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Synthesis and Characterization of Two New Telluroindates: $K_6In_2Te_6{\cdot}4C_2H_8N_2$ and $(Ph_4P)_2In_2Te_6$

Chwanchin Wang and Robert C. Haushalter*,†

NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08540

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Main-group chalcogenides have recently attracted a great deal of attention because of their technological applications in low band gap semiconductors, photovoltaics, and IR detection.[1−4] Studies directed toward the synthesis of new materials have been facilitated by the use of several convenient low-temperature synthetic methods, including solvent extraction,[5−7] reaction involving alkali- and/or alkaline-earth-metal polychalcogenide salts (fluxes),[8,9] cathodic dissolution of intermetallic phases,[10] chemical reduction,[11,12] and solventothermal reaction.[13−18] Using these synthetic techniques, numerous binary, ternary, and even quaternary compounds with unique structures have been discovered and structurally characterized. However, only two examples of binary telluroindates have been reported: a 1-D chain compound $(n\text{-}Bu_4N)_2In_2Te_4$[19] and a discrete cluster compound $(Et_4N)_5In_3Te_7{\cdot}0.5Et_2O$,[12] synthesized by cathodic dissolution of an In_2Te_5 electrode and by chemical reduction using K/NH_3, respectively. Among the aforementioned synthetic methods, solventothermal reactions have also been widely used for the exploration of new materials, mainly concentrated on the sulfide and selenide systems. Relatively little synthetic efforts have been focused on the telluride systems.[18,20,21] Investigation of ternary A−In−Te systems (A = main-group elements), by employing the solventothermal technique in ethylenediamine (en), has led to the discovery of two new binary telluroindates. In this communication, we report the synthesis and structural characterization of these two compounds, $K_6In_2Te_6{\cdot}4en$ and $(Ph_4P)_2In_2Te_6$.

The telluride $K_6In_2Te_6{\cdot}4en$ was synthesized by mixing K_2Te and In_2Te_3 in a mole ratio of 3:1 with 1 mL of ethylenediamine in an evacuated Pyrex tube (∼10 mL). $(Ph_4P)_2In_2Te_6$ was synthesized by mixing 0.3 g (0.4 mmol) of an alloy of nominal composition $K_2InSbTe_4$, prepared from the fusion of K_2Te, In, Sb, and Te in stoichiometric proportions, and 0.3 g (0.8 mmol) of tetraphenylphosphonium bromide with 1 mL of ethylenediamine in an evacuated Pyrex tube (∼10 mL). The reaction tubes were heated to 150 °C over 12 h and maintained at 150 °C for 3 days followed by cooling to room temperature at a rate of 15 °C/h. Yellow plate crystals of $K_6In_2Te_6{\cdot}4en$ and red-brown needle crystals of $(Ph_4P)_2In_2Te_6$ were isolated and separated from byproducts in approximately 40% and 12% yields, respectively. Energy dispersive X-ray analysis on selected crystals from the products gave approximate ratios of 3:1:3 and 1:1:3 for K:In:Te and P:In:Te, respectively.

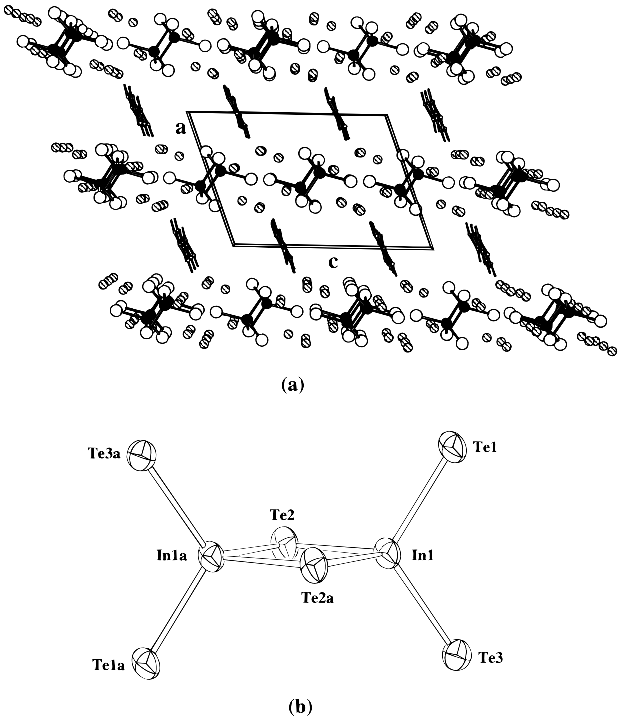

Figure 1. Approximate (010) projection of $K_6In_2Te_6{\cdot}4en$ (a). The cations and anions form a layerlike structure with the layers separated by ethylenediamine. The K, In, and Te atoms are shown as hatched, black, and open circles, respectively. The compound contains an isolated $In_2Te_6^{6-}$ dimer (50% probability ellipsoids) (b) which is composed of two edge-sharing $InTe_4$ tetrahedra. Distances (Å): In1−Te1, 2.738(1); In1−Te3, 2.741(1); In1−Te2, 2.850(1); In1a−Te2, 2.852(1).

The structure of $K_6In_2Te_6{\cdot}4en$[22] projected on the *ac* plane is shown in Figure 1a. Interestingly, cations and anions are aligned

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[†] Current address: Symyx Technologies, 3100 Central Expressway, Santa Clara, CA 95051.

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(22) Crystal data for $K_6In_2Te_6{\cdot}4en$: $C_8H_{32}N_8K_6In_2Te_6$, monoclinic space group $P2_1/c$ (No. 14), $a = 11.939(3)$ Å, $b = 9.878(2)$ Å, $c = 16.663(2)$ Å, $\beta = 110.08(1)°$, $V = 1845.7(6)$ Å^3, $Z = 2$, $D_{calc} = 2.654$ g cm^{-3}, μ(Mo Kα) = 65.88 cm^{-1}, crystal dimension 0.23 × 0.20 × 0.10 mm, $R = 0.031$, $R_w = 0.031$. The data were collected ($+h,+k,\pm l$) at 293 K on a Rigaku AFC7R four-circle diffractometer equipped with a RU300 18KW rotating anode, in the range of $2\theta < 40°$ using a $\omega - 2\theta$ scan at a scan rate of 8 deg/min. A total of 1973 reflections were measured, of which 1637 reflections with $I \geq 3\sigma(I)$ were considered as observed. An empirical absorption correction using the program DIFABS was applied (transmission 1.000−0.811). The structure was solved by direct methods and refined by the teXsan crystallographic software package of Molecular Structure Corp. All atoms were refined anisotropically except H atoms were fixed. One of nitrogen atoms in ethylenediamine was refined with a disordered model.

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parallel to the *bc* plane forming a layerlike structure. The layers are then separated by ethylenediamine which show strong interaction with the K^+ ions (K−N distances range between 2.59 and 3.14 Å). This strong K−N interaction is also observed in $(Ph_4P)_2[K_2Au_4Te_4(en)_4]$.[6] The telluride $K_6In_2Te_6{\cdot}4en$ possesses a highly charged dimeric $[In_2Te_6]^{6-}$ anion (Figure 1b) which is composed of two edge-sharing $InTe_4$ tetrahedra. There are four $In-Te_{terminal}$ bond distances, 2 × 2.741(1) and 2 × 2.738(1) Å, which are about 0.11 Å shorter than the $In-Te_{bridging}$ bond distances, 2 × 2.850(1) and 2 × 2.852(1) Å. Similar observations were also reported in both isoelectronic sulfide and selenide analogs.[23,24] There are three crystallographically unique K^+ ions that surround the $[In_2Te_6]^{6-}$ anions and have close contact with both the Te atoms (3.523(3)−3.966(3) Å) and the In atoms (3.830(3)−4.137(3) Å). Similar close contacts are also observed in KAuTe[25] and $(Ph_4P)_2[K_2Au_4Te_4(en)_4]$.[6] The dimer $[In_2Te_6]^{6-}$ shows even shorter $In-Te_{terminal}$ and longer $In-Te_{bridging}$ bond distances than those of the isolated $[InTe_4]^{5-}$ tetrahedra in Na_5InTe_4 (2.758−2.811 Å)[26] and the one-dimensional $[In_2Te_4]^{2-}$ chain in $(n\text{-}Bu_4N)_2In_2Te_4$ (2.786−2.814 Å),[19] respectively. It should be noted that the In_2Te_2 rings in $K_6In_2Te_6{\cdot}4en$ and $(n\text{-}Bu_4N)_2In_2Te_4$ become more strained as the structure extends from the dimer to a 1-D chain. This is manifested by the wider In−Te−In angles in the dimer which also results in a longer In−In distance (3.898 Å vs average 3.728 Å of a 1-D chain).

During our investigation of the ternary Sb−In−Te system, we discovered $(Ph_4P)_2In_2Te_6$.[27] Although the anion of $(Ph_4P)_2In_2Te_6$ has the same composition as that of the dimer, it instead adopts a one-dimensional chain structure. While the $InTe_4$ tetrahedra share opposite edges to form 1-D $[In_2Te_4]^{2-}$ chains in $(n\text{-}Bu_4N)_2In_2Te_4$, the $InTe_4$ tetrahedra in $(Ph_4P)_2In_2Te_6$ structure are instead linked together by sharing two Te corners and by joining the two other Te corners to form two Te_2^{2-} units with neighboring tetrahedra (Figure 2). These repeating $[InTe_{2/2}(Te_2)_{2/2}]$ units propagate along the *c*-axis in the formation of one-dimensional $[In_2Te_6]^{2-}$ chains separated by tetraphenylphosphonium ions. The In−Te bond distances within the $In_2(Te_2)Te$ five-membered ring are in the range 2.726 − 2.819 Å which are comparable to those of $(n\text{-}Bu_4N)_2In_2Te_4$, $MInTe_2$ (M = Na, K),[28] and $M'In_2Te_4$ (M′ = Ca, Sr, Ba).[28,29] The Te−Te distance in the Te_2^{2-} unit, 2.715(7) Å, falling between 2.70 Å ($MgTe_2$)[30] and 2.77 Å ($BaTe_2$),[31] is in good agreement with the Te−Te covalent bond distance, 2.74 Å.[32] The transannular In−In distances in these rings are 3.973(2) Å, which is about 0.2 Å longer than those compounds containing 1-D $[In_2Te_4]^{2-}$ chains. While 1-D $[In_2Te_4]^{2-}$ chains are found with both organic and inorganic cations, to our knowledge, 1-D $[In_2Te_6]^{2-}$ chains have not yet been discovered with inorganic ones. An isolated dimer, $[Sn_2Te_7]^{4-}$, with a similar five-membered ring was reported in $Cs_4Sn_2Te_7$.[33]

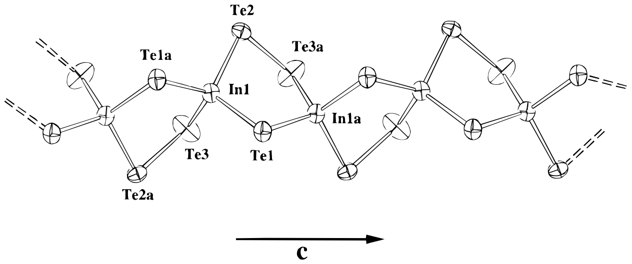

Figure 2. Perspective view of the $In_2Te_6^{2-}$ chain (50% probability ellipsoids) in $(Ph_4P)_2In_2Te_6$ along the *c*-axis. Distances (Å): In1−Te1, 2.753(6); In1−Te2, 2.819(6); In−Te3, 2.787(6); In1a−Te1, 2.726(6); Te2−Te3a, 2.715(7).

In summary we isolated two new telluroindates by employing solventothermal reactions in ethylenediamine and showed that telluride Zintl anions could be obtained by this method. The successful isolation of the $[In_2Te_6]^{6-}$ dimer suggests the possible discovery of oligomers as seen in the sulfide and selenide analogs.[23,24] On the contrary, the isolation of a new 1-D $[In_2Te_6]^{2-}$ chain also indicates the possibility in breaking down the chain and obtaining the dimer, $[In_2Te_7]^{6-}$, isoelectronic with the $[Sn_2Te_7]^{4-}$ ion. Work on the exploration of the In−Te system is underway.

Supporting Information Available: Tables of crystal data, atomic coordinates and thermal parameter, anisotropic displacement parameters, and bond distances and angles for $(Ph_4P)_2In_2Te_6$ and $K_6In_2Te_6{\cdot}4en$ (12 pages). Ordering information is given on any current masthead page.

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