Crystal structure of potassium antimony hexathiodiphosphate, $KSbP_2S_6$

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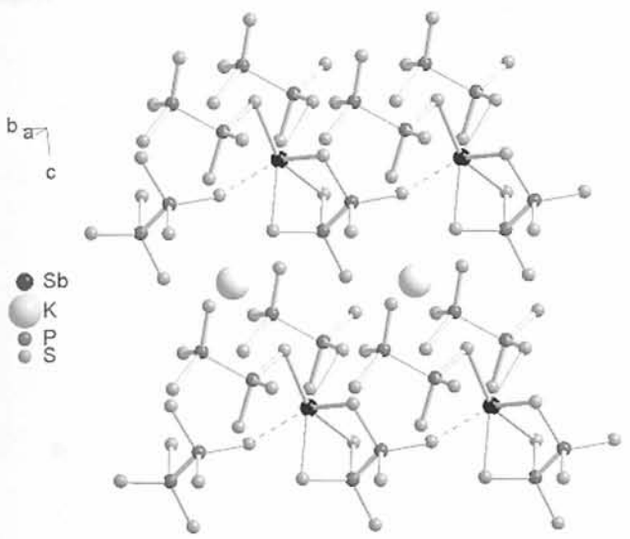

Abstract

$KSbP_2S_6$, monoclinic, $P12_11$ (No. 4), $a = 6.605(1)$ Å, $b = 7.651(2)$ Å, $c = 9.754(2)$ Å, $\beta = 92.11(3)°$, $V = 492.6$ Å^3, $Z = 2$, $R_{gt}(F) = 0.018$, $wR_{ref}(F^2) = 0.044$, $T = 293$ K.

Source of material

For the synthesis of $KSbP_2S_6$, the corresponding high purity element powders (99.99%) supplied by Aldrich were mixed in the stoichiometric amounts, sealed in evacuated quartz tubes, and heated at 1023 K for two weeks. After the reaction was completed, the sample was slowly cooled to room temperature. All manipulations were carried out under Ar atmosphere

Discussion

In the course of our work on chalcogen phosphates [1,2], we have preparated the quaternary antimony hexathiodiphosphate $KSbP_2S_6$. This compound is isostructural to $KBiP_2S_6$ [3]. As expected, the Sb—S bonds in $KSbP_2S_6$ are shorter that the Bi—S bonds in $KBiP_2S_6$. Also, the smaller radius of Sb^{3+} results in a decreased coordination number. Thus, each Sb^{3+} is coordinated by five S atoms compared with the six-coordinated Bi^{3+} ions in the isostructural compound. In the title compound, each Sb^{3+} ion is tri-coordinated by one ethane-like $[P_2S_6]^{4-}$ ligand and mono-coordinated by two $[P_2S_6]^{4-}$ groups forming chains, while a sixth S atom connect the Sb^{3+} to a neighboring chain, through a Sb–S contact of 3.4187(9) Å, to form a layer in the *bc* plane. The layer are separated by the K^+ ions. The bond lengths d(Sb—S) range from 2.545(1) Å to 3.1471(5) Å. The compounds KMP_2S_6 (M = Sb, Bi) are structurally related to $Na_{0.16}Bi_{1.28}P_2S_6$ [4] and β-KMP_2Se_6 [5].

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.089 × 0.104 × 0.224 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	47.43 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART CCD, φ/ω
$2\theta_{max}$:	55.84°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4075, 2078
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2037
$N(param)_{refined}$:	91
Programs:	SHELXL-97 [6], DIAMOND [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	2*a*	0.81740(3)	0.76783(2)	0.98199(2)	0.0247(1)	0.0193(1)	0.0235(1)	–0.0014(1)	–0.00049(9)	–0.0024(1)
K	2*a*	0.6955(1)	1.0534(1)	0.50699(9)	0.0300(5)	0.0380(5)	0.0314(5)	–0.0002(4)	–0.0020(4)	–0.0003(4)
P(1)	2*a*	0.6923(1)	0.3492(1)	0.82655(9)	0.0176(5)	0.0174(4)	0.0167(4)	–0.0019(4)	–0.0007(3)	0.0009(4)
P(2)	2*a*	0.7957(1)	0.5678(1)	0.69610(9)	0.0191(4)	0.0199(4)	0.0172(4)	–0.0019(4)	–0.0001(3)	0.0016(4)
S(1)	2*a*	0.6716(1)	0.4642(1)	1.01839(8)	0.0297(5)	0.0219(4)	0.0174(5)	–0.0062(4)	0.0032(4)	–0.0019(4)
S(2)	2*a*	0.9110(1)	0.1592(1)	0.8275(1)	0.0230(5)	0.0213(4)	0.0247(5)	0.0034(4)	–0.0038(4)	–0.0015(4)
S(3)	2*a*	0.4285(1)	0.2626(2)	0.74772(8)	0.0194(4)	0.0263(4)	0.0233(4)	–0.0057(5)	–0.0035(3)	0.0011(5)
S(4)	2*a*	1.0547(1)	0.6438(1)	0.8062(1)	0.0180(4)	0.0297(4)	0.0232(5)	–0.0036(4)	0.0002(4)	–0.0025(4)
S(5)	2*a*	0.5878(1)	0.7546(2)	0.73068(9)	0.0251(4)	0.0226(4)	0.0268(4)	0.0045(5)	–0.0041(3)	–0.0007(5)
S(6)	2*a*	0.8271(2)	0.4844(2)	0.5078(1)	0.0308(6)	0.0367(6)	0.0184(5)	–0.0037(5)	0.0023(4)	–0.0030(4)

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