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Synthesis and structural characterization of the new arsenic telluride $Rb_4As_2Te_4 \cdot (en)$

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Abstract—The ethylenediamine (en) extraction of an alloy of nominal composition $Rb_4As_2Te_4$ and subsequent concentration of the solution gave $Rb_4As_2Te_4 \cdot (en)$ (**1**) as dark red crystals in 40% yield. The single crystal X-ray diffraction data revealed a novel dimeric $[As_2Te_4]^{4-}$ anion, which consists of an As—As bonded As_2^{4+} dimer bonded to four Te atoms. Each of the As atoms are in a trigonal pyramidal coordination environment. © 1997 Elsevier Science Ltd

Keywords: arsenic tellurides; extraction of intermetallic phases; crystal structure.

INTRODUCTION

There has been a considerable interest in the chemistry and physics of the compounds containing Group 15 and 16 elements due to their potential applications in optical and electronics devices [1]. Pioneering work by Sheldrick and coworkers on the isolation of arsenic sulfide anions from the binary solid-state materials upon treatment with organic amines [2], and their subsequent efforts involving solvothermal reactions in methanol, elucidated a number of novel arsenic sulfides and selenides [3]. Kolis and coworkers [4] have synthesized other arsenic selenide compounds, such as $AsSe_4^{3-}$ [4b] and $As_2Se_3^{4-}$ [4b]. However, there are only a few arsenic telluride polyanions known to date, such as $As_{10}Te_3^{2-}$ [5], $As_{11}Te^{3-}$ [6], $As_2Te_6^{2-}$ [7] and $As_4Te_6^{4-}$ [8]. Recently, a unique method involving the cathodic dissolution of alloy electrodes that has led to several novel tellurides, such as $Au_3Te_4^{3-}$ [9], $GaTe_2(en)_2$ [10], $In_2Te_4^{2-}$ [11], $Hg_3Te_7^{4-}$ [12], $Sb_4Te_4^{4-}$ [13], $Sb_9Te_6^{3-}$ [13], $Sb_2Te_5^{4-}$ [14] and $Sb_6Te_9^{4-}$ [14], has also afforded the novel one dimensional arsenic telluride, $(Et_2N)_2[As_2Te_5]$ [15]. We and others [16] have also employed the solvent extraction of intermetallic phases and have successfully demonstrated that this method is capable of producing novel clusters and low-dimensional solids which are not readily accessible from conventional solution phase of solid-state reactions. Novel metal telluride complexes exhibiting unusual and diverse structural features, as seen in $Au_2Te_4^{2-}$ [17], $Au_4Te_4^{4-}$ [18], $KAu_9Te_7^{4-}$ [18], $Hg_4Te_{12}^{4-}$ [19], $Hg_2Te_5^{2-}$ [19], $Hg_2Te_4^{2-}$ [12], $Au_2Te_{12}^{2-}$ [20], $Ge_4Te_{10}^{4-}$ [21], $HgSnTe_4^{2-}$ [22] and $Cu_4SbTe_{12}^{3-}$ [23], have, for example, been isolated by this technique. In this paper we report the extension of the extractive method to the Group 15–16 intermetallic phases, which has resulted in the successful isolation and structural characterization of the new arsenic telluride complex $Rb_4As_2Te_4 \cdot (en)$ (**1**).

EXPERIMENTAL

All manipulations were performed under oxygen-free helium. Rb_2Te_2 was obtained by combining stoichiometric amounts of Rb metal and very fine Te powder in liquid ammonia under a nitrogen atmosphere. The alloy of nominal composition $Rb_4As_2Te_4$ was prepared from the fusion of Rb_2Te, As powder and elemental Te in the appropriate molar ratios in a quartz ampoule under nitrogen. The alloy was crushed to a very fine black powder and stored under a helium atmosphere. The ethylenediamine (en) was purchased from Aldrich (99.5+% double distilled), purified by

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distillation from CaH_2 followed by a second distillation from a red solution of K_4Sn_9, and stored under He.

Syntheses of $Rb_4As_2Te_4 \cdot (en)$ (**1**)

Telluride **1** was prepared by ethylenediamine extraction of an alloy of nominal composition $Rb_4As_2Te_4$. The red–brown extract obtained by the addition of 10 cm^3 of ethylenediamine to 1.00 g of $Rb_4As_2Te_4$ alloy was filtered and carefully concentrated by the slow removal of solvent *in vacuo* to ~5 cm^3. After 2 weeks, deep red crystals of **1** were isolated in an approximate 40% yield. A preliminary composition of the title compound was determined by quantitative analysis on several crystals in an electron microscope by energy dispersive X-ray analysis which gave an average composition of $Rb_{1.64}As_{1.00}Te_{1.90}$.

Crystallography

A single crystal of **1** was flame sealed into a thin-walled glass capillary under He for data acquisition. The crystallographic data were collected at 22°C on a Rigaku AFC7R four-circle diffractometer equipped with a RU300 18 kW rotating anode using ω–2θ scans. Accurate unit-cell dimensions were determined from 20 reflections in the range of $20 < 2\theta < 45°$. The intensities of three check reflections were monitored every 150 reflections during the course of data collection to check the crystal integrity. A decay in intensities of 7.0% was observed in **1** and a polynomial decay correction was applied to the data. The structure was solved by direct methods and refined on F by full-matrix least-squares using the *teXsan* crystallographic software package from Molecular Structure Corporation. All of the atoms in **1** were refined anisotropically, except for the en molecules which were refined isotropically due to a paucity of data. Further details of the X-ray structural analysis are given in Table 1 and some selected interatomic distances and angles are given in Table 2. Atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre.

Table 1. Crystallographic data for $Rb_4As_2Te_4 \cdot (en)$

Formula	$Rb_4As_2Te_4N_2C_2H_8$
F_W	1062.21
Crystal color, habit	Red, plate
a (Å)	8.356(4)
b (Å)	10.986(5)
c (Å)	10.809(4)
α (°)	90.00
β (°)	90.45(4)
γ (°)	90.00
V (Å^3)	992.2(7)
Z	2
Space group	$P\,2_1/n$ (no. 14)
D_{calc} (g cm^{-3})	3.555
μ (cm^{-1})	188.40
Crystal size (mm)	0.10 × 0.10 × 0.05
2θ max (°)	60
No. of data collected	2424
Data $I \geqslant 3\sigma(I)$	445
No. of variables	54
Final R/R_w	0.056/0.044

$R = \Sigma(|F_o - |F_c|)/\Sigma|F_o|$, $R_w = [(\Sigma w(|F_o| - |F_c|)/\Sigma w|F_o|^2)]^{/2}$.

Table 2. Selected bond lengths (Å) and bond angles (°) in $Rb_4As_2Te_4 \cdot (en)$

Te(1)—As(1)	2.585(8)
Te(2)—As(1)	2.583(8)
As(1)—As(1)	2.47(1)
Te(1)—Rb(1)	3.743(7)
Te(1)—Rb(1)	3.634(8)
Te(1)—Rb(2)	3.781(9)
Te(1)—Rb(2)	3.890(8)
Te(1)—Rb(2)	3.794(7)
Te(2)—Rb(1)	3.717(8)
Te(2)—Rb(1)	3.689(9)
Te(2)—Rb(2)	3.849(8)
Te(2)—Rb(2)	3.816(9)
Te(2)—Rb(2)	3.759(7)
Rb(1)—As(1)	3.67(1)
Rb(1)—N(1)	3.27(7)
Rb(1)—N(1)	3.44(7)
Te(1)—As(1)—Te(2)	104.6(3)
Te(1)—As(1)—As(1)	98.3(4)
Te(2)—As(1)—As(1)	98.7

RESULTS AND DISCUSSION

During our investigation of ternary Rb–As–Te alloys, we prepared an intermetallic alloy having the nominal composition $Rb_4As_2Te_4$. The extraction of this alloy with en and subsequent slow evaporation of the solvent gave deep red crystals of $Rb_4As_2Te_4 \cdot (en)$ (**1**). The single crystal X-ray diffraction data revealed that **1** contains the unprecedented $[As_2Te_4]^{4-}$ anion (Fig. 1). The $[As_2Te_4]^{4-}$ polyanion has a crystallographically imposed center of symmetry and consists of trigonal pyramidal As atoms containing As—As bonded As_2^{4+} dimers. The other two arsenic coordination sites in the $[As_2Te_4]^{4-}$ anion are satisfied by monotelluride (Te^{2-}) ligands.

The arsenic–arsenic bond length of 2.47(1) Å in the As_2^{4+} dimer can be compared with As—As distances of 2.517 Å in the α-form of elemental arsenic [24] as well as the bond lengths in the range 2.357–2.498 Å, as found in As_7^{3-} [25] or As_{11}^{3-} [26]. The As—Te distances in the $[As_2Te_4]^{4-}$ anion, which are either 2.585(8) or 2.583(8) Å, are similar to the As—Te distances observed in previously characterized arsenic tellurides [5, 6, 7, 8, 15].

The packing of the atoms in the unit cell of Rb_4As_2

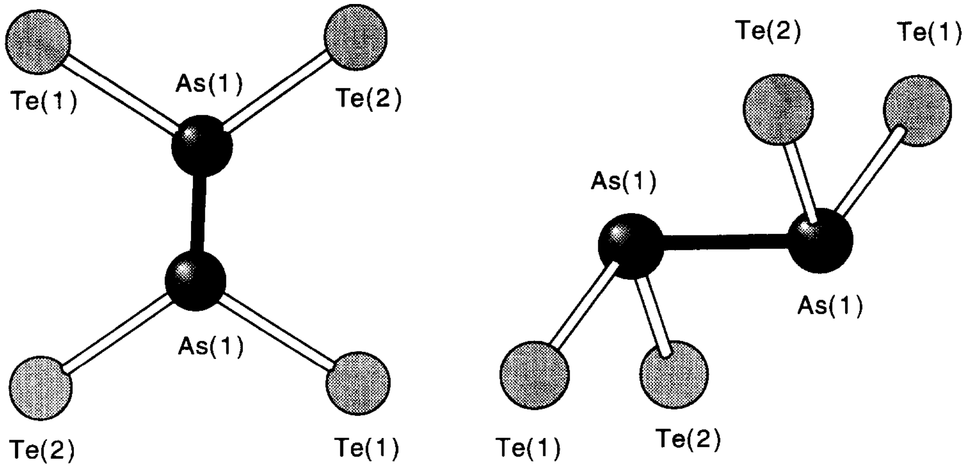

Fig. 1. Two views of the $[As_2Te_4]^{4-}$ anion in **1**.

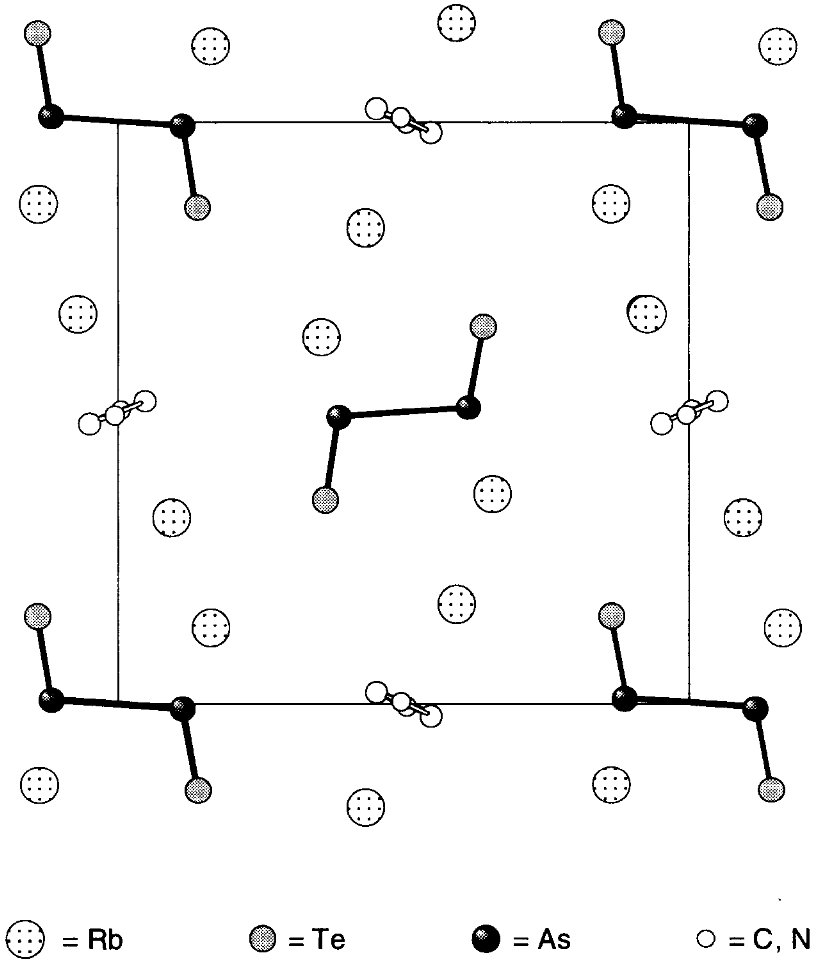

Fig. 2. Unit-cell view of the structure of $Rb_4As_2Te_4 \cdot (en)$ (**1**). The en molecules are hydrogen bonded to the Rb atoms.

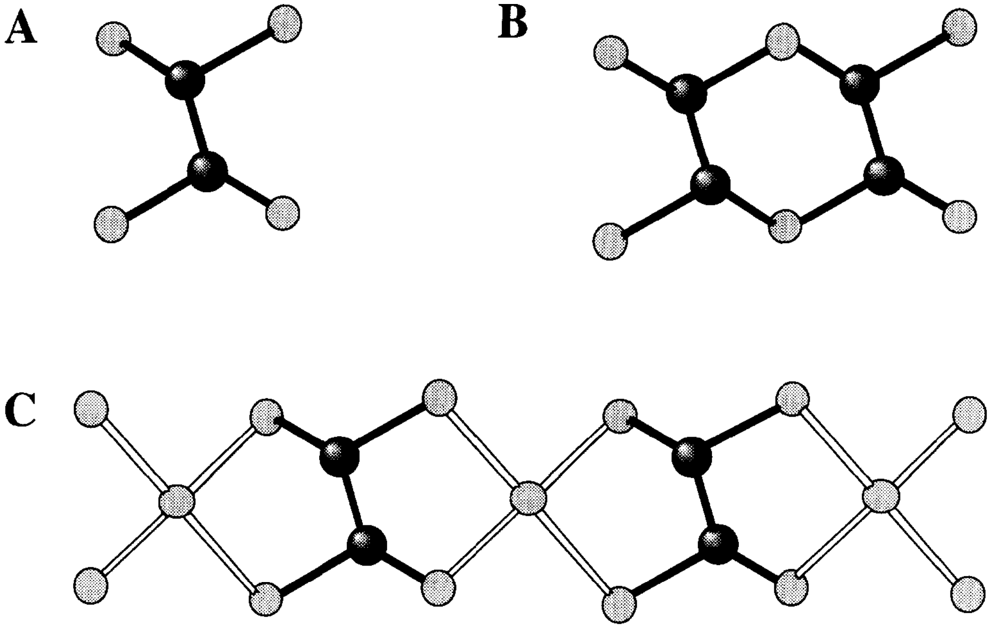

Fig. 3. The As_2Te_4 motif (a) isolated in (**1**) and its incorporation in the structures of $[As_4Te_6]^{4-}$ (b) and $[As_2Te_5]^{2-}$ (c).

$Te_4 \cdot (en)$ (**1**) is shown in Fig. 2. The unit cell consists of isolated $[As_2Te_4]^{4-}$ anions, Rb cations and ethylenediamine molecules. It is interesting to note that the nitrogen atoms of the en molecules in the $[As_2Te_4]^{4-}$ anion of **1** have rather short contacts with the Rb cations, these contacts ranging between 3.27 and 3.44 Å. The Rb atoms also have ionic interactions with the Te atoms which are in the range 3.634–3.890 Å. These and other selected bond distances and angles for $Rb_4As_2Te_4 \cdot (en)$ are given in Table 2.

Telluride $Rb_4As_2Te_4 \cdot (en)$ (**1**) is soluble in DMF and ethylenediamine, and are only slightly soluble in acetonitrile. The compound is also extremely air-sensitive, decomposing into black solids on exposure to the atmosphere. Our experiments in this system have also shown that when the en extract of $Rb_4As_2Te_4$ is treated with an additional solution of tetrapropylammonium iodide in en, single crystals of $(Pr_4N)_2[As_2Te_6]$ are produced in high yield. The compound $(Pr_4N)_2[As_2Te_6]$ contains the previously characterized $As_2Te_6^{2-}$ anion, which was first identified by Belin in the material (Crypt 2,2,2,-K)$_2$As$_2$Te$_6$ [7]. The $As_2Te_6^{2-}$ anion is composed of an As_2Te_4 six-membered ring having a chair conformation consisting of two Te_2^{2-} units and two trigonal pyramidal As^{3+} moieties. In contrast to the $As_2Te_4^{4-}$ anion, the $As_2Te_6^{2-}$ anion does not contain an As—As bond and the coordination environment of the arsenic atoms is satisfied by exocyclic Te atoms in *trans* positions. Not surprisingly, both the bond distances and angles in $(Pr_4N)_2[As_2Te_6]$ are similar to those reported for (Crypt 2,2,2,-K)$_2$As$_2$Te$_6$.

As shown in Fig. 3, the arsenic–arsenic bonded As_2Te_4 moiety [Fig. 3(A)] of **1** is found to be a common building block in the previously characterized $As_4Te_6^{4-}$ [8, 15] and $As_2Te_5^{2-}$ [15] species. As Fig. 3(B) illustrates, two As_2Te_4 units can, through the loss of two Te atoms, combine to form the $As_4Te_6^{4-}$ anion. In Fig. 3(C), the As_2Te_2 unit can be seen in each repeat unit of the infinite one-dimensional $As_2Te_5^{2-}$ polymer.

In summary, the synthesis and structural characterization of the new arsenic telluride $Rb_4As_2Te_4 \cdot (en)$ (**1**) substantiates the fact that extraction of ternary intermetallic phases is capable of yielding novel metal tellurides not necessarily accessible by other synthetic techniques. We are currently exploring the reaction of the title compound with post transition metals in ethylenediamine and characterizing the species thus formed.

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