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Cationic Main-Group Metal Chalcogenide with a 1-D Polymeric Structure, $[\{In(dien)\}_2(InTe_4)]\cdot Cl$

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Coordination of unsaturated $[In(amine)]^{3+}$ onto indium telluride structure, where the complex ion has higher positive charge, not only forms an organic−inorganic hybrid polymeric structure, but also offers an indium telluride with positive charge. Based on this strategy, cationic networks of metal chalcogenide may be expected.

Low-dimensional chalcogenides are currently the focus of interest for novel functional materials.[1] These compounds exhibit unique anisotropy effects,[2] because of the presence of different combined forces (van der Waals or covalent forces) along the distinct orientations. Numerous low-dimensional polymeric chalcogenides had been synthesized previously by solid-state reactions at high temperature or the very effective flux method at medium temperature. For example, $MInTe_2$ (M = Na, K, Rb, Tl) and AIn_2Te_4 (A = Ca, Sr, Ba)[3] are some pure inorganic tellurides with 1-D In_2Te_4 anionic chains constructed by MTe_4 tetrahedra sharing opposite edges. Lately, many low-dimensional compounds have been prepared by utilizing a hydrothermal or solvothermal synthetic technique at relatively low temperature. This method is usually used to obtain unique organic−inorganic hybrid materials with novel structures from 1-D to 3-D topology.[4−9] The cations of these compounds are tetraalkylammonium, protonated amines, or metal complex ions, and the main-group 13−15 chalcogenidometalates invariably act as polyanions, such as those for 1-D indium tellurides $[(C_4H_9)_4N]InTe_2$,[5] $[La(en)_4Cl]In_2Te_4$,[6] $[M(en)_3]In_2Te_6$ (M = Fe, Zn),[7] $[Ni(dap)_3]_{0.5}[InS_2]$,[8] $[Ni(dien)_2]_{0.5}[InS_2]$,[8] $[Zn(taa)(\mu\text{-tren})_{0.5}][InTe_2]Cl$,[9] $[M(en)_3]In_2Te_4\cdot en$ (M = Ni, Co),[9] and $[M(en)_3]_2In_4Te_8\cdot 0.5en$ (M = Mn, Fe, Zn).[9] Very recently, a number of compounds have been reported in which the metal complex segment is covalently bonded to an anionic framework and acts as a structural-modifying moiety.[10−15] We have obtained a series of 1-D neutral chalcogenidometalates like these types of compounds, such as 1-D chalcogenidostannates $[\{Mn(en)_2\}_2(\mu\text{-en})(\mu\text{-}Sn_2S_6)]_n$[10] and $[Mn(tepa)\cdot Sn_3Se_7]_n$,[11] 1-D thioantimonates $[Ln(en)_3(H_2O)_x(\mu_{3-x}$-

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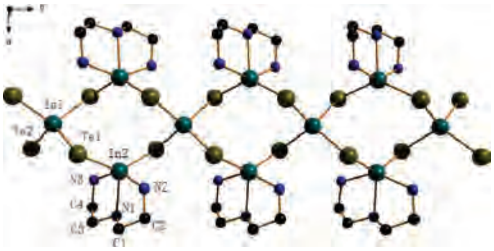
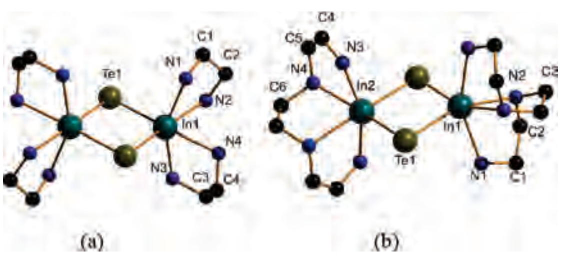


Figure 1. 1-D chain structure of the polymeric cation in **1** with a labeling scheme. H atoms are omitted for clarity.



(a) (b)

Figure 2. Crystal structures of dinuclear cations in **2** (a) and **3** (b) with a labeling scheme. All H atoms and I^- ions are omitted for clarity.

$SbS_4)]_n$ (Ln = La, $x = 0$; Ln = Nd, Sm, $x = 1$),[12] 1-D thiogallate $[Mn(atep)Ga_2S_4]_n$[13], and 1-D thioindate $\{[Ni(tepa)]_2[In_4S_7(SH)_2]\cdot H_2O$.[8] In these cases, in spite of the neutral structure of the chains, the chalcogenidometalate cores still take a negative charge.

In this paper, we report a novel 1-D polymeric indium telluride $[\{In(dien)\}_2(InTe_4)]\cdot Cl$ (**1**), which has been obtained and characterized during our successive exploration of solvothermal routes for the synthesis of main-group chalcogenidometalates. To the best of our knowledge, compound **1** is the first polymeric cationic metal chalcogenide. As a concomitant result, two new cationic organic hybrid indium telluride compounds, $[InTe(amine)]_2\cdot 2I$ [amine = en (**2**), teta (**3**)], are also presented herein.

Single-crystal X-ray diffraction analysis revealed that compound **1** crystallizes in monoclinic space group *P*2/*c* with two formula units in a unit cell and is composed of a cationic chain in stoichiometric $[\{In(dien)\}_2(InTe_4)]^+$ and a free Cl^- ion. The cationic chain structure can be viewed as a string of fused eight-membered In_4S_4 rings, sharing two opposite In atoms, and propagating along the crystallographic *c* axis (Figure 1). There are two structurally distinct In atoms in the chain, including distorted tetrahedral $InTe_4$ and distorted trigonal dipyramid $InTe_2N_3$, in which the N atoms come from the amine (dien) covalently bonded to the inorganic framework. The bond distances of In−Te in the $InTe_4$ tetrahedron [2.7691(5) Å for In1−Te1 and 2.7662(5) Å for In1−Te2] are longer than those in the $InTe_2N_3$ trigonal dipyramid [2.6998(6) Å for In2−Te2 and 2.7175(5) Å for In2−Te1]. These In−Te distances indicate that the unsaturated indium amine complex is a strong chalcophilic unit unlike the transition-metal complexes, which usually form weaker covalent bonds with chalcogenidometalate anions.[10–13]

Single-crystal X-ray analysis revealed that compounds $[InTe(en)_2]_2\cdot 2I$ (**2**) and $[InTe(teta)]_2\cdot 2I$ (**3**) have a dimeric cation with a similar In_2Te_2 rhomboidal core. The In center is six-coordinated by four N atoms from one teta or two en amine ligands and two bridging Te^{2-} ions, as shown in Figure 2. Both compounds display an inversion center in the middle of the In_2Te_2 core. The structural feature of **2** or **3** is that both of them contain main-group metal chalcogenide cations, similar to that of **1**. The I^- ions act as counterions and incorporate into the final products.

The organic−inorganic hybrid chalcogenides prepared in recent years display a new type of crystal structure and have attracted great interest. The metal complex cations usually act as templating components and are discrete to the anions,[6–9] while in some compounds, the cationic segments of the metal complex are covalently bonded to an anionic framework, acting as structural-modifying moieties. The complex modification contributes to the increased complexity and functionality of the chalcogenide. For examples, compound $[Mn(tepa)\cdot Sn_3Se_7]_n$ is a chiral structure,[11] and $[Mn(teta)(en)]\cdot[Mn(teta)][Mn(SnTe_4)_2\cdot Mn(teta)]$ displays a helical chain.[14] In most cases, the coordination center is a transition-metal or lanthanide metal ion,[10–14] and the main-group metals are invariably included in the anionic segments. Although main-group metal complexes with amine and S-donor ligands have been reported,[16] the polymeric hybrid chalcogenides with decorated main-group metal complexes are unfamiliar. On the other hand, it is also noteworthy that the reported chalcogenidometalates covalently linked with metal complex cations are usually nonionic structures (neutral) or ionic structures with negative charges. However, compound **1** displays a rare polychalcogenide structure with a positive charge. Therefore, the structure of **1** represents a new structural motif for chalcogenides of main-group metal complexes. This unusual structural character should result from the higher positive charge (3+) of the In ion and its comparable coordination ability to neutral amines and to chalcogen anions, which lead to part of the positive charge not being compensated for. The halogen ions Cl^- and I^- are also indispensable in the growth of the ionic crystals.

Halogen ion-directed supramolecular self-assembly has produced fascinating results in the crystal design and engineering of various topologies with interesting properties.[17] In the research of secondary building topology including cation, anion, and solvent, the halogen−H bond can be employed as an active joining during the assembly. There are many important halogen−H bonds between the 1-D cationic chain and the free Cl^- ion in **1** (N−H···Cl···H−N). By these hydrogen-bond interactions, the chains are assembled into a 2-D extended layer structure, shown in Figure 3. In addition, other interchain weak hydrogen bonds between Te atoms and organic amine (SI-Table 1 in the Supporting Inforamtion) further stabilize the chain skeleton structure of

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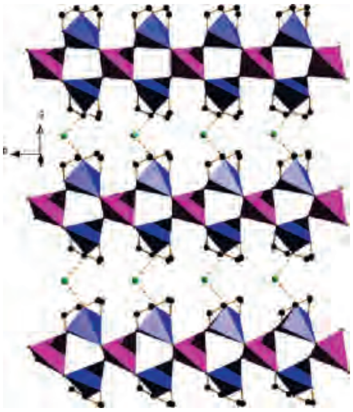

Figure 3. 2-D extended layer structure of **1** assembled by the N−H···Cl hydrogen bonds.

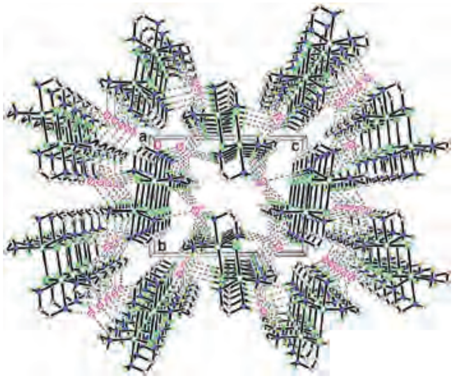

Figure 4. Molecular packing of **2**, showing the N−H···I interactions (I^- in pink).

1. In compounds **2** and **3**, the dimeric cations interact with the I^- anions via N−H···I nonclassical hydrogen bonds, assembling into a 3-D network structure (Figure 4).

IR spectra of three compounds show the typical bands of $-NH_2$ groups (Supporting Inforamtion). The UV−vis spectrum of **1** was recorded in the solid state at room temperature (Figure 5). The band gap can be estimated as 2.43 eV from the abrupt absorption edge, which is assigned to the electronic excitations located at the polymeric cation. Thermogravimetric analysis of **1** (SI-Figure 1 in the Supporting Inforamtion) shows an initial weight loss of 2.59% below 100 °C (physisorbed water), followed by a two-step weight loss of 19.25%, accompanied by two endothermic peaks at temperatures of 285.90 and 343.54 °C, respectively, corresponding to the decomposition of dien ligands (calcd 18.81%).

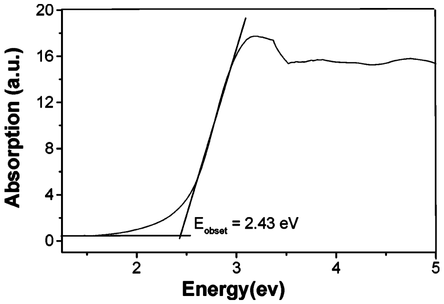

Figure 5. (a) Solid-state optical absorption spectrum of **1** at room temperature.

Although a number of main-group metal complexes with anionic or neutral structures as building units have been reported, no report of main-group metal polychalcogenide with a positive charge has been documented to date. In this paper, we have reported a new type structure of the main-group metal telluride with a positive charge. It is important to note that coordinating main-group metal $[M(amine)]^{n+}$ moiety onto the chalcogenide structure can offer a polymeric structure with a positive charge. If we are able to modify the structural construction and control the charge distribution, appropriate cationic metal chalcogenides are expected. This result has demonstrated a new tactic in synthesis and will broaden the potential application of the metal chalcogenides. Although application of these types of compounds is still unknown, on the basis of this strategy, cationic networks of metal chalcogenide may be expected, which are potential materials for anion separation. The N−H···X (X = halogen) hydrogen bonds have been discussed for these compounds, which are responsible for the structure topology and the formation of hydrogen-bond networks.

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Supporting Information Available: X-ray crystallographic data in CIF format and experimental preparation, IR data, table of X-ray crystallographic data, molecular packings, and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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