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$\{[\mathrm{Ga}(en)_3]_2(\mathrm{Ge}_2\mathrm{Te}_{15})\}_n$: A Polymeric Semiconducting Polytelluride with Boat-Shaped $\mathrm{Te}_8{}^{4-}$ Rings and Cross-Shaped $\mathrm{Te}_5{}^{6-}$ Units

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The reaction of the Zintl compound $\mathrm{K_4Ge_9}$ with Te and $\mathrm{Ga_2Te_3}$ in ethylenediamine (*en*) at 190 °C gave the germanium polytelluride $\{[\mathrm{Ga}(en)_3]_2[(\mathrm{GeTe})_2(\mathrm{Te}_5)^{6-}(\mathrm{Te}_8)^{4-}]\}_n$ (**1**). The single-crystal structure analysis revealed that **1** has two different polytelluride fragments: cross-shaped 36-e$^-$ $\mathrm{TeTe_4}^{6-}$ anions and boat-shaped 52-e$^-$ $\mathrm{Te_8}^{4-}$ rings. The new material is a p-type semiconductor at room temperature and switches to n-type at 380 K.

Metal polytellurides display rich structural chemistry[1−3] and interesting physical properties such as charge density waves,[4] spin density waves,[5] glass formation,[6] and superconductivity.[7] The polytellurides generally differ from the traditional binary or ternary metal tellurides[8−10] and feature a diverse collection of unusual species that vary in shape, coordinating numbers, and ability to interact with each other in three-dimensions via Te···Te attractions. Such so-called nonclassicality[2b] comes from the violation of the octet rules in their structures. Recently, the strong interaction among chalcogenides has been found to have a big impact on physical properties such as thermoelectric and resistivity switching.[11] Especially, very important secondary chalcogenide−chalcogenide interactions will favor the thermoelectric properties.[11b,c] An extensive understanding of the structures of polytellurides is required to explain observed properties and in the planned synthesis of new materials. Furthermore, structurally well-defined polytellurides can serve as model systems to provide structural insights into materials with less well-defined structures such as glasses.

Typical Te-rich species are short chain-like ($\mathrm{Te_2}^{2-}$, $\mathrm{Te_3}^{2-}$, $\mathrm{Te_4}^{2-}$,$\mathrm{Te_6}^{2-}$, $\mathrm{Ba_2SnTe_5}$),[12] T-shaped ($\mathrm{TeTe_3}^{n-}$ in $\mathrm{NaTe_3}$[13] or $\mathrm{CsTe_4}$[14]), cross-shaped ($\mathrm{TeTe_4}^{2-}$ in $\mathrm{Rb_2Te_5}$[15] and $\mathrm{Cs_2Te_5}$,[16] $\mathrm{TeTe_4}^{6-}$ in $(\mathrm{Ga}^{3+})_2\mathrm{Te}_5$,[17] and $\mathrm{M_2SnTe_5}$ (M = K, Rb)[18]),

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neutral crown-shaped Te_8 in Cs_3Te_{22},[19] and bicyclical rings (spiro[3,4]Te_8 ring in $[K(15\text{-}C\text{-}5)_2]_2Te_8$[20] and [2,2,2]$Te_8^{2+}$ ring in $Te_8(WCl_6)_2$[21]). In addition, polytellurides can easily form chains (linear, helical, kinked, branched or spirocyclic), puckered layers, and strictly planar networks.[1a] The occurrence of multiple Te-rich building units into one structure is rare.

Here, we report a novel semiconducting polytelluride $[Ga(en)_3]_2(Ge_2Te_{15})$ (**1**, *en* = ethylenediamine), which contains two different Te-rich building linkers: slight-distorted square-planar 36-e^- $TeTe_4^{6-}$ blocks and boat-shaped 52-e^- Te_8^{4-} rings. The synthesis was accomplished under solvothermal conditions in ethylenediamine (*en*) at 190 °C using the Zintl anions $[Ge_9^{4-}]$[22] as strong reducing agents to activate tellurium.[23] The single-crystal (Figure S1, Supporting Information) structure of **1** was determined from single-crystal X-ray diffraction data collected at 100 K.[24] The X-ray powder diffraction pattern of **1** agrees with the one calculated from the single-crystal diffraction analysis (Figure S2, Supporting Information). The existence of *en* molecules was confirmed by FT-IR spectroscopy (Figure S3 in Supporting Information), and the quantification was made through thermogravimetric analysis (TGA; Figure S4, Supporting Information). The atomic Ga/Ge/Te ratio, determined from the single-crystal structure analysis, is in agreement with energy dispersive X-ray spectroscopic analysis (EDS; Figure S5, Supporting Information).[25]

The new tellurium-rich $\{[Ga(en)_3]_2(Ge_2Te_{15})\}_n$ (**1**) has a polar structure. It crystallizes in the monoclinic space group $P2_1$ and contains infinite anionic chains and $[Ga(en)_3]^{3+}$ cations (Figure 1). The chains contain two Ge^{4+} sites (Ge(1) and Ge(2) atoms), which adopt tetrahedral coordination geometry (i.e., $GeTe_4^{4-}$) and are linked through edge-sharing with a slightly distorted square-planar building unit 36-e^- $[TeTe_4]^{6-}$ to form a larger repeating unit [(GeTe)($TeTe_4$)(GeTe)]. These units are bridged by boat-shaped 52-e^- Te_8^{4-} rings to produce a chain-like structure (Figure 2a). The two terminal Te atoms (Te(9) and Te(10) atoms) in the Ge centers point in opposite directions. This arrangement creates anionic chains expressed as $^1/_\infty\{[(GeTe)_2]^{4+}(Te_5)^{6-}(Te_8)^{4-}\}$. In the tetrahedrally coordinated Ge sites, the bonding distances to Te atoms range from 2.5437(16) Å to 2.6233(16) Å.

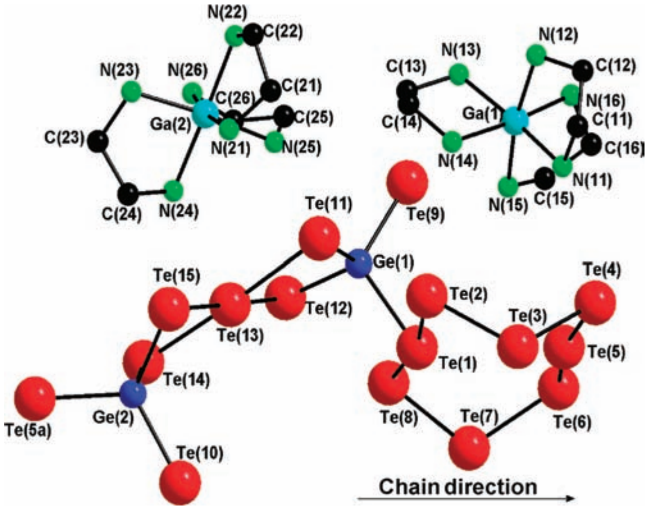

Figure 1. Ball-and-stick model of the relevant fragments of compound **1** with atomic labels. Blue, Ge; cyan, Ga; red, Te; green, N; and black, C. The range of N−Ga distances and N−Ga−N angles are 2.054(12)−2.111(13) Å and 81.4(5)−173.6(5)°, respectively.

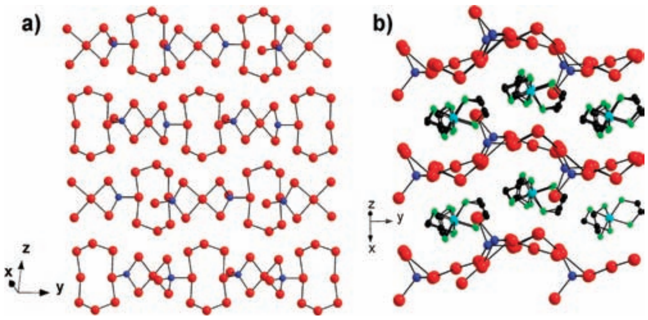

Figure 2. (a) A view of the parallel arrangement of the chains. (b) Parallel packing of adjacent single chain with $[Ga(en)_3]^{3+}$ cations in between. Blue, Ge; cyan, Ga; red, Te; green, N; black, C.

The chains in **1** are packed in a parallel manner (Figure 2a), and the remaining empty spaces are occupied by the $[Ga(en)_3]^{3+}$ complexes (Figure 2b). In one unit, two octahedral $[Ga(en)_3]^{3+}$ complexes are chiral. The Ga(1) center has a Λ configuration, while Ga(2) is a Δ isomer. In addition to the dissymmetry generated by the tris(chelate) structure of the octahedral complexes, the enantiomeric conformations of gauche ethylenediamine also have dissymmetry. Considering all factors, these two complexes can be written as $\Lambda^{M\lambda\delta\lambda}$-$[Ga(1)(en)_3]^{3+}$ and $\Delta^{M\lambda\delta\lambda}$-$[Ga(2)(en)_3]^{3+}$, respectively.

The unique structural feature in **1** is the boat-shaped 52-e^- Te_8^{4-} rings. This represents a four-electron-reduced version of the neutral crown-shaped 48-e^- Te_8 ring (isostructural with S_8) reported by Sheldrick and Wachhold.[19a] In the neutral Te_8 rings, each Te atom adopts sp^3 hybridization, which gives each Te atom a V-shaped local coordination. When four electrons are added into two Te atoms (here, Te(1) and Te(5) atoms in Figure 3a), the orbital hybridization in Te(1) and Te(5) is changed into dsp^3. This imposes a trigonal bipyramidal geometry of the electron pairs around these Te atoms and forces a linear coordination for these tellurium centers. According to valence-shell electron-pair repulsion theory, the Te(1) and Te(5) sites should adopt a linear

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[24] Single-crystal X-ray diffraction data were collected at 100 K using a STOE imaging-plate diffraction system (IPSD-2) with graphite-monochromatized Mo Kα radiation. A numerical absorption correction was applied using the X-area suite of programs. Direct methods and full-matrix least-squares refinements against F^2 were performed with the SHELXTL package. The PLATON program (A. L. Spek *J. Appl. Crystallogr.* **2003**, *36*, 7) could not suggest additional symmetry. Crystal data for $\{[Ga(en)_3]_2[(GeTe)_2Te_{15}]\}_n$ (**1**): Monoclinic $P2_1$, Z = 2, a = 10.1433(6) Å, b = 14.2390(5) Å, c = 16.0788(9) Å, β = 96.131(4)°, V = 2309.0(3) Å^3, temperature = 100 K, $2\theta_{max}$ (Mo Kα) = 54.32°, D_{calcd} = 3.681 g/cm^3, $F(000)$ = 2124, parameters = 270, GOF = 1.016, and R_1 = 6.88% and wR_2 = 16.84% for $I > 3\sigma(I)$.

[25] The calculated ratio for Ge, Ga, and Te is 1:1:7.5, and the result from EDS is 1:1:8.0.

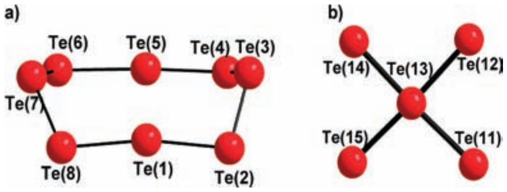

Figure 3. Two polytelluride building blocks: (a) boat-shaped 52 e$^-$ Te$_8^{4-}$ ring and (b) slightly distorted square-planar building unit 36 e$^-$ TeTe$_4^{6-}$. The typical distances of Te−Te are Te(1)−Te(2) 3.0011(25) Å; Te(2)−Te(3) 2.7667(27) Å; Te(3)−Te(4) 2.7865(28) Å; Te(4)−Te(5) 2.9619(26) Å; Te(5)−Te(6) 3.1829(26) Å; Te(6)−Te(7) 2.7916(27) Å; Te(7)−Te(8) 2.7690(28) Å; Te(8)−Te(1) 3.0961(26) Å; Te(11)−Te(13) 3.0799(26) Å; Te(12)−Te(13) 3.0215(25) Å; Te(13)−Te(14) 2.9762(12); Te(13)−Te(15) 2.9546(13) Å.

structure, which is very similar to that of the central iodine atom in the linear I$_3^-$ ion. The boat-shaped 52-e$^-$ Te$_8^{4-}$ ring is stabilized through direct coordination of the two reduced Te sites (Te(1) and Te(5) atoms) to the electrophilic Ge^{4+} centers (Ge1 and Ge2). Because of this Ge−Te bond formation, the angles of Te(2)−Te(1)−Te(8) and Te(4)−Te(5)−Te(6) change from the ideal 180° to 167.51(4)°. Other Te$_8$-type species with different structures are found in ring structures such as the two-electron reduced spiro[3,4]Te$_8$ ring in [K(15-C-5)$_2$]$_2$Te$_8$[20] and the oxidized [2,2,2]Te$_8^{2+}$ ring in Te$_8$(WCl$_6$)$_2$.[21]

It is worth noting that the charge of the 36-e$^-$ cross-shaped TeTe$_4$ species is −6, instead of −2 in the 32-e$^-$ isostructural unit of TeTe$_4$ found in Rb$_2$Te$_5$[15] and Cs$_2$Te$_5$.[16] Such a highly charged TeTe$_4^{6-}$ unit is also found in Ga$_2$Te$_5$[17] and M$_2$SnTe$_5$ (M = K, Rb).[18] The Te−Te distances in TeTe$_4^{6-}$ range from 2.9546(13) to 3.0799(26) Å, which is in agreement with the analogous distances in Ga$_2$Te$_5$ and M$_2$SnTe$_5$ (M = K, Rb), whereas the Te−Te distances in 32-e$^-$ TeTe$_4^{2-}$ are shorter at 2.8216(10) Å. In order to reduce the electronic charge density and increase the stability of the 36-e$^-$ TeTe$_4^{6-}$ species, these fragments have to form covalent bonds with strongly electrophilic centers (here are Ge^{4+} sites: Ge(1) and Ge(2)) via terminal Te atoms (Te(11), Te(12), Te(14) and Te(15)).

The electrical conductivity of **1** was measured on single-crystal samples and was found to be of semiconducting character with a value of ~7.42 × 10^{-3} S/cm at room temperature. With increasing temperature, the conductivity decreased rapidly to ~1.5 × 10^{-3} S/cm at 380 K, indicating thermally activated behavior (Figure 4a). Measurements could not be obtained at temperatures above 380 K because of the apparent thermal decomposition of compound **1**. The absolute value of the Seebeck coefficient is positive at room temperature, indicating p-type (hole) conduction. With increasing temperature, the Seebeck changes from about 400 μV/K at 310 K to at −400 μV/K at 380 K (Figure 4b). The change in sign from positive to negative with rising temperature indicates a transition from p-type (hole) to n-type (electron) conductivity and likely a very narrow energy band gap.

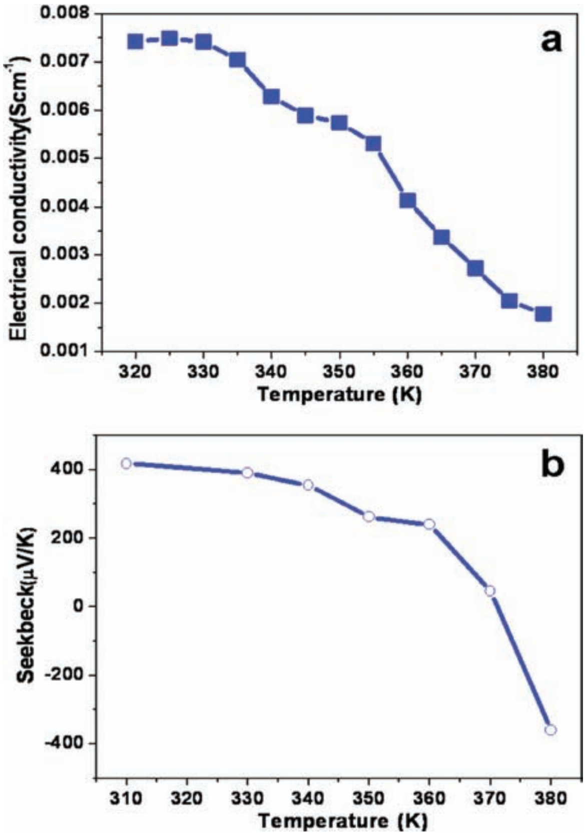

Figure 4. Electrical conductivity (a) and Seebeck (b) of a single-crystal sample of compound **1** as a function of the temperature.

In conclusion, the novel germanium polytelluride [Ga(*en*)$_3$]$_2$[(GeTe)$_2$(Te$_5$)$^{6-}$(Te$_8$)$^{4-}$]}$_n$ (**1**) forms under solvothermal conditions by activation of Te with Zintl anion Ge$_9^{4-}$. The new material has a unique structure composed of two new Te-rich units: cross-shaped TeTe$_4^{6-}$ blocks and boat-shaped Te$_8^{4-}$ rings. To the best of our knowledge, the Te$_8^{4-}$ ring is the first species of its kind in the chalcogenide family. This implies that the corresponding isoelectronic S$_8^{4-}$ and Se$_8^{4-}$ rings (currently unknown) may also be stable. Compound **1** appears to be a narrow gap semiconductor with p-type conductivity at room temperature and switches to n-type at the temperatures above 380 K.

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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**. These materials are available free of charge via the Internet at http://pubs.acs.org.