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Activation of Tellurium with Zintl Ions: $^{1}/_{\infty}\{[Ge_5Te_{10}]^{4-}\}$, An Inorganic Polymer with Germanium in Three Different Oxidation States

Qichun Zhang, Gerasimos Armatas, and Mercouri G. Kanatzidis*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208

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The solvothermal reaction among tellurium, manganese, and the Zintl compound K_4Ge_9 has led to the formation of a polymeric mixed-valent complex $\{[Mn(en)_3]_2(Ge_5Te_{10})\}_n$ (**1**; en = ethylenediamine). The most interesting structural feature of this material is the presence of three different oxidation states of germanium centers and the formation of Ge−Ge bonds in the infinite polymeric chains $^{1}/_{\infty}\{[Ge_5Te_{10}]^{4-}\}$. X-ray photoelectron spectroscopy characterization confirms the different oxidation states of germanium.

Germanium chalcogenides are of interest for potential applications in different technological areas such as thermoelectric,[1] gas separation,[2] phase-change memory,[3] nonlinear optical performance,[4] proton conductivity,[5] optical property,[6] ferro- and pyroelectrics,[7] and photocatalysis.[8] Normally, thio(seleno)germanates readily form a variety of structures by arranging and connecting the tetrahedra (GeQ_4^{4-} or $Ge_4Q_{10}^{4-}$, Q = S or Se) in space;[9−11] however, germanium telluride based anions (larger than $[GeTe_4]^{4-}$[13]) are rare. Some examples include $A_4Ge_4Te_{10}$ (A = K, Et_4N)[12] and $[Mn(en)_3]_2(Ge_4O_6Te_4)$ (en = ethylenediamine).[14]

Recently, by employing metal zintl anions/phases[15,16] as strong reducing agents to activate elemental tellurium, we have already reported the layered indium telluride compound $\{[In(en)_3]_2[In_5Te_9(en)_2]\cdot 0.5en\}_n$ based on supertetrahedral T2 clusters.[17] We describe here a new type of polymeric Ge/Te species based on repeating $[Ge_5Te_{10}]^{4-}$ cluster units. Among the unusual features of the $^{1}/_{\infty}\{[Ge_5Te_{10}]^{4-}\}$ chains is the multivalent germanium sites containing Ge^{2+}, Ge^{3+}, and Ge^{4+} centers. To the best of our knowledge, this is the first reported example with three different oxidation states of germanium being observed in a single compound.

Germanium is always tetravalent if it adopts tetrahedral coordination with chalcogenide ions. However, lower oxidation states are possible, resulting in Ge−Ge bond formation or nontetrahedral coordination geometries reflecting the sterochemical expression of the so-called lone pair of electrons in this germanium center. For example, Ge^{2+} centers have been observed in the binary compounds GeQ (Q = S, Se),[18] $Tl_2Ge^{2+}Ge^{4+}S_4$,[19] and $Ba_2Ge^{2+}Ge^{4+}Se_5$,[20] while Ge^{3+} are found to form homonuclear Ge−Ge bonds in the glassy phase Ge_2Q_3 (Q = S, Se)[21] and ternary compounds such as $A_6Ge_2Q_6$ (A = Na, K; Q = S, Se, Te),[22] $Na_8Ge_4Te_{10}$,[23] and $Sr_2Ge_2Se_5$.[24] Prior to this work, lower oxidation states

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*To whom correspondence should be addressed. E-mail: m-kanatzidis@northwestern.edu.

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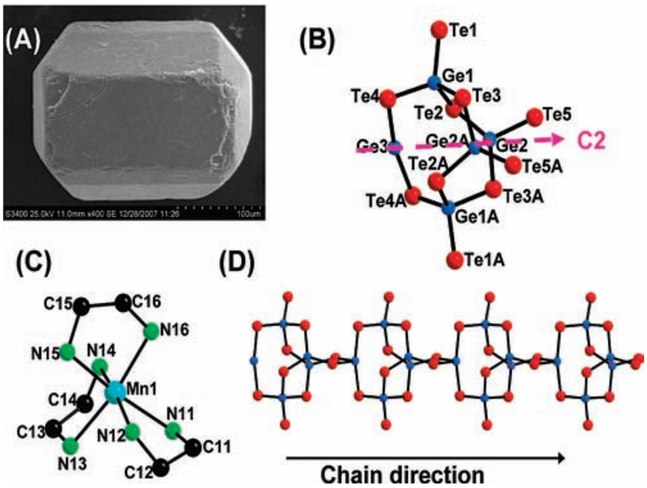

Figure 1. (A) SEM image of a millimeter-sized crystal of **1**. (B) Repeating unit of **1** with labeling. (C) Cation $\Delta^{M\delta\lambda\lambda}$-$[Mn(en)_3]^{2+}$ with labeling. (D) Segment of the polymeric chain. Blue balls: Ge atoms. Red balls: Te atoms. Cyan balls: Mn atoms. Green balls: N atoms. Black balls: C atoms. Selected bond lengths (Å) and angles (deg) are as follows: Te1−Ge1 2.5262(16), Ge1−Te2 2.6092(16), Ge1−Te3 2.6615(17), Ge1−Te4 2.5414(16), Ge2−Te2 2.5587(18), Ge2−Te3 2.5956(16), Ge2−Te5 2.5450(16), Ge2−Ge2A 2.420(3), Ge3−Te4 2.8936(14), Ge3−Te5 2.8573(17); Ge1−Te4−Ge3 94.24(6), Te1−Ge1−Te4 113.49(6), Te1−Ge1−Te2 104.33(5), Te4−Ge1−Te2 112.34(6), Te1−Ge1−Te3 112.96(5), Te4−Ge1−Te3 106.99(6), Te2−Ge1−Te3 106.62(6), Te5−Ge3−Te5 99.34(8), Te5−Ge3−Te4 89.83(4), Te5−Ge3−Te4 98.41(4), Te5−Ge3−Te4 98.41(4), Te5−Ge3−Te4 89.83(4), Te4−Ge3−Te4 167.28(10), Ge2−Ge2−Te5 108.44(5), Ge2−Ge2−Te2 103.92(8), Te5−Ge2−Te2 108.83(6), Ge2−Ge2−Te3 104.58(6), Te5−Ge2−Te3 116.01(6), Te2−Ge2−Te3 114.13(6).

on germanium in chalcogenides were obtained from high-temperature reactions. There are no reported examples being formed at low temperature (< 200 °C). Very recently, a mixed-valent tin molecular complex $[(RSn^{4+})_4(\mu\text{-}S)_2]_3$-$Sn^{3+}{}_2S_6$ was reported (R = organic group).[25]

To prepare crystals of **1**, 30 mg of manganese, 250 mg of tellurium, 100 mg of K_4Ge_9, and 4.0 mL of dried en (distilled from sodium) were mixed in a 23 mL Teflon-lined stainless steel autoclave in a nitrogen-filled drybox. The mixture was stirred for 10 min, and the vessel was then sealed and heated at 190 °C for 6 days. The autoclave was subsequently allowed to cool to room temperature. The product formed as black shining crystals (Figure 1A) in 35% yield (based on germanium) and is not stable in air. The crystal structure was determined from single-crystal X-ray diffraction (XRD) data collected at 100 K.[26] The existence of en molecules was confirmed by IR spectroscopy (Figure S1 in the Supporting Information), and quantification was made through thermogravimetric analysis (TGA; Figure S2 in the Supporting Information). The calculated atomic Mn/Ge/Te ratio from the single-crystal structure analysis is in agreement with energy-dispersive X-ray spectroscopy (EDS) analysis (Figure S3 in the Supporting Information).[27]

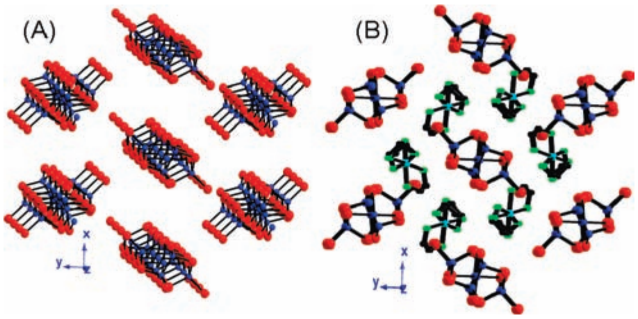

Figure 2. Stacking view of compound **1** along the *c* axis: (A) without cations; (B) with cations. Blue spheres: Ge atoms. Red spheres: Te atoms. Cyan spheres: Mn atoms. Green spheres: N atoms. Black spheres: C atoms.

Compound **1** crystallizes in the orthorhombic space group $P2_12_12$. It has a chainlike structure with $[Ge_5Te_{10}]^{4-}$ clusters as repeating units (Figure 1B) and $\Delta^{M\delta\lambda\lambda}$-$[Mn(en)_3]^{2+}$ cations as charge-balance species (Figure 1C). The structure of the chain (Figure 1D) is unique. The ${}^1/_\infty\{[Ge_5Te_{10}]^{4-}\}$ entity is polar and has a 2-fold axis running along its axis (Figure 2B). Each cluster consists of five germanium sites and itself possesses 2-fold rotation axis. The Ge1 site adopts tetrahedral geometry and coordinates to four Te atoms, where three Te atoms (Te2, Te3, and Te4) are shared with Ge2, Ge2A, and Ge3, respectively, and Te1 is a terminal atom. The Ge2 site is occupied by one Ge2A atom and three bridged Te atoms (Te2, Te5, and Te3A), while the Ge3 site has a "see-saw" four coordination of Te4, Te5, Te4A, and Te5A. This configuration might be due to the so-called lone-pair electrons' pushing in the Ge3 site or ring strain in the five-membered rings that they belong to or both. The building units align in the same direction and join to form a polar chain through coordination between Te5 atoms and Ge3 from another unit. The total charge of the unit is 4−, which is balanced by two octahedral $\Delta^{M\delta\lambda\lambda}$-$[Mn(en)_3]^{2+}$ complexes. The ranges of Mn−N bond distances and N−Mn−N angles are 2.261(10)−2.327(10) Å and 77.8(4)−170.1(4)°, respectively.

A remarkable feature of compound **1** is the presence of three different oxidation states of germanium (namely, Ge^{2+}, Ge^{3+}, and Ge^{4+}). The Ge^{3+} atoms form Ge−Ge-bonded dimers with a distance of 2.4198(19) Å. The Ge^{4+} center has a tetrahedral coordinate environment, while the Ge3 center adopts a four-coordinate "see-saw" geometry. The bond distances of Ge3−Te [2.857(14)−2.894(16) Å] are longer than the bond distances in Ge1−Te [2.528(15)−2.662(17) Å] and Ge2−Te [2.545(16)−2.596(18) Å]. Using Brown's bond-valence model,[28,29] the calculated valence sums surrounding Ge1, Ge2, and Ge3 are 3.78, 2.95, and 1.71, respectively, which is in agreement with the assigned valences. X-ray photoelectron spectroscopy (XPS; Figure S4 in the Supporting Information) analysis showed the presence of three different binding energies (31.2, 32.9, and 35.4 eV), which can be assigned respectively to three oxidation states (Ge^{2+}, Ge^{3+}, and Ge^{4+}) in compound **1**. The atomic ratio acquired from the area of the XPS peaks of Ge^{2+}, Ge^{3+}, and

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(26) Single-crystal XRD data were collected at 100 K with a STOE imaging-plate diffraction system (IPSD-2) with graphite-monochromatized Mo Kα radiation. A numerical absorption correction was applied. Direct methods and full-matrix least-squares refinements against F^2 were performed with the *SHELXTL* package. Crystal data for $\{[Mn(en)_3]_2(Ge_5Te_{10})\}_n$ (**1**): orthorhombic $P2_12_12$, $Z = 2$, $a = 10.735(2)$ Å, $b = 23.417(5)$ Å, $c = 8.9325(18)$ Å, $V = 2245.5(8)$ Å^3, $T = 100$ K, $2\theta_{max}$(Mo Kα) = 40°, $D_{calc} = 3.049$ g/cm^3. Total reflections = 1884, unique reflections $[F_o{}^2 > 2\sigma(F_o{}^2)] = 1884$, parameters = 187, GOF = 1.066, R1 = 2.38, and wR2 = 5.77 for $I > 2\sigma(I)$.

(27) The calculated ratio for manganese, germanium, and tellurium is 1:2.5:5, and the result from EDS is 1:2.2:4.6.

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Ge^{4+} is 0.4:1:0.8, which is very close to the calculated result (0.5:1:1) from the crystal structure. XPS also shows peaks of 37.7 and 40.6 eV, which can be assigned to Te 4d core-level signals (see Figure S4 in the Supporting Information).

A material with three different oxidation states of germanium centers is unprecedented. The unique structure and mixed-valent character of $^{1}/_{\infty}\{[Ge_5Te_{10}]^{4-}\}$ attests to the synthetic usefulness of using Zintl anions such as Ge_9^{4-} as starting materials to activate chalcogens in solvothermal reaction chemistry.

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Supporting Information Available: IR spectrum, EDS analysis, XPS spectrum, TGA graph, powder XRD, and X-ray crystallographic files in CIF format for the structure determination of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.