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Ta5Sb4

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Ta₅Sb₄

Abstract
The title compound, pentatantalum tetraantimonide, was obtained as a by-product of the reaction between Ba and Sb mixed in a 1:2 molar ratio using tantalum as a reaction container. This compound adopts the Ti₅Te₄ structure type, which consists of chains of vertex-sharing Ta₆Sb₈ face-capped octahedral clusters. The resulting formulation is Ta₄Ta₂/2Sb₈/2. Distance ranges are: Ta--Ta 2.930(1)-3.301 (1) Å and Ta--Sb 2.775 (2)-3.074 (1) Å; there are no bonding Sb--Sb distances. Closer inspection reveals that the Ta substructure also resembles chains cut out from bcc packing.

Disciplines
Materials Chemistry | Other Chemistry | Physical Chemistry

Comments
Refinement

Refinement on $F^2$

$R(F^2) = 0.033$

$wR(F^2) = 0.090$

$S = 1.018$

2471 reflections

3 standard reflections

frequency: 60 min

intensity decay: 4.4%

Table 1. Selected geometric parameters ($\AA$, °)

<table>
<thead>
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<th>Symmetry codes</th>
<th>Fe1—O4</th>
<th>Sr1—O1</th>
<th>O3—P1—O1ii</th>
<th>O1v—O6vii</th>
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<tr>
<td>(i)</td>
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<td>2.533 (2)</td>
<td>1.138 (13)</td>
<td>112.94 (13)</td>
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<tr>
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<td>2.199 (2)</td>
<td>2.559 (2)</td>
<td>1.513 (2)</td>
<td>112.94 (13)</td>
</tr>
<tr>
<td>(iii)</td>
<td>1.502 (2)</td>
<td>2.566 (2)</td>
<td>1.513 (2)</td>
<td>112.94 (13)</td>
</tr>
<tr>
<td>(iv)</td>
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<td>2.637 (2)</td>
<td>1.513 (2)</td>
<td>112.94 (13)</td>
</tr>
<tr>
<td>(v)</td>
<td>1.502 (2)</td>
<td>2.648 (2)</td>
<td>1.513 (2)</td>
<td>112.94 (13)</td>
</tr>
<tr>
<td>(vi)</td>
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<td>2.657 (3)</td>
<td>1.513 (2)</td>
<td>112.94 (13)</td>
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<tr>
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<td>2.722 (2)</td>
<td>1.513 (2)</td>
<td>112.94 (13)</td>
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<tr>
<td>(viii)</td>
<td>1.502 (2)</td>
<td>2.776 (2)</td>
<td>1.513 (2)</td>
<td>112.94 (13)</td>
</tr>
<tr>
<td>(ix)</td>
<td>1.502 (2)</td>
<td>2.776 (2)</td>
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<td>112.94 (13)</td>
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<tr>
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<td>2.898 (2)</td>
<td>1.513 (2)</td>
<td>112.94 (13)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) $-x,-y,-z$; (ii) $x,-y,-z$; (iii) $-x,-y,1-z$; (iv) $x,-y,1-z$; (v) $-x,-y,1-z$; (vi) $x,-y,1-z$; (vii) $x$, $y$, $z$; (viii) $x$, $y$, $z$; (ix) $x$, $y$, $z$; (x) $x$, $y$, $z$; (xi) $x$, $y$, $z$.

Absorption corrections were attempted (Gaussian method), but they did not improve the results of the refinement. The rather complex shape of the crystal makes a good numerical correction difficult to obtain. Thus, the results are based on observed structure factors with no absorption correction. Only about half the reflections in the $hkl$ range indicated could be measured, but all independent reflections were measured at least once.


The authors thank Professor M. Leblanc (Université du Maine) for his help in data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1225). Services for accessing these data are described at the back of the journal.

References


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TaSb$_4$

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Abstract

The title compound, pentatantalum tetraantimonide, was obtained as a by-product of the reaction between Ba and Sb mixed in a 1:2 molar ratio using tantalum as a reaction container. This compound adopts the Ti$_5$Te$_4$ structure type, which consists of chains of vertex-sharing Ta$_6$Sb$_8$ face-capped octahedral clusters. The resulting formulation is Ta$_4$Ta$_2$/2Sb$_8$/2. Distance ranges are: Ta-Ta $= 2.930 (1) - 3.301 (1)$ and Ta-Sb $= 2.775 (2) - 3.074 (1)$ Å; there are no bonding Sb···Sb distances. Closer inspection reveals that the Ta substructure also resembles chains cut out from bcc packing.

Comment

During investigations on the binary barium–antimony system using sealed tantalum containers for their preparation, the compound Ta$_5$Sb$_4$ was obtained as a side product. Previously, this compound was prepared by direct reaction between the elements and characterized by X-ray powder diffraction (Boller & Nowotny, 1964; Furuseth et al., 1965). Ta$_5$Sb$_4$ is isostructural with tetragonal Ti$_5$Te$_4$ (Grönvold et al., 1961), which adopts the space group $I4/m$. Unit-cell parameters for Ta$_5$Sb$_4$ have been determined to be $a = 10.2357 (14)$ and $c = 3.5425 (7)$ Å. The shortest interatomic distances

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are Ta-Ta 2.930 (1) and Ta-Sb 2.775 (2) Å. These distances are close to the shortest distance found in elemental tantalum \((bcc, 2.86 \text{ Å}; \text{Mueller, 1977})\) and the sum of the metallic radii of Ta and Sb \((\text{Barrett et al., 1963})\), which is 2.88 Å. The closest Sb-Sb distance in this compound is 3.525 Å, which indicates that there is no bonding interaction between Sb atoms, as this is much longer than twice the metallic radius of Sb.

The \(\text{Ti}_6\text{Te}_4\) structure has been discussed with respect to the condensation of \(\text{Ti}_6\text{Te}_8\) face-capped octahedral clusters via opposite vertices, which leads to a quasi-infinite chain of composition \(\text{Ti}_{2/2}\text{Te}_{8/2} = \text{TiS} \text{Te}_4\) \((\text{Simon, 1992})\). In \(\text{TasSb}_4\), as in the other examples, the octahedra are compressed by approximately 22%; the eight octahedral edges involving the apex atoms are 2.930 (1) Å long, whereas the four edges in the waist are 3.297 (1) Å long. This distance, within standard error, equals the shortest Ta-Ta distance found between adjacent chains of 3.301 (1) Å, the apex Ta atoms are bonded to four Sb atoms arranged in a square-planar structure at a distance of 3.074 (1) Å, the other Ta atoms being coordinated by a distorted square pyramid of Sb atoms; in the equatorial plane, the Ta-Sb distances are 2.790 (1) and 2.827 (1) Å, while the remaining distance to an adjacent column is 2.775 (2) Å. This strong donor-acceptor interaction between Ta atoms in the waist with Sb atoms from neighboring chains in the axial position of the local square pyramid may explain the distortion of the octahedra \((\text{Simon, 1992})\), but the alternative explanation uses the assumption that the shared apex Ta atoms prefer a \(bcc\)-type environment with eight nearest-neighbor Ta atoms \((\text{Chen & Franzen, 1972})\).

As indicated by \(\text{Simon (1992)}\), this structure type occurs for a wide range of electron counts from 44 \((\text{TiSTe}_4)\) to 50 valence electrons \((\text{MoS}_2\text{As}_4)\). \(\text{TasSb}_4\) exhibits 45 valence electrons. According to band-structure calculations of \(M_2X_4\) chains \((\text{Kumar & Heine, 1984a,b})\), minima in their electronic energy densities of states occur for 44–45 and 49–50 valence electrons. \(\text{TasSb}_4\) is in good agreement with the lower values.

**Experimental**

The title compound was obtained as a by-product when elemental Ba [rod, Aesar (99.99%)] and Sb [powder, 100 mesh, Aesar (99.999%)] in a 1:2 molar ratio were loaded into a tantalum tube \((\text{Noble-Met. Ltd, }> 99.85\%, 0.375 \text{ OD})\) in an argon-filled glove-box, sealed in an arc melter under argon, and then heated to 1173 K for 3 d in a fused-silica jacket. The reaction container was slowly cooled to 673 K at 10 K h\(^{-1}\) and then quenched to room temperature. When the tantalum tube was opened in the argon-filled glove-box, thin grey needle-shaped crystals of the title compound were found in the product. Suitable single crystals were mounted in 0.2 mm thin-walled capillaries for subsequent diffraction experiments.

**Crystal data**

\[
\begin{align*}
\text{TasSb}_4 & & \text{Mo K}\alpha \text{ radiation} \\
M_r & = 1391.75 & \lambda = 0.71073 \text{ Å} \\
& \text{Tetragonal} & \text{Cell parameters from 39} \\
\frac{a}{m} & = 10.2357 (14) \text{ Å} & \text{reflections} \\
c & = 3.5425 (7) \text{ Å} & \theta = 7.28-14.66^\circ \\
V & = 371.15 (10) \text{ Å}^3 & \mu = 87.556 \text{ mm}^{-1} \\
Z & = 2 & T = 293 (2) \text{ K} \\
D_t & = 12.454 \text{ Mg m}^{-3} & \text{Needle} \\
D_m & \text{not measured} & 0.10 \times 0.03 \times 0.03 \text{ mm} \\
& & \text{Grey}
\end{align*}
\]

**Data collection**

Rigaku AFC-6R diffractometer

\(2\theta-\omega\) scans

Absorption correction: \(\psi\) scan \((\text{North et al., 1968})\)

\(T_{\text{min}} = 0.138, T_{\text{max}} = 0.199\)

655 measured reflections

314 independent reflections

218 reflections with \(I > 2\sigma(I)\)

\(R_{\text{int}} = 0.096\)

\(\theta_{\text{max}} = 30.05^\circ\)

\(h = -14 \rightarrow 14\)

\(k = 0 \rightarrow 14\)

\(l = 0 \rightarrow 4\)

3 standard reflections

every 150 reflections

intensity decay: 0.4%

**Refinement**

Refinement on \(F^2\)

\(R(F^2 > 2\sigma(F^2)) = 0.029\)

\(wR(F^2) = 0.065\)

\(S = 1.062\)

314 reflections

16 parameters

\(w = 1/[\sigma^2(F_o^2) + 18.3209P]\)

where \(P = (F_o^2 + 2F_c^2)/3\)

\((\Delta/\sigma)_{\text{max}} < 0.001\)

\(\Delta \rho_{\text{max}} = 4.49 \text{ e Å}^{-3}\)

\(\Delta \rho_{\text{min}} = -4.60 \text{ e Å}^{-3}\)

Extinction correction: \(\text{SHELXL97}\)

Extinction coefficient: 0.00108 (8)

Scattering factors from \(\text{International Tables for Crystallography (Vol. C)}\)
The crystal structure was solved by direct methods (SHELXS97; Sheldrick, 1990). The space groups $I4$, $I4$ and $I4/m$ were allowed based upon the observed systematic absences. The space group $I4/m$ was selected for initial refinements, and this group was confirmed by comparing the refinement results using the other two groups, which were identical with $I4/m$ within three s.u.'s. The Ta and Sb atoms were readily located from the $F$ map and refined with anisotropic displacement parameters. The reflection (110) with $2\theta = 5.62^\circ$ was omitted from the refinement due to the close proximity and possible interference from the beam stop of the X-ray diffractometer. The largest residuals in the final difference map were $4.49 \text{ e}^{-3}$ at a distance of $1.82 \AA$ from Tal and $-4.60 \text{ e}^{-3}$.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{Å}^2$)

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<tr>
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</table>


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**Strontium tetramolybdate dihydrate, SrMo$_4$O$_{13}$·2H$_2$O**

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(Received 6 August 1998; accepted 19 October 1998)

**Abstract**

SrMo$_4$O$_{13}$·2H$_2$O contains infinite sheets of distorted MoO$_6$ and MoO$_5$ moieties sharing edges and vertices. Inter-layer nine-coordinate Sr$^{2+}$ cations [\(d_{av}(\text{Sr}--\text{O}) = 2.678 (3) \text{ Å}\)] and water molecules complete the structure, which is isostructural with that of BaMo$_4$O$_{13}$·2H$_2$O.

**Comment**

SrMo$_4$O$_{13}$·2H$_2$O (Fig. 1) is confirmed to be isostructural with BaMo$_4$O$_{13}$·2H$_2$O (Harrison et al., 1995). The polyhedral connectivity of the Mo/O groups results in buckled anionic sheets of stoichiometry [Mo$_4$O$_{13}$]$_{2-}$, which propagate normal to [100]. Both vertex-sharing and edge-sharing of the MoO$_6$ and MoO$_5$ groups occurs in this phase, which has essentially the same sheet structure as BaMo$_4$O$_{13}$·2H$_2$O.

The Sr$^+$ atom is nine-coordinate to O atoms [\(d_{av}(\text{Sr}--\text{O}) = 2.678 (3) \text{ Å}\)] in irregular coordination (Fig. 2). Four of these neighbours are the O atoms of

---

<Fig. 1. Fragment of the SrMo$_4$O$_{13}$·2H$_2$O structure, drawn with 50% displacement ellipsoids. The very long Mo$^2$--O$_{11}$ bond is indicated by a thin line (see text). Symmetry codes are as in Table 1.>