Crystal structure of potassium bismuth hexathiodiphosphate, KBiP_2S_6

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Abstract

BiKP_2S_6 , monoclinic, $P12_11$ (No. 4), $a = 6.6200(6)$ Å, $b = 7.4058(7)$ Å, $c = 9.9002(9)$ Å, $\beta = 92.108(1)^\circ$, $V = 485.0$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.027$, $wR_{\text{ref}}(F^2) = 0.060$, $T = 293$ K.

Source of material

All manipulations were carried out under Ar atmosphere. For the synthesis of KBiP_2S_6 stoichiometric amounts of the corresponding high purity (99.99%) elements, supplied by Aldrich, were mixed and sealed in quartz tubes after evacuation. The mixture was then heated at 1123 K for two weeks. The reacted matter was slowly cooled (0.4 K/min) to room temperature.

Experimental details

The absolute configuration was tested and the $wR(F^2)$ values for the two possible orientations were 0.0586 and 0.1907. The first one represents the absolute structure of the crystal studied. The corresponding Flack parameter is 0.012(7).

Discussion

In the course of our work on chalcophosphate [1,2] we have prepared the quaternary bismuth hexathiodiphosphate KBiP_2S_6 . The title compound has a complicated layered structure, which contains the ethane-like $[\text{P}_2\text{S}_6]^{4-}$ ligand. KBiP_2S_6 is structurally related to $\text{Na}_{0.16}\text{Bi}_{1.28}\text{P}_2\text{S}_6$ [3] and KBiP_2Se_6 [4]. The structure is characterized by layers of condensed S_6 distorted octahedra alternately centered by P_2 pairs and Bi atoms. The staircase layers of $[\text{BiP}_2\text{S}_6]^{1-}$ groups in the a - b plane are held together by a single layer of K^+ ions. The bond lengths in the hexathiodiphosphate $[\text{P}_2\text{S}_6]^{4-}$ are $d(\text{P}-\text{P}) = 2.219(3)$ Å and $d(\text{P}-\text{S})$ in the range from 1.962(3) Å to 2.058(3) Å. The ethane-like $[\text{P}_2\text{S}_6]^{4-}$ ligand chelates to 4 Bi atoms, the bond lengths $d(\text{Bi}-\text{S})$ range from 2.706(2) Å to 3.143(2) Å.

Table 1. Data collection and handling.

Crystal:	red dark prism, size $0.075 \times 0.075 \times 0.2$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	201.48 cm ⁻¹
Diffractometer, scan mode:	Siemens SMART CCD, φ/ω
$2\theta_{\text{max}}$:	56°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	3908, 2071
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1901
$N(\text{param})_{\text{refined}}$:	91
Programs:	SHELXL-97 [5], ATOMS [6]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	2a	0.79399(4)	0.77391(6)	0.98012(3)	0.0245(2)	0.0188(1)	0.0223(2)	-0.0012(2)	0.0009(1)	-0.0048(2)
K	2a	0.7017(3)	0.0236(3)	0.5016(2)	0.032(1)	0.035(1)	0.026(1)	-0.0025(9)	-0.001(1)	0.0003(9)
P(1)	2a	0.6876(3)	0.3148(2)	0.8258(2)	0.017(1)	0.014(1)	0.013(1)	-0.0003(7)	-0.0014(8)	0.0005(7)
P(2)	2a	0.7956(3)	0.5409(3)	0.7003(2)	0.015(1)	0.0139(9)	0.014(1)	-0.0008(8)	-0.0017(8)	0.0004(8)
S(1)	2a	0.6585(3)	0.4287(3)	0.0136(2)	0.026(1)	0.020(1)	0.013(1)	-0.0044(9)	0.0015(9)	-0.0015(8)
S(2)	2a	0.9127(3)	0.1262(3)	0.8259(2)	0.019(1)	0.0153(9)	0.020(1)	0.0016(8)	-0.0028(9)	-0.0003(9)
S(3)	2a	0.4251(3)	0.2268(2)	0.7458(2)	0.018(1)	0.020(1)	0.020(1)	-0.0050(7)	-0.0033(8)	-0.0004(8)
S(4)	2a	0.0521(3)	0.6229(3)	0.8071(2)	0.015(1)	0.023(1)	0.019(1)	-0.0013(8)	-0.0010(8)	-0.0024(9)
S(5)	2a	0.5845(3)	0.7341(2)	0.7305(2)	0.021(1)	0.019(1)	0.021(1)	0.0043(8)	-0.0048(8)	-0.0008(8)
S(6)	2a	0.8230(4)	0.4592(3)	0.5134(2)	0.029(1)	0.031(1)	0.013(1)	-0.004(1)	0.0017(9)	-0.0020(9)

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