiconductor clusters and bulk materials is a problem of fundamental and technological importance.[1] One basic question is how properties and structures of small molecular clusters evolve when going to bulk materials. Although the step-wise growth of large transition metal clusters has been clearly elucidated, similar routes to main group semiconductor clusters are scarce.[2] Moreover, evidence for the direct synthesis of bulk solid elemental semiconductors by kinetic-controlled cluster assembly and reactions has been lacking or inconclusive.[1, 3] Progress toward this goal has been slow mainly due to the lack of unequivocal structural and mechanistic relationships between solid-state phases and their relevant cluster derivatives.

Members of a unique family of "naked" metal cluster ions, collectively known as Zintl ions, have been isolated from solution and characterized. They represent one end of the cluster-to-solid spectrum.[4] In particular, Group 14 homopolyatomic anionic clusters may be considered as close derivatives of the technologically important elements. Hence, chemical and physical studies of novel Zintl cluster ions may provide valuable clues to understanding the evolution of molecular clusters into nanophases and bulk solid-state structures of Si, Ge, Sn, and Pb.[1, 5]

Numerous Zintl cluster ions have been isolated and classified.[4] Use of sequestering agents has led to several isolable homopolyatomic germanium anions such as $\mathrm{Ge}_9{}^{n-}$ ($n = 2$,[6] 3,[7] 4[6]), $\mathrm{Ge}_5{}^{2-}$,[8], $\mathrm{Ge}_{10}{}^{2-}$,[7a] and $\mathrm{Ge}_{18}{}^{6-}$.[9] A different synthetic route also provided $[\mathrm{Ge}_6\{\mathrm{Cr(CO)}_5\}_6]^{2-}$, which features an octahedral *closo*-$\mathrm{Ge}_6{}^{2-}$ unit.[10] It should be noted that the nine-atom *nido*-$\mathrm{Ge}_9{}^{4-}$ clusters are remarkably resilient and are stable in solution and in the solid state.[4c, 6, 11] Moreover, oxidation of *nido*-$\mathrm{Ge}_9{}^{4-}$ clusters resulted in the formation of related cluster species such as the paramagnetic radical $\mathrm{Ge}_9{}^{3-}$, $\mathrm{Ge}_{18}{}^{6-}$ dimers, and *closo*-$\mathrm{Ge}_9{}^{2-}$. Recent questions about the nature of $\mathrm{Ge}_9{}^{n-}$ clusters have been posed addressed at the validity of the disproportionation allocation of charges in $[\mathrm{K([2.2.2]crypt)}]_6\mathrm{Ge}_9\mathrm{Ge}_9$ into $\mathrm{Ge}_9{}^{2-}$ and $\mathrm{Ge}_9{}^{4-}$.[4c, 6, 12] Our investigation, focused on the isolation and characterization of *closo*-$\mathrm{Ge}_9{}^{2-}$ clusters, has led to the synthesis of a unique polymeric Zintl anion. Herein we report the synthesis as well as the crystal and electronic structures of $[\mathrm{K([18]crown\text{-}6)}]_2\mathrm{Ge}_9 \cdot \mathrm{en}$ (en = ethylenediamine), which features an unprecedented polymer of vertex-linked *nido*-$\mathrm{Ge}_9{}^{2-}$ clusters. The polymer can be considered as being formed from a two-electron oxidative polymerization of *nido*-$\mathrm{Ge}_9{}^{4-}$ polyhedral clusters.

The title compound $[\mathrm{K([18]crown\text{-}6)}]_2\mathrm{Ge}_9 \cdot \mathrm{en}$ (**1**) was prepared by allowing binary alloys, having nominal composition "KGe_4", to react with crown ether [18]crown-6 in neat ethylenediamine and toluene. Careful use of slow diffusion techniques, over a two-week period, resulted in the formation and growth of transparent light blue-green crystals of **1**, which were investigated by single-crystal X-ray diffraction. Although the use of non-cryptand sequestering agents in the isolation of Zintl anions has been suggested, there has only been one report on the successful use of crown ethers in this regard—the isolation and characterization of $[\mathrm{K([18]crown\text{-}6)}]_3\mathrm{KSn}_9$.[13]

Compound **1** crystallizes in the noncentric orthorhombic space group $P2_12_12_1$.[14] The asymmetric unit consists of one $\mathrm{Ge}_9{}^{2-}$ monomer, two types of $[\mathrm{K([18]crown\text{-}6)}]^+$ complex ions, and one solvent molecule. The crystal structure (Figure 1) features zigzag chains of $_{1\infty}[\mathrm{Ge}_9{}^{2-}]$ anions that lie along the 2_1 screw axes along *a*. The polymer of unligated clusters is illustrated as an "up" and "down" chain arrangement of Ge_9 clusters, with one diagonal of the cluster basal planes lying along the polymer axis. The polymer is completed by intercluster *exo* bonds that link the basal vertices of neighboring polyhedral clusters. The *exo* bonds (2.486(1) Å) are comparable to known Ge–Ge single bonds,[15a] and form an angle of 171° with each cluster base.

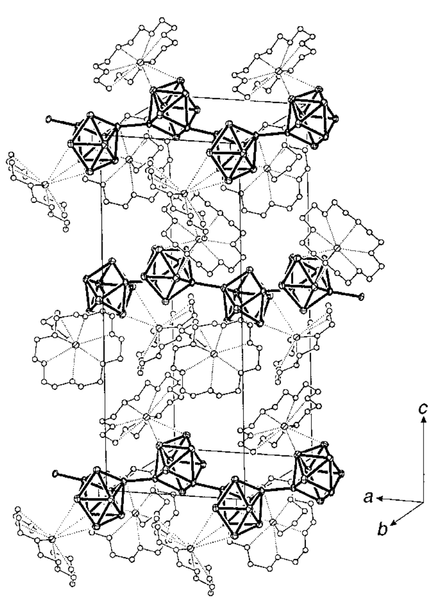

Figure 1. A view of the unit cell of **1**. Non-germanium atoms are represented as circles (K = crossed; C, O, N = open). Ellipsoids for germanium atoms are drawn at 50% probability. For clarity, only one orientation of the disordered [18]crown-6 molecule of the "noncapping" cation is drawn.

The complex cations $[\mathrm{K([18]crown\text{-}6)}]^+$ serve as "face-capping" and "spacer" units that effectively surround and isolate each anionic polymer. One type of cation caps the apical triangular faces of a polyhedral cluster unit in the polar

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chains (Figure 2) and reflect the lack of an inversion center in the crystal structure. The remaining noncapping complex cations, which exhibit configurational disorder of the crown ether, are coordinated by solvent molecules and serve as spacers.[14] The resulting distance between the axes of nearest neighboring polymers is over 14 Å.

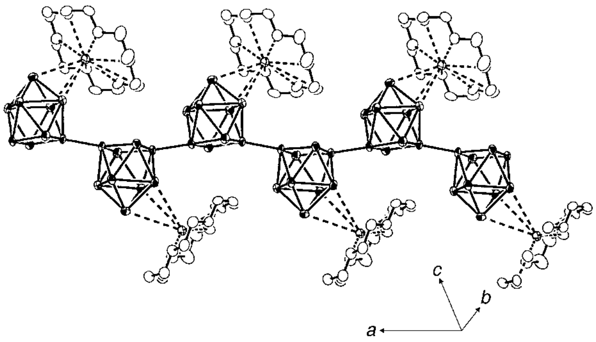

Figure 2. View of a section of the polymeric anion chain and "capping" [K([18]crown-6)]$^+$ cations of **1**. All thermal ellipsoids are drawn at 50% probability.

The Ge_9^{2-} cluster unit (Figure 3) closely resembles a monocapped square antiprism that is distorted to C_{2v} symmetry. The observed Ge–Ge bond lengths within the cluster range from 2.552(1) to 2.864(1) Å and compare well with the distances for the isolated *nido*-Ge_9^{4-} cluster.[6, 11] The longest cluster edges are located at the nearly rectangular cluster "waist", with the face-capping cation closest to the longest edge of the cluster waist. The accompanying angular distortions from ideal C_{4v} symmetry are most noticeable at the basal planes. A rhomboidal distortion of the basal planes is depicted by a contraction along the chain axis, resulting in basal angles of 102.5° and 77.5° at the *exo*-bonded and nonbonded vertices, respectively. The distortion also results in basal diagonal distances of 3.194(1) Å and 3.942(1) Å between *exo*-bonded vertices and nonbonded vertices, respectively. However, the planarity of the basal plane remains intact.

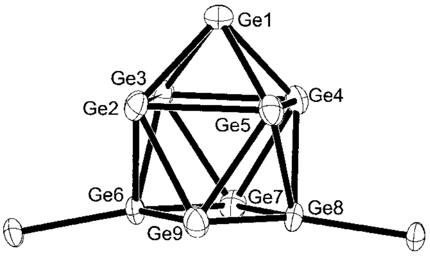

Figure 3. ORTEP representation of one $[Ge_9]^{2-}$ cluster unit of the polymeric anion. Ellipsoids are drawn at 50% probability. The *exo*-bonded atoms have been added. Bond lengths [Å] within the cluster: Ge1–Ge2 2.601, Ge1–Ge3 2.585, Ge1–Ge4 2.577, Ge1–Ge5 2.588, Ge2–Ge3 2.864, Ge2–Ge5 2.705, Ge2–Ge6 2.620, Ge2–Ge9 2.625, Ge3–Ge4 2.734, Ge3–Ge6 2.615, Ge3–Ge7 2.658; Ge4–Ge5 2.855, Ge4–Ge7 2.627, Ge4–Ge8 2.622, Ge5–Ge8 2.633, Ge5–Ge9 2.639; Ge6–Ge7 2.563, Ge6–Ge9 2.552, Ge7–Ge8 2.554, Ge8–Ge9 2.554. The *exo*-bond distance, Ge6–Ge8, is 2.486 Å. The standard deviation for all distances is 0.001 Å.

On the basis of cluster bond distances and angles, the point symmetry of the cluster unit is close to C_{2v} and can be derived from a "compression" of a base diagonal in a C_{4v} monocapped square antiprism. The distortion contrasts the well-described geometric transformation of nine-atom *nido* clusters, which is accompanied by a "butterfly" distortion of the cluster base.[4c, 6, 12] The slight distortions from ideal C_{2v} geometry may be attributed to the effects of the face-capping [K([18]crown-6)]$^+$ ion and close packing of the noncentric lattice. Application of Wade's rules of electron counting[15b] to the Ge_9^{2-} cluster unit leads to the following distribution: 38 total e^- – 14 lone-pair e^- – 2 *exo*-bond e^- = 22 skeletal bond e^-, effectively yielding an electron count for a *nido* cluster.

The surprising formation of the polymeric anion is counterintuitive to known two-electron oxidation behavior of *nido* clusters and contrasts the existence of an isoelectronic *closo*-Ge_9^{2-} cluster.[4, 16] Moreover, synthesis of elemental clusters through the reduction of metal salts has been clearly established.[2, 17] The addition of [2.2.2]crypt to an aliquot portion of "KGe_4" in solution results in high-yield formation of [K([2.2.2]crypt)]$_2$Ge$_9$ with *closo*-Ge_9^{2-} clusters.[16] The unique polymerization implies that energy barriers between different geometric conformations of the monomeric cluster are small. Moreover, the electronic and geometric resiliency of *nido*-Ge_9^{4-} is emphasized. These factors and the packing effects of the disclike shape of the cations allow for the formation of bonds between *nido* clusters.

Theoretical calculations on related nine-atom *nido* clusters show that the HOMO states are mainly derived from cluster orbitals at the basal vertices.[18] Consequently, this correlates with the oxidative formation of *exo* bonds between basal *trans* vertices in the polymer. Whereas isolated Zintl cluster ions are mainly associated with Groups 14 and 15, extended structures of clusters that exhibit classical deltahedral bonds have been entirely allied with Zintl phases containing "electron-deficient" triels (Group 13).[4c, 19] Hence, polymeric [K([18]crown-6)]$_2$Ge$_9$·en nicely bridges the electronic and structural gap between isolated Zintl cluster anions and the extended structures of Zintl phases.

Extended-Hückel band calculations performed on a $[Ge_9^{2-}]$ polymer indicate a direct band gap of 2.86 eV. The electronic states immediately above and below the Fermi level (E_f) are 4p-based cluster antibonding and bonding states and do not exhibit significant band dispersion. Intercluster bonding states derived from basal atoms are stabilized, and lie 2–3 eV below E_f. Corresponding antibonding states are destabilized and lie more than 5 eV above E_f. Moreover, the increased 4s–4p hybridization of the *exo*-bonded atoms correlates with the observed increase in the basal bond angles. The semiconducting "bare" metal polymer satisfies descriptions for a quantum-wire structure, predicted to exhibit unique optical and electronic properties associated with quantum confinement.[20] Preliminary optical absorption measurements indicate the material is strongly photoluminescent, consistent with the calculated band gap. Detailed investigations on the optical, SHG (Secondary Harmonic Generation), and spectroscopic properties of the novel material are currently in progress.

Experimental Section

All manipulations and reactions were carried out under an argon atmosphere. All solvents were degassed, distilled, and dried accordingly. The crown ether was oven- and vacuum-dried before use.

A sample (0.104 g) of the binary alloy "KGe_4", prepared by high-temperature reactions of pure elements (Aldrich) within sealed Nb tubing, was dissolved in neat en (5 mL), forming a dark green solution. A separate solution of [18]crown-6 (0.048 g, 0.182 mmol) in neat toluene (4 mL) was slowly added and layered on the alloy solution. Formation of transparent light blue-green rodlike crystals was observed after two weeks. The moisture-sensitive crystals were preserved in mother liquor and were found to be of compound **1** (yield 30–40 %).

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[14] Crystal structure data for **1**: $M_r = 1320.24$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 11.2796(7)$, $b = 14.7049(9)$, $c = 27.8321(17)$ Å, $V = 4616.4(5)$ Å^3, $Z = 4$, $\rho = 1.900$ g cm^{-3}, $\mu = 6.003$ mm^{-1}, $\lambda = 0.71073$ Å ($Mo_{K\alpha}$), $2\theta_{max} = 46.5°$; of 20849 total reflections, 6629 were independent and 6605 were observed ($> 3\sigma_I$); 455 total variables; final R indices $R1 = 0.0328$, $wR2 = 0.0772$ ($I > 4\sigma(I)$) and $R1 = 0.0488$, $wR2 = 0.0978$ (all data). The analysis, using a Siemens SMART diffractometer equipped with a CCD area detector, was carried out at −50 °C. Empirical absorption correction was applied on a hemisphere of data, and redundant reflections were averaged. The structure was solved by direct methods and refined by full-matrix least-squares calculations. One of the two crown ether molecules is disordered over two different positions (50:50). The potassium atom K2 attached to it binds to an en solvent molecule, which is also disordered. Owing to disorder, the exact amount of en cannot be determined. One en molecule per K2 atom was assumed for all the calculations. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133996. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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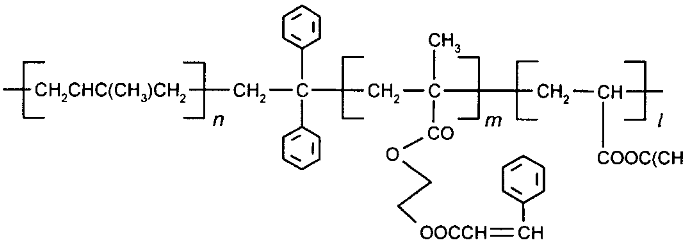
Block Copolymer Nanotubes[**]

Sean Stewart and Guojun Liu*

The preparation of nanometer-sized structures with well-defined shape and narrow size distribution, "nanostructures", has attracted much attention mainly to meet the demand for smaller electronic devices.[1] Nanostructures are also useful in the preparation of strong nanocomposite materials or sensors that may imitate enzymes in molecular recognition. Nanostructures of block copolymers[2] are interesting because they span the size range from 5 to 500 nm and fill the gap between nanostructure sizes obtainable from traditional lithographic techniques and those from small-molecule self-assembly processes. In this communication we report the preparation of solvent-dispersible nanotubes from a triblock copolymer, polyisoprene-*block*-poly(2-cinnamoylethyl methacrylate)-*block*-poly(*tert*-butyl acrylate), PI-*b*-PCEMA-*b*-P*t*BA (**1**), with 130 isoprene, 130 CEMA, and 800 *t*BA units.



1, PI-*b*-PCEMA-*b*-P*t*BA

Although there have been many reports in the past decade on the preparation and study of nanotubes, our nanotubes are unique in composition and properties. Excluding those dealing with nanochannels formed in inorganic oxides,[3–6] glass,[7] metals,[8] or polymer matrices,[9, 10] the majority of publications in the past eight years have been on carbon[11–14] or metal

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