

Electrochemical Synthesis of a New Indium Telluride Containing One-Dimensional Chains: Structure of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{In}_2\text{Te}_4$

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Received September 23, 1993; accepted December 14, 1993

A new indium telluride, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{In}_2\text{Te}_4$, has been synthesized at room temperature by the cathodic dissolution of an In_2Te_5 alloy electrode in an ethylenediamine solution of tetrabutylammonium iodide. The title compound is characterized by single-crystal X-ray diffraction at -120°C and crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 14.86(2)$, $b = 15.740(4)$, $c = 18.262(4)$ Å, $\beta = 96.48(6)^\circ$, $V = 4243(3)$ Å³, and $Z = 4$ with $R(R_w) = 0.038$ (0.040) for 3409 reflections ($I > 3\sigma(I)$) and 356 variables. The structure consists of one-dimensional $(\text{In}_2\text{Te}_4)^{2-}$ chains which run parallel to the crystallographic a axis and are separated by tetrabutylammonium cations. The $(\text{In}_2\text{Te}_4)^{2-}$ chains are isotopic to the chains found in the SiS_2 and KFeS_2 structure types. © 1994 Academic Press, Inc.

INTRODUCTION

Our investigation into the electrochemically controlled cathodic dissolution of alloy electrodes to produce crystalline solids has led to the discovery of a variety of novel compounds containing main-group element metal clusters (1). This technique, which involves the constant current electrolysis of a tellurium-rich alloy electrode in a concentrated supporting electrolyte of organic cations, produces conditions ideal for crystal growth and represents a new approach to the synthesis of Zintl compounds. Whereas previous techniques used to synthesize and isolate these compounds have relied on the high-temperature fusion of the elements and/or extraction methods (2), our technique relies on the constantly increasing concentration of anions as they are discharged from the cathode, is performed at room temperature, and in many cases yields X-ray quality single crystals in as little as 3–5 days. This technique may also allow the preparation of compounds which are not accessible by the more standard high-temperature and extraction techniques. Apart from Zintl's early electrochemical work (3) and two brief communications [the first relating to the preparation of solutions of Pb–Sn anionic clusters for NMR studies (4) and the second an electrochemical study of the utility of the Zintl anion salt R_4N^+

Hg_4^- to prepare quaternary ammonium salts (5)], the electrochemical synthesis of Zintl anions has not been thoroughly investigated. Our study of this technique continues with the electrolysis of In_2Te_5 alloy electrodes which, in the presence of concentrated tetrabutylammonium iodide solutions in ethylenediamine, yield the new one-dimensional indium telluride $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{In}_2\text{Te}_4$.

EXPERIMENTAL

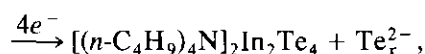
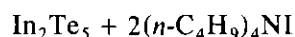
Crystals of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{In}_2\text{Te}_4$ were prepared by the cathodic dissolution of an In_2Te_5 alloy electrode which was made by melting stoichiometric amounts of the elements under N_2 in a quartz tube. The resulting shiny black regulus was then crushed into a fine powder and recast into cylindrical electrodes of approximate 1 cm² area each. The electrodes were then soldered to copper wires with 50/50 In–Sn solder and sealed into glass jackets with epoxy such that only the In_2Te_5 alloy was exposed. The synthesis was done in a two-compartment, liquid junction, air-tight electrochemical cell equipped with a nickel plate counter electrode. The cell was filled with a solution of 0.40 M tetrabutylammonium iodide in ethylenediamine (en) which served as both a source of cations for the crystallization process and the supporting electrolyte. The en was purified before use by distillation from a red solution of K_4Sn_9 , and all manipulations were carried out in a high purity (<1 ppm O_2) He atmosphere.

The cathodic dissolution of an In_2Te_5 alloy electrode (area ≈ 1 cm²) running at a constant current of 1 mA immediately gave rise to a deep red stream of anions which surrounded the cathode and then sank to the bottom of the cathode chamber. After 1 day the solution in the cathode chamber was dark red in color and transparent yellow plate-like crystals had been deposited on the In_2Te_5 electrode and throughout the cathode chamber. The deposition of this yellow crystalline layer (the elemental microprobe analysis of which showed an In : Te ratio of 1 : 1.97) on the In_2Te_5 electrode reduced the current flow to 300 μA where it was held for another 4 days. The dark red

TABLE 1
Crystal Data for $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{In}_2\text{Te}_4$

| | |
|---|--|
| Empirical formula | $\text{C}_{32}\text{H}_{72}\text{N}_2\text{In}_2\text{Te}_4$ |
| Formula weight (g/mol) | 1224.97 |
| Crystal color, habit | Yellow, plate |
| Crystal dimensions (mm) | $0.10 \times 0.14 \times 0.05$ |
| Crystal system | Monoclinic |
| Lattice parameters: | |
| a (Å) | 14.86(2) |
| b (Å) | 15.470(4) |
| c (Å) | 18.262(4) |
| β (°) | 96.48(6) |
| V (Å ³) | 4243(3) |
| Z | 4 |
| Space group | $P2_1/c$ (No. 14) |
| D_{calc} (g/cm ³) | 1.917 |
| Radiation | MoK_α (graphite monochromatized) |
| μ_{MoK_α} (cm ⁻¹) | 38.03 |
| T (°C) | -120 |
| Scan type | ω -2 θ |
| Scan rate (°/min) | 32 |
| Reflections measured | |
| Total | 8096 |
| Unique | 7780 ($R_{\text{int}} = 0.069$) |
| Used in refinement ($I > 3\sigma(I)$) | 3409 |
| No. variables | 356 |
| Goodness of fit indicator | 1.11 |
| Max (min) electron density in final difference map ($e^-/\text{Å}^3$) | 0.68 (-0.89) |
| $R(R_w)$ | 0.038(0.040) |

catholyte solution was then filtered under a He atmosphere leaving transparent yellow plate-like crystals which were isolated in an approximate 35% yield (electrochemical yield = 12%) (6). Exactly how the cathodic dissolution of an In_2Te_5 electrode in a concentrated solution of tetrabutylammonium iodide yields the one-dimensional chain compound $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{In}_2\text{Te}_4$ is unclear at this time, but may occur according to the equation



where Te_x^{2-} may be present as excess polytellurides in the catholyte solution, left as unreacted Te metal in the cathode, or perhaps some combination of both.

Crystals of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{In}_2\text{Te}_4$ were the only solid products obtained from the dissolution reaction and were not obtained from a control experiment of powdered In_2Te_5 and tetrabutylammonium iodide in en. They are unstable with respect to oxygen and moisture, decomposing immediately into a gray-black solid on exposure to the atmosphere.

STRUCTURAL DETERMINATION

A thin yellow plate crystal of approximate dimensions $0.10 \times 0.14 \times 0.05$ mm was mounted in a glass capillary. X-ray and intensity data were collected on a Rigaku AFC7R automatic four-circle diffractometer with graphite monochromated MoK_α radiation and a RU200 12-kW rotating anode generator. Cell constants and an orientation matrix for data collection were obtained from the setting angles of 24 carefully centered reflections in the range $20.45^\circ < 2\theta < 27.18^\circ$ and corresponded to a primitive monoclinic cell with the unit cell dimensions given in

TABLE 2
Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å²) for $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{In}_2\text{Te}_4$

| Atom | x | y | z | B_{eq} |
|-------|------------|-------------|-------------|-----------------|
| Te(1) | 0.97300(6) | -0.09087(7) | 0.41739(5) | 2.46(2) |
| Te(2) | 0.73774(6) | 0.11576(6) | 0.43548(5) | 2.14(2) |
| Te(3) | 0.76364(6) | -0.07096(6) | 0.59611(5) | 2.44(2) |
| Te(4) | 0.49304(6) | 0.09224(7) | 0.58180(5) | 2.48(2) |
| In(1) | 0.87546(7) | 0.01257(6) | 0.50631(5) | 1.95(2) |
| In(2) | 0.62460(7) | 0.01109(6) | 0.50832(5) | 1.91(2) |
| N(1) | 0.7733(7) | 0.2269(6) | 0.1694(5) | 1.9(2) |
| N(2) | 0.2621(7) | 0.2236(7) | 0.1722(6) | 2.4(3) |
| C(1) | 0.8318(8) | 0.2336(10) | 0.1069(7) | 2.5(3) |
| C(2) | 0.863(1) | 0.147(1) | 0.0800(8) | 3.9(4) |
| C(3) | 0.917(1) | 0.156(1) | 0.0168(9) | 4.8(5) |
| C(4') | 0.835 | 0.142 | -0.0504 | 3.5 |
| C(4) | 0.953(2) | 0.081(2) | -0.005(2) | 6.9(7) |
| C(5) | 0.6923(9) | 0.1685(2) | 0.1515(8) | 2.7(3) |
| C(6) | 0.6339(9) | 0.186(1) | 0.0819(8) | 3.4(4) |
| C(7) | 0.563(1) | 0.114(1) | 0.0703(10) | 5.2(5) |
| C(8) | 0.501(2) | 0.129(2) | 0.006(1) | 7.7(7) |
| C(9) | 0.7414(8) | 0.3173(9) | 0.1807(8) | 2.2(3) |
| C(10) | 0.6850(10) | 0.3284(9) | 0.2451(8) | 2.8(4) |
| C(11) | 0.6769(10) | 0.419(1) | 0.2672(9) | 3.6(4) |
| C(12) | 0.619(1) | 0.436(1) | 0.3279(9) | 4.6(5) |
| C(13) | 0.8273(9) | 0.1910(9) | 0.2383(7) | 2.4(3) |
| C(14) | 0.9066(9) | 0.2430(9) | 0.2722(8) | 2.7(3) |
| C(15) | 0.9513(10) | 0.200(1) | 0.3405(7) | 3.1(4) |
| C(16) | 1.0361(9) | 0.244(1) | 0.3739(8) | 3.7(4) |
| C(17) | 0.2878(9) | 0.1931(10) | 0.0970(7) | 2.6(3) |
| C(18) | 0.2207(9) | 0.2176(9) | 0.0317(7) | 2.7(3) |
| C(19) | 0.2471(9) | 0.1776(9) | -0.0381(8) | 2.7(3) |
| C(20) | 0.235(1) | 0.083(1) | -0.0437(10) | 5.4(5) |
| C(21) | 0.1677(9) | 0.1958(9) | 0.1846(7) | 2.5(3) |
| C(22) | 0.1499(9) | 0.1023(9) | 0.1753(8) | 3.0(3) |
| C(23) | 0.066(1) | 0.078(1) | 0.2092(9) | 4.4(4) |
| C(24) | 0.037(1) | -0.013(1) | 0.2026(10) | 4.7(5) |
| C(25) | 0.2635(9) | 0.3215(9) | 0.1729(7) | 2.5(3) |
| C(26) | 0.235(1) | 0.3613(9) | 0.2431(8) | 3.3(4) |
| C(27) | 0.260(1) | 0.4533(10) | 0.2461(8) | 3.2(4) |
| C(28) | 0.358(1) | 0.471(1) | 0.262(1) | 6.6(6) |
| C(29) | 0.3305(9) | 0.1869(9) | 0.2319(7) | 2.8(3) |
| C(30) | 0.4261(10) | 0.209(1) | 0.2305(9) | 4.3(4) |
| C(31) | 0.4842(9) | 0.168(1) | 0.2931(8) | 3.4(4) |
| C(32) | 0.472(1) | 0.206(1) | 0.366(1) | 5.4(5) |

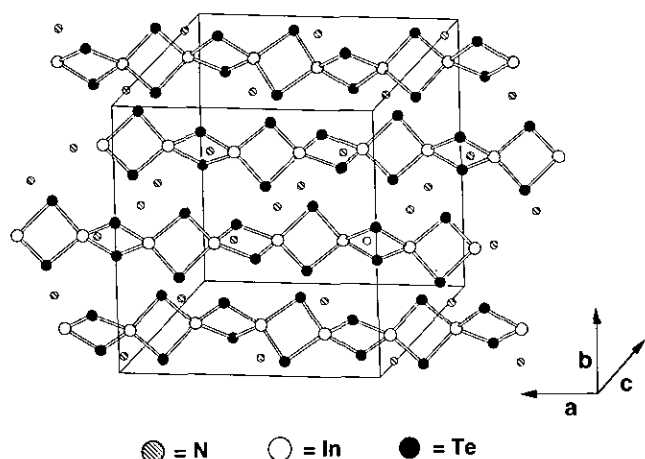


FIG. 1. Unit cell view of the $\text{In}_2\text{Te}_4^{2-}$ chains that run parallel to the crystallographic a axis. The carbon atoms of the tetrabutylammonium cations were omitted for clarity.

Table 1. The systematic absences of $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, uniquely determined the space group to be $P2_1/c$ (No. 14).

The data collection consisted of scans of $(1.26 + 0.35 \tan \theta)^\circ$ in the range $5^\circ < 2\theta < 50^\circ$ which were made at a speed of $32^\circ/\text{min}$ (in omega). The weak reflections [$I < 15.0\sigma(I)$] were rescanned a maximum of three times. The intensities of 3 standard reflections were measured after every 150 reflections, and over the course of the data collection decreased in intensity by 6.3%. A linear correction factor was applied to account for this phenomenon. An empirical correction using the program DIFABS (7) was also applied and resulted in transmission factors ranging from 0.802 to 1.234. The data were also corrected for Lorentz and polarization effects.

The structure was solved by direct methods and refined on F by full-matrix least squares using the *teXsan* crystallographic software package of Molecular Structure Corporation (8). All nonhydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were included, but not refined. One of the carbon atoms, C4,

TABLE 3
Selected Bond Distances (Å) and Angles ($^\circ$) for
 $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{In}_2\text{Te}_4$

| Bond distances | | | |
|----------------------|-----------|----------------------|-----------|
| Te-In | | | |
| Te(1)-In(1) | 2.814(2) | Te(1)-In(1*) | 2.797(3) |
| Te(2)-In(1) | 2.811(2) | Te(2)-In(2) | 2.795(2) |
| Te(3)-In(1) | 2.792(2) | Te(3)-In(2) | 2.786(2) |
| Te(4)-In(2) | 2.801(2) | Te(4)-In(2*) | 2.786(2) |
| Te-Te (transannular) | | In-In (transannular) | |
| Te(1)-Te(1*) | 4.170(2) | In(1)-In(1*) | 3.755(5) |
| Te(2)-Te(3) | 4.140(1) | In(1)-In(2) | 3.732(5) |
| Te(4)-Te(4*) | 4.188(2) | In(2)-In(2*) | 3.697(5) |
| Bond angles | | | |
| In(1)-Te(1)-In(1*) | 84.01(8) | In(1)-Te(2)-In(2) | 83.46(9) |
| In(1)-Te(3)-In(2) | 84.00(9) | In(2)-Te(4)-In(2*) | 82.88(8) |
| Te(1)-In(1)-Te(1*) | 95.99(8) | Te(1)-In(1)-Te(2) | 117.67(6) |
| Te(1*)-In(1*)-Te(3*) | 116.48(5) | Te(1*)-In(1)-Te(2) | 118.55(6) |
| Te(1)-In(1*)-Te(3*) | 114.45(6) | Te(2)-In(1)-Te(3) | 95.27(9) |
| Te(2)-In(2)-Te(3) | 95.76(9) | Te(2)-In(2)-Te(4) | 116.67(6) |
| Te(2)-In(2)-Te(4*) | 115.72(6) | Te(3)-In(2)-Te(4) | 116.62(6) |
| Te(3)-In(2)-Te(4*) | 116.39(6) | Te(4)-In(2)-Te(4*) | 97.12(8) |

of one of the crystallographically independent tetrabutylammonium cations was disordered over two sites and given site occupancy of 60% (C4) and 40% (C4') in the final model. The final least-squares refinement was based on 3409 observed reflections [$I > 3.0\sigma(I)$] and 356 variable parameters and converged with $R(R_w) = 0.038(0.040)$. Further details of the X-ray structural analysis are given in Table 1. The final positional and equivalent isotropic thermal parameters are given in Table 2.

DESCRIPTION OF STRUCTURE

The structure of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{In}_2\text{Te}_4$ consists of InTe_4 tetrahedra which are linked together by sharing opposite edges to form one-dimensional $\text{In}_2\text{Te}_4^{2-}$ chains as shown

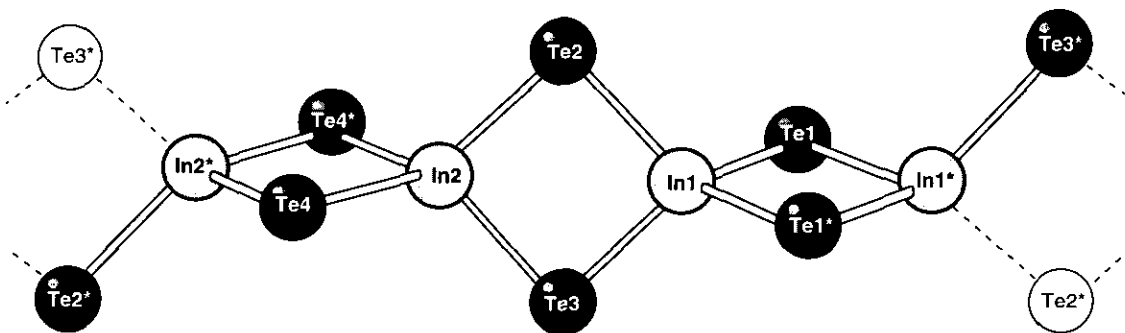


FIG. 2. One of the $\text{In}_4\text{Te}_{10}$ chain fragments in the unit cell of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{In}_2\text{Te}_4$.

in Fig. 1. The $\text{In}_2\text{Te}_4^{2-}$ chains run parallel to the crystallographic a axis and are effectively isolated from one another by tetrabutylammonium cations. These chains are isotopic with those found in the SiS_2 and KFeS_2 -type compounds (9) and are closely related to the ones found in the solid-state compounds $X\text{InTe}_2$ ($X = \text{Na}, \text{K}$) (10) and $Y\text{In}_2\text{Te}_4$ ($Y = \text{Ca}, \text{Ba}$) (11), but to our knowledge $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{In}_2\text{Te}_4$ represents the first example of a telluride compound with this structure type containing organic cations and completely isolated metal chains.

The unit cell of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{In}_2\text{Te}_4$ contains four separate $\text{In}_4\text{Te}_{10}$ chain fragments per unit cell translation along a , one of which is shown in Fig. 2. In–Te bond distances in the In_2Te_2 four-membered rings within these units are in the range 2.786(2)–2.814(2) Å. The transannular In–In distances in these rings are in the range 3.697(5)–3.732(5) Å, and those of the Te–Te are 4.140(1)–4.188(2) Å. Specific In–Te bond distances and selected bond angles are given in Table 3.

Comparison of the title compound with other structurally characterized indium tellurides shows numerous structural similarities (based on the InTe_4 tetrahedral unit) and a general agreement in In–Te bond distance values. The structure of Na_5InTe_4 , for example, consists of isolated InTe_4 tetrahedra with an average In–Te bond length of 2.788 Å (12). A similar structure, $\text{Na}_5\text{In}_2\text{Te}_6$, also consists of InTe_4 tetrahedra, this time connected through common vertices to form “Zweiereinfach”-chains which are further joined together into ribbons through intermittent neighboring Te–Te bridges (12). The average In–Te bond length in $\text{Na}_5\text{In}_2\text{Te}_6$ is 2.799 Å. Other compounds include the solid-state materials LiInTe_2 (13), InTeCl (14), and K_3InTe_4 (15), the first of which crystallizes in the chalcopyrite structure type with In–Te bond distances of 2.768 Å. The compound InTeCl contains complex layers of strongly distorted InTe_3Cl tetrahedra with In–Te bond distances varying from 2.752 to 2.883 Å. The structure of K_5InTe_4 has not been determined, the compound to date being characterized by X-ray powder diffraction and elemental analysis studies. All of these compounds have been prepared by the high-temperature fusion of stoichiometric amounts of the elements.

Structural similarities also exist between the title compound and indium sulfides and selenides. The compounds $\text{Rb}_6\text{In}_2\text{S}_6$ and $\text{Rb}_4\text{In}_2\text{S}_5$, for instance, consist of edge-sharing InS_4 tetrahedra that form isolated $\text{In}_2\text{S}_6^{6-}$ anions in the former and polymeric $\text{In}_2\text{S}_5^{4-}$ chains by corner sharing in the latter (16). The compound $\text{Rb}_6\text{In}_2\text{Se}_5$ is isostructural to $\text{Rb}_6\text{In}_2\text{S}_5$ with the same one-dimensional chains (17). Finally, in the compound KInSe_2 , InSe_4 tetrahedra form adamantane-like $\text{In}_4\text{Se}_{10}$ groups that are linked two-dimensionally via corners to form a layered material (17). Other examples of compounds with the very common InX_4

($X = \text{S}, \text{Se}, \text{Te}$) tetrahedral unit are likely to exist or will almost certainly be synthesized in the future.

In summary, our efforts in the electrochemical generation of Zintl anions from the cathodic dissolution of alloy electrodes have produced the novel indium telluride compound $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{In}_2\text{Te}_4$ described here as well as a wide variety of other polyanions (1). This preparative method is an ideal crystal growth technique and, considering the endless choice of both electrode materials and cations, should be amenable to many other systems. We have recently isolated crystals from the As, Ge, and Sn telluride systems, for example, which we will report in the near future.

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