Crystal structure of a new modification of potassium tetrathioantimonate, β -K₃SbS₄

W. Bensch and P. Dürichen

Universität Frankfurt, Institut für Anorganische Chemie, Marie-Curie-Str. 11, D-60439 Frankfurt/Main, Germany

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Source of material: During our investigations in the system A/Nb/Sb/S the compound β -K₃SbS₄ was obtained under the following conditions. K₂S₃, Nb, Sb and S, in a 4/1/2/8 ratio, were thoroughly mixed in a dry box. K₂S₃ was prepared by the reaction of stoichiometric amounts of K and S in liquid ammonia under an argon atmosphere. The mixture was then loaded into a pyrex-glass ampoule which was subsequently evacuated (4×10^{-5} mbar) and sealed. The ampoule was heated to 623 K for 6 days and afterwards was cooled to roomtemperature with 3K/h. The resulting black-red melt was washed with DMF and dried in vacuum. The product consisted of two components, red crystals of K₆Nb₄S₂₅ and white transparent crystals of β -K₃SbS₄. β -K₃SbS₄ is hygroscopic and must be stored under dry conditions. For X-ray crystal structure determination, a suitable crystal was mounted on a glass fiber and completely covered with glue. Despite these measure the crystal slightly decomposed during

data collection. The standard reflections showed a decrease of nearly 20% intensity.

Ternary thio- and selenoantimonates (V) A₃SbQ₄ (A= Rb, Cs, NH₄⁺; Q= S, Se) crystallize either in the cubic (NH₄)₃SbS₄ structure type (space group *I*43*m*) or in the orthorhombic (NH₄)₃AsS₄ structure type (space group *Pnma*) (see refs. 1-3). The title compound crystallizes in the acentric orthorhombic space group *Cmc*2₁. The Sb–S distances of 2.340 Å and 2.353 Å and the S–Sb–S angles of 108.9°–109.8° are in the range observed in other thioantimonates(V), and reveal that the tetrahedra are only slightly distorted. Assuming an origin shift of 1/4 in *b* the centers of the SbS₄ tetrahedra would occupy all corners and face centers of this "new" unit cell. The K1 ion is coordinated by six S with K–S distances ranging from 3.173 Å to 3.457 Å. The resulting polyhedron may be viewed as a strong distorted trigonal prism. The K2 center shows five short K–S distances (3.105 Å – 3.276 Å) and two significantly longer contacts of 3.721 Å. Hence, the coordination number for K2 is 5+2.

K₃S₄Sb, orthorhombic, *Cmc*2₁ (No. 36), *a* = 10.712(2) Å, *b* = 11.289(2) Å, *c* = 7.705(2) Å, *V* = 931.7 Å³, *Z* = 4, *R*(*F*) = 0.053, *R*_w(*F*²) = 0.156.

Table 1. Parameters used for the X-ray data collection

Crystal:	white-transparent, irregular, size 0.14 x 0.16 x 0.18 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	51.08 cm ⁻¹
Diffractometer:	STOE AED-II
Scan mode:	$\omega/2\theta$
<i>T</i> _{measurement} :	293 K
$2\theta_{\max}$:	55°
<i>N</i> (<i>hkl</i>) _{unique} :	749
Criterion for <i>I</i> ₀ :	<i>I</i> ₀ > 2 σ (<i>I</i> ₀)
<i>N</i> (<i>param</i>) _{refined} :	43
Programs:	SHELXS-86, SHELXL-93

Table 2. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Sb(1)	4 <i>a</i>	0	0.75467(8)	0.9804	0.0206(6)	0.0146(6)	0.0182(6)	0	0	–0.0012(6)
S(1)	4 <i>a</i>	0	0.9091(4)	0.7765(9)	0.029(2)	0.022(2)	0.025(2)	0	0	0.003(2)
S(2)	8 <i>b</i>	0.1778(4)	0.7692(3)	1.1556(6)	0.027(2)	0.028(1)	0.028(2)	0.003(1)	–0.007(2)	–0.004(2)
S(3)	4 <i>a</i>	0	0.5710(4)	0.8361(9)	0.038(3)	0.018(2)	0.023(2)	0	0	0.004(2)
K(1)	8 <i>b</i>	0.2232(3)	0.9699(3)	0.489(1)	0.039(1)	0.034(1)	0.047(2)	0.014(1)	0.005(3)	0.005(2)
K(2)	4 <i>a</i>	0	0.7007(4)	0.481(1)	0.081(3)	0.026(2)	0.024(2)	0	0	0.001(3)

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