

# A Wheel-Shaped Indium–Telluride Nanocluster $[\text{In}_{18}\text{Te}_{30}(\text{dach})_6]^{6-}$ : Its Formation and Structure

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## S Supporting Information

**ABSTRACT:** The preparation and crystal structure of a large wheel-shaped indium–telluride compound are reported. The inorganic cluster is decorated with 1,2-diaminocyclohexane molecules that play an important role in the formation of the nanoring. A related new 1D polymeric InTe compound is also presented in order to understand the effect of acidity on the formation of the ring structure.

Semiconductor nanomaterials and nanoclusters can be exploited as building blocks or dots for the design of photonic, electronic, and magnetic devices as well as for use in sensing and optical applications. In particular, the fabrication of nanoring structures has attracted significant attention, owing not only to their aesthetically pleasing nature but also to their fascinating potential application as optical and electronic resonators.<sup>1</sup> There are approximately two types of known wheel-like or ring-shaped nanoclusters. The first is the organic–inorganic covalently assembled wheels, in which the metal atoms are bridged by O atoms or chalcogen atoms of the organic ligands. In the past decade, such molecular wheels are of growing interest especially the alcoholate- or carboxylate-bridged molecular wheels with paramagnetic transition metals, such as Fe, Co, Cr, Cu, Mn, and Ni.<sup>2</sup> Thiolate-bridged Fe and Ni ring-shaped compounds have also been reported.<sup>3</sup> The second is the pure inorganic rings, in which the metal atoms are covalently bridged by inorganic oxygen ( $\text{O}^{2-}$ ) or chalcogen anions ( $\text{Q}^{2-}$ , where  $\text{Q} = \text{S}, \text{Se}, \text{and Te}$ ). In contrast to the organic ligand-bridged compounds, large inorganic ring-shaped compounds are limited. Such known clusters are of the giant polyoxomolybdate rings,<sup>4</sup> the oxothiomolybdate,<sup>5</sup> and the FeS wheels.<sup>6</sup>

On the other hand, significant progress has recently been made in main-group metal (In, Ga, and Ge) chalcogenometalates prepared by the solvothermal method. The super-tetrahedral clusters ( $T_n$ ) seem to be the dominating subunit structure of the  $\text{M}_x\text{Q}_y$  clusters ( $\text{M} = \text{Ga}, \text{In}, \text{and Ge}$ ;  $\text{Q} = \text{S}$  and  $\text{Se}$ ), which assemble to 2D and 3D porous structures.<sup>7</sup> However, the corresponding tellurides are usually a 1D structure<sup>8a–d</sup> except a recently reported 2D compound.<sup>8e</sup> The large ring-shaped clusters of main-group metals  $\text{Ga}_x$ ,  $\text{In}_x$ , and  $\text{Ge}_x$  ( $x > 6$ ) are rarely documented.<sup>2g,9,10</sup> The two known large

$\text{Ga}_{10}$  and  $\text{Ga}_{18}$  rings are bridged by organic OMe and OAc ligands.<sup>2g,10</sup> The large chalcogenometalate rings of  $\text{Ga}_x$ ,  $\text{In}_x$ , and  $\text{Ge}_x$  have not been reported. In our continual efforts to explore the rich synthetic and structural chemistry of chalcogenometalates using coordinative ligands as structural decorating moieties,<sup>8c,d,11</sup> we obtained a novel indium–telluride cluster with a nanoscale wheel-shaped structure. The 18-membered indium structure is bridged by 30 telluride ions to form a pure inorganic nanoring, which is decorated (not bridged) by an organic amine, 1,2-diaminocyclohexane (dach). In this Communication, we report the preparation and structure of the novel compound  $[\text{Mn}(\text{dach})_3]_2[\text{In}_{18}\text{Te}_{30}(\text{dach})_6] \cdot 2\text{Hdach} \cdot \text{H}_2\text{O}$  (**1**). In comparison with the inorganic wheels of polyoxomolybdate<sup>4</sup> and FeS,<sup>6</sup> the wheel-shaped InTe structure of compound **1** is decorated by organic ligand dach. However, it still belongs to the second type of wheel-like compounds. A related new 1D polymeric InTe compound  $\{[\text{Mn}(\text{dach})_3]_2[\text{In}_5\text{Te}_{10}] \cdot 2\text{H}_2\text{O}\}_\infty$  (**2**) is also presented here in order to understand the effect of acidity on the formation of the ring structure.

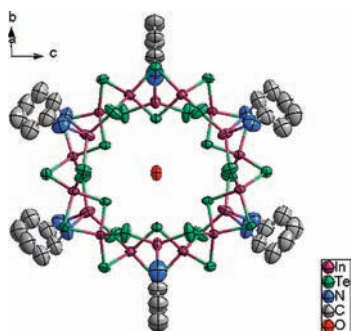
Compound **1** was prepared by a solvothermal technique. The element Mn and  $\text{InCl}_3$  reacted with tellurium powder in a mixed solvent of dach and  $\text{H}_2\text{O}$  (7:3 in volume). The optimized mole ratio of In:Mn:Te is 1:1:2. The optimized reaction temperature and time are 140 °C and 4 days. The 1D compound **2** was prepared by a method similar to that used for **1** except that the pure water was replaced by HCl (2 mol/L). In this case, crystals were obtained after 14 days. Details of the preparation can be found in the Experimental Section in the Supporting Information (SI). The weak acidity is the point for the formation of **1**, because at higher acidity, the dach molecules are protonated and difficult to coordinate to the In atom. The crystal samples for physical measurements are collected by a careful hand-picking method, and they are stable in open air. The experimental X-ray diffraction (XRD) pattern of **1** is in agreement with the simulated pattern from single-crystal XRD data (Figure S1 in the SI), which indicates the purity of the sample used for measurement. The broad vibrational bands of IR at about 3440 and 3250  $\text{cm}^{-1}$  indicate the presence of the  $-\text{NH}_2$  group and  $\text{H}_2\text{O}$  molecules. The

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sharp intense peak at  $1384\text{ cm}^{-1}$  is clearly the vibration of the  $-\text{NH}_2$  group. Those at about  $2920$  and  $2840\text{ cm}^{-1}$  are assigned to the C–H vibrational bands of dach (Figure S2 in the SI).

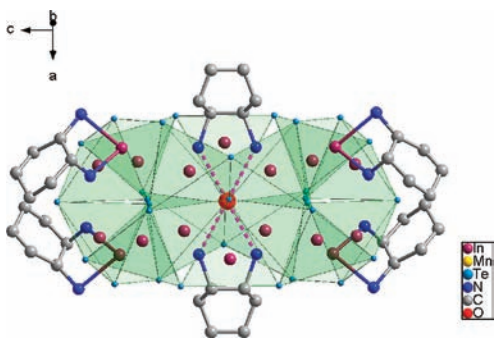
Single-crystal XRD analysis reveals that crystal **1** is orthorhombic and belongs to the  $Pnmm$  space group. Relevant crystal data, collection parameters, and refinement results can be found in Table S1 in the SI. The compound is comprised of a centrosymmetric wheel-shaped anion  $[\text{In}_{18}\text{Te}_{30}(\text{dach})_6]^{6-}$  (Figures 1 and S3 in the SI), two  $[\text{Mn}(\text{dach})_3]^{2+/3+}$  complex



**Figure 1.** Anion structure of compound **1** with 50% thermal ellipsoids. H atoms are omitted for clarity. The water molecule in the center is displayed.

cations, two protonated dach molecules, and one  $\text{H}_2\text{O}$  molecule. The structure of the  $[\text{In}_{18}\text{Te}_{30}(\text{dach})_6]^{6-}$  ring can be viewed as six  $\text{In}_2\text{Te}_6$  subunits (green in Figure S3b in the SI) grouped with six trigonal-bipyramidal  $[\text{InTe}_3(\text{dach})]$  (yellow in Figure S3b in the SI) via corner-sharing. The inorganic ring structure shows a pseudo- $D_{3d}$  symmetry, but it is an accurate  $C_i$  point group if considered as decorated organic dach molecules. The bond distances (Table S2 in the SI) of In–Te are  $2.7196(2)$ – $2.848(2)$  Å for tetrahedral In1, In3, and In4 and  $2.701(2)$ – $2.939(2)$  Å for trigonal-bipyramidal In2 and In5. In2 is chelated by dach with In–N distances of  $2.55(3)$  and  $2.29(3)$  Å, while In5 is chelated by dach with one strong In–N bond and one In–N interaction with distances of  $2.18(3)$  and  $2.77(3)$  Å, respectively.

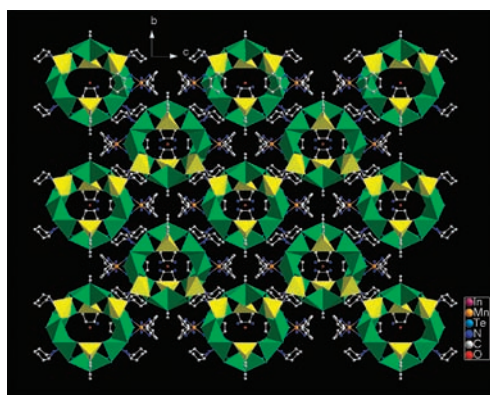
It is noteworthy that the  $\text{H}_2\text{O}$  molecule locates just at the center of the  $\text{In}_{18}\text{Te}_{30}$  ring and it is hydrogen-bonded by two protonated dach molecules, forming a  $\text{H}_2\text{O}/2\text{Hdach}$  unit (Figure 2), which acts as the template in the formation of the



**Figure 2.** Hydrogen-bonding  $\text{H}_2\text{O}/2\text{Hdach}$  unit that is located just at the center of the  $\text{In}_{18}\text{Te}_{30}$  ring of **1**. Two dach molecules bonded in the front and back of the  $\text{In}_{18}\text{Te}_{30}$  ring are omitted for clarity.

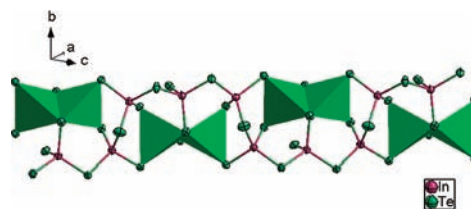
ring compound. The isolated  $[\text{Mn}(\text{dach})_3]^{2+}$  cations reside at the space outside the rings with both  $\Delta$  and  $\Lambda$  configurations. A

notable feature of compound **1** is the nanoscale ring size. The average outer diameter  $15.54$  Å (ca.  $1.5$  nm) and the inner diameter  $8.25$  Å of the ring are estimated from the distance of two opposite Te centers, and the van der Waals radii of the In atoms have not been taken into account. Figures 3 and S4 in the SI are the crystal packing of **1**, showing a ring matrix with body-centered anion packing.



**Figure 3.** Polyhedral views of the molecular packing of **1**, viewed along the  $a$  direction.

The structure of **2** is monoclinic and belongs to the  $P2_1/n$  space group with three formula units in a unit cell. Five  $\text{InTe}_4$  tetrahedra share edges and corners, forming a 1D polymeric structure with two discrete  $[\text{Mn}(\text{dach})_3]^{2+}$  complex cations and two  $\text{H}_2\text{O}$  molecules (Figures S5 and S6 in the SI). The chain structure can be described as  $\text{In}_2\text{Te}_6$  subunits (green in Figure

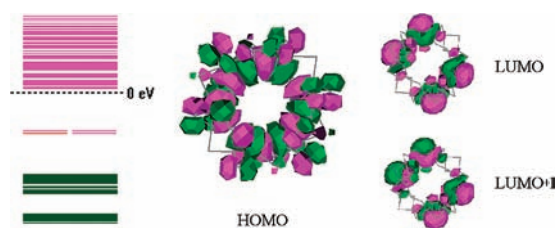


**Figure 4.** 1D structure of compound **2**, with the regular  $\text{In}_2\text{Te}_6$  subunits being shown in polyhedra.

4) connected by corner-sharing  $\text{InTe}_4$  tetrahedra. When the structure of **2** is compared with that of **1**, it is found that the dach molecule is not coordinated onto the In atom because of the higher acidity of the reaction medium (most of the amines are protonated). The bond distances of In–Te are  $2.738(2)$ – $2.924(2)$  Å, comparable to those of **1** (Table S3 in the SI). The subunits of  $\text{In}_2\text{Te}_6$ , formed by two  $\text{InTe}_4$  tetrahedra cosharing one edge, are bent about  $28^\circ$  with the face-to-face angle of  $83.507(44)^\circ$  and  $140.019(32)^\circ$  in **1** (Figure S7 in the SI), while the  $\text{In}_2\text{Te}_6$  subunits in **2** are no longer bent. The dach coordinating to the In atom is concerned with the bend of the  $\text{In}_2\text{Te}_6$  subunits, and that is also one of the reasons for the ring formation of **1**, except the templating effect of the  $\text{H}_2\text{O}/2\text{Hdach}$  unit.

Related calculations by the extended Hückel method<sup>6b,c,12</sup> provided useful insights into the electronic structure of the  $[\text{In}_{18}\text{Te}_{30}]^{6-}$  nanoring. The following are the principal conclusions from the molecular orbital (MO) calculations: (i) the ring structure is stable considering the lower energy of the highest occupied MOs (HOMOs); (ii) the compositions of the

MOs imply extensive electron delocalization; (iii) there are two energy gaps, one of which is the HOMO to lowest unoccupied MO (LUMO) and LUMO+1 gap, and the other of which is the LUMO+4 and LUMO+5 to LUMO+6 gap (Figures 5 and S8



**Figure 5.** Calculated electronic band structure and the HOMO and LUMO population of the  $[\text{In}_{18}\text{Te}_{30}]^{6-}$  nanoring.

in the SI). The band-gap value extracted from the UV–vis diffuse reflectance of **1** is 2.35 eV (Figure S9 in the SI), which is narrower than the calculated value.

In summary, the incorporation of dach chelation into the InTe structure has led to a large wheel-shaped InTe anion. It is noted that compound **1** is the first large nanoring compound found for main-group metal chalcogenides, in which the bridge is the inorganic divalent tellurium anion. The dach molecules play important roles in the formation of the wheel-like topology. The chelating coordination of dach molecules to six In ions forms unusual five-coordinated In centers,  $[\text{InTe}_3(\text{dach})]$ , and such trigonal bipyramids as linkwork bend and link the  $\text{In}_2\text{Te}_6$  subunits to form the ring structure. The other role is the templating function of the hydrogen-bonded  $\text{H}_2\text{O}/2\text{Hdach}$  unit. The nanoscale inorganic  $\text{In}_{18}\text{Te}_{30}$  cluster shows a double-decker ring structure, and the matrix in the single crystal might have applications as optical and electronic resonators. The scientists in materials and physics would be interested in such compounds.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Crystallographic data (CIF), experimental details, XRD, IR, thermogravimetric analysis, and diffuse-reflection spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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