

Rb₃Ti₃Te₁₁

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Tirubidium trititanium undecatelluride, Rb₃Ti₃Te₁₁, has been synthesized from the reaction of titanium, tellurium, and Rb₂Te₃ at 773 K. Its structure has been determined from single-crystal X-ray data. It is composed of one-dimensional [Ti₃Te₁₁³⁻] chains built by face-sharing pentagonal TiTe₇ bipyramids and distorted TiTe₆ octahedra. These chains adopt hexagonal closest packing along the [101] direction. Rb atoms are located among these chains. The wide range of Te–Te interactions makes the assignment of formal oxidation states impossible. The compound is isostructural with Cs₃Ti₃Te₁₁.

Comment

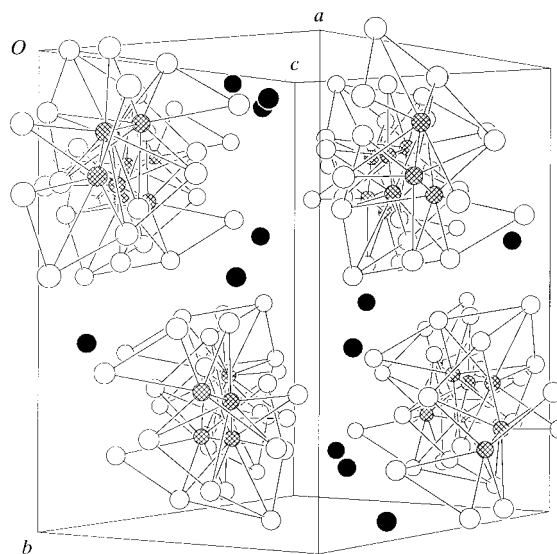
The study of low-dimensional solids is a central one in solid-state chemistry (Rouxel, 1986; Monceau, 1985). Such solids exhibit interesting physical properties, including superconductivity and charge–density waves (Withers & Wilson, 1986; Chaussy *et al.*, 1976; Monceau, 1985; Monceau *et al.*, 1976). Many one-dimensional polychalcogenides *A/M/Q* (*A* = Na, K, Rb, Cs; *M* = Ti, Zr, Hf; *Q* = S, Se, Te; Sunshine *et al.*, 1987*a,b*; Kang & Ibers, 1988; Keane & Ibers, 1991; Cody & Ibers, 1994; Pell & Ibers, 1996, 1997; Anderson *et al.*, 2000) have been synthesized with the aid of an *A*₂*Q*_{*x*} (*x* ≥ 1) reactive flux, since K₄Ti₃S₁₄ was first synthesized by the reactive flux method (Sunshine *et al.*, 1987*a,b*). These polychalcogenides contain linear infinite [*M/Q*] chains that are hexagonally closest packed. The polysulfide and polyselenide chains contain, almost exclusively, *Q*₂²⁻ dimers and *Q*²⁻ monomers (Pell & Ibers, 1997). The known polytellurides are K₄M₃Te₁₇ (*M* = Zr, Hf; Keane & Ibers, 1991), A₄Zr₃Te₁₆ (*A* = Rb, Cs; Cody & Ibers, 1994; Anderson *et al.*, 2000), Cs₃Ti₃Te₁₁ (Pell & Ibers, 1996), and Cs₅Hf₅Te₂₆ (Pell & Ibers, 1996). The Te–Te interactions in these [*M/Te*] chains are much more complicated in many of these compounds, showing a variety of distances intermediate between the single-bond distance and the van der Waals distance (about 2.76 and 4.10 Å, respectively; Shannon, 1976). Accordingly, formal oxidation states are usually impossible to assign in such compounds. We describe here the one-dimensional polytelluride Rb₃Ti₃Te₁₁, which is isostructural with Cs₃Ti₃Te₁₁.

The structure of Rb₃Ti₃Te₁₁ is displayed in Fig. 1. It consists of hexagonal closest packing of [Ti₃Te₁₁³⁻] chains along the

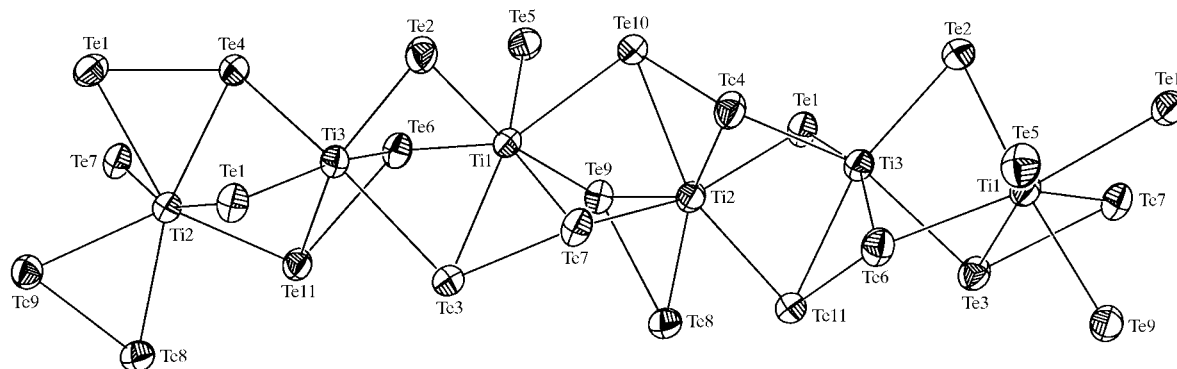
[101] direction. These chains are separated from each other by Rb atoms. Three unique Rb atoms in the structure are coordinated to ten, nine, and twelve Te atoms, respectively. The Rb–Te distances range from 3.5510 (8) to 4.2091 (8) Å. In contrast, two unique Rb atoms in Rb₄Te₃Te₁₆ are coordinated to eleven and twelve Te atoms, respectively, and Rb–Te distances vary from 3.614 (2) to 4.316 (3) Å (Cody & Ibers, 1994).

Each [Ti₃Te₁₁³⁻] chain contains three unique Ti atoms and eleven unique Te atoms. Two of the Ti atoms adopt a pentagonal bipyramidal geometry, and the other Ti atom has a distorted octahedral geometry. These polyhedra link together by three face-sharing Te atoms, as shown in Fig. 2. Here, the shortest Ti–Ti distance is 3.174 (1) Å, which does not differ from that in Cs₃Ti₃Te₁₁ [3.172 (2) Å]. The shortest non-bonding Ti–Ti distance in Na₂Ti₂Se₈ is 3.253 Å (Kang & Ibers, 1988), and that in TiO₂ is 3.07 (4) Å (Simons & Dachille, 1967). Therefore, no Ti–Ti bonding occurs in Rb₃Ti₃Te₁₁. Since the energy levels of 3*d* orbitals for Ti⁴⁺ are higher than those of the valence orbitals for *Q*²⁻, Ti atoms are presumed to be formally Ti⁴⁺ in the polychalcogenides. The Ti–Te distances range from 2.636 (1) to 2.912 (1) Å, consistent with those in Cs₃Ti₃Te₁₁ [2.628 (2) to 2.952 (2) Å; Pell & Ibers, 1996].

As is well known, tellurium has a greater propensity than the other chalcogens to exhibit *Q–Q* interactions of intermediate strength. The present compound, Rb₃Ti₃Te₁₁, illustrates this nicely. Only atoms Te1 and Te2 are Te²⁻ monomers, since they are not bonded to any other Te atoms. Each Te atom in the other nine is bonded to more than one Te atom, and the Te–Te distances range from 2.79 to 3.82 Å. Only Te–Te bonding distances from 2.7910 (6) to 3.2306 (6) Å are shown in Table 1. There are four Te–Te distances less than 3.0 Å, as shown in Fig. 2. Clearly, it is not possible to assign formal oxidation states in Rb₃Ti₃Te₁₁.

**Figure 1**

The unit cell of Rb₃Ti₃Te₁₁ viewed down [101]; filled, cross-hatched and open circles represent Rb, Ti and Te atoms, respectively.


Figure 2

The $[\text{Ti}_3\text{Te}_{11}]^{3-}$ chain along $[011]$ in $\text{Rb}_3\text{Ti}_3\text{Te}_{11}$ shown with 90% probability displacement ellipsoids. Pairs of Te atoms closer than 3.0 Å are connected by lines.

Experimental

Crystals of $\text{Rb}_3\text{Ti}_3\text{Te}_{11}$ were obtained from an initial mixture of Ti (1.0 mmol) (Alfa, 99.9%), Te (4.0 mmol) (Aldrich, 99.8%), and Rb_2Te_3 (0.5 mmol), synthesized from the reaction of stoichiometric amounts of elemental Rb (Aldrich, 98%) and Te in liquid ammonia. The mixture was loaded under argon, sealed under 10^{-4} Torr (1 Torr = 133.322 Pa) in a fused-silica tube, heated in a furnace to 773 K at 1 K min^{-1} , kept at 773 K for 3 d, cooled at 0.05 K min^{-1} to 373 K, and finally cooled to room temperature. The reaction mixture was washed with dimethylformamide, and then dried with acetone. It contained black needles and blocks of $\text{Rb}_3\text{Ti}_3\text{Te}_{11}$. The yield of these crystals was about 80–90%. Analysis of these crystals with an EDX-equipped Hitachi S-4500 SEM showed the presence of Rb, Ti and Te in the ratio 1:1:4.

Crystal data

$\text{Rb}_3\text{Ti}_3\text{Te}_{11}$	$D_x = 5.104 \text{ Mg m}^{-3}$
$M_r = 1803.71$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 14466 reflections
$a = 10.5757 (6) \text{ \AA}$	$\theta = 1.93\text{--}28.00^\circ$
$b = 15.0449 (8) \text{ \AA}$	$\mu = 20.560 \text{ mm}^{-1}$
$c = 14.7710 (8) \text{ \AA}$	$T = 153 (2) \text{ K}$
$\beta = 92.9540 (10)^\circ$	Needle, black
$V = 2347.1 (2) \text{ \AA}^3$	$0.150 \times 0.022 \times 0.017 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART 1000 CDD diffractometer	4676 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.033$
Absorption correction: numerical face indexed	$\theta_{\text{max}} = 28.00^\circ$
$T_{\text{min}} = 0.321$, $T_{\text{max}} = 0.511$	$h = -9 \rightarrow 13$
14466 measured reflections	$k = -19 \rightarrow 19$
5422 independent reflections	$l = -18 \rightarrow 15$
	Intensity decay: <2%

Refinement

Refinement on F^2	154 parameters
$R(F) = 0.028$	$w = 1/[\sigma^2(F_o^2) + (0.0400F_o^2)^2]$
$wR(F^2) = 0.066$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.037$	$\Delta\rho_{\text{max}} = 2.33 \text{ e \AA}^{-3}$
5422 reflections	$\Delta\rho_{\text{min}} = -1.89 \text{ e \AA}^{-3}$

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

Table 1

Selected geometric parameters (Å).

Rb1—Te5 ⁱ	3.7012 (8)	Rb3—Te3	4.1953 (8)
Rb1—Te3 ⁱⁱ	3.7101 (8)	Rb3—Te10 ^v	4.2091 (8)
Rb1—Te4 ⁱⁱⁱ	3.7270 (8)	Ti1—Te2	2.7187 (11)
Rb1—Te6 ⁱ	3.8179 (8)	Ti1—Te3 ^{xv}	2.7844 (11)
Rb1—Te9 ⁱⁱ	3.8518 (8)	Ti1—Te5 ^{xvi}	2.7910 (11)
Rb1—Te2	3.8756 (8)	Ti1—Te7 ⁱⁱⁱ	2.8275 (11)
Rb1—Te10	3.9319 (8)	Ti1—Te10	2.8531 (11)
Rb1—Te8 ⁱⁱ	3.9345 (8)	Ti1—Te6 ^{xvi}	2.8644 (11)
Rb1—Te11	3.9415 (8)	Ti1—Te9 ^{xv}	2.9121 (11)
Rb1—Te6 ^{iv}	4.1518 (8)	Ti2—Te1	2.7813 (11)
Rb2—Te5	3.5510 (8)	Ti2—Te9	2.7893 (11)
Rb2—Te1 ^v	3.6177 (8)	Ti2—Te8	2.7970 (11)
Rb2—Te1 ^{vi}	3.6413 (8)	Ti2—Te4 ^{xii}	2.8435 (11)
Rb2—Te8 ^v	3.6572 (8)	Ti2—Te10 ^{xvii}	2.8691 (11)
Rb2—Te7 ^{vii}	3.7932 (8)	Ti2—Te7 ^{xii}	2.8815 (11)
Rb2—Te3 ^{viii}	3.8476 (8)	Ti2—Te11 ^{xiii}	2.8829 (11)
Rb2—Te3 ^{ix}	4.0293 (8)	Ti3—Te1	2.6363 (11)
Rb2—Te2 ^{vi}	4.0602 (8)	Ti3—Te2	2.6399 (12)
Rb2—Te11 ^x	4.1034 (8)	Ti3—Te11 ^{xiii}	2.8024 (11)
Rb3—Te1 ^{viii}	3.6248 (7)	Ti3—Te6 ^{xvi}	2.8143 (11)
Rb3—Te5 ^{xi}	3.6954 (8)	Ti3—Te4 ^{xii}	2.8162 (12)
Rb3—Te2 ^{xii}	3.7040 (7)	Ti3—Te3 ^{xv}	2.9454 (11)
Rb3—Te8	3.7498 (8)	Te3—Te7 ^{xii}	2.8103 (6)
Rb3—Te10 ^{xiii}	3.7978 (8)	Te4—Te10 ^{xviii}	2.8870 (6)
Rb3—Te7 ^{xii}	3.8485 (8)	Te5—Te10 ^x	3.1316 (6)
Rb3—Te11 ^{xiii}	3.9324 (8)	Te5—Te6	3.1411 (6)
Rb3—Te9 ^{viii}	3.9915 (7)	Te5—Te9 ^{xix}	3.2306 (6)
Rb3—Te4 ^{xiv}	4.0196 (8)	Te6—Te11 ^{iv}	2.8909 (6)
Rb3—Te1 ^{xii}	4.0770 (8)	Te8—Te9	2.7910 (6)

Symmetry codes: (i) $x, 1+y, z$; (ii) $x, y, 1+z$; (iii) $x-1, y, z$; (iv) $1-x, 1-y, 2-z$; (v) $-x, 1-y, 1-z$; (vi) $x, y-1, z$; (vii) $x-1, y-1, z$; (viii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ix) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (x) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (xi) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (xii) $x-\frac{1}{2}, \frac{3}{2}-y, z-\frac{1}{2}$; (xiii) $x, y, z-1$; (xiv) $x-1, y, z-1$; (xv) $x-\frac{1}{2}, \frac{3}{2}-y, \frac{1}{2}+z$; (xvi) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (xvii) $\frac{1}{2}+x, \frac{3}{2}-y, z-\frac{1}{2}$; (xviii) $1+x, y, z$; (xix) $1-x, 1-y, 1-z$.

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1300). Services for accessing these data are described at the back of the journal.

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