Crystal structure of trirubidium tetrathiophosphate, Rb_3PS_4

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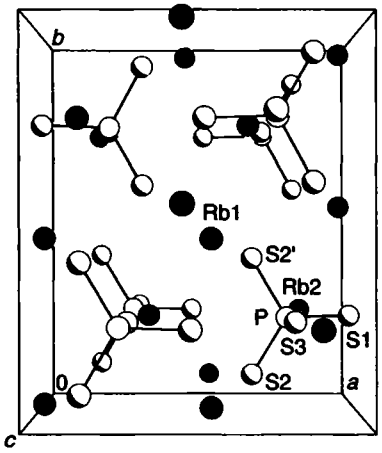

Abstract

PRb_3S_4, orthorhombic, *Pnma* (no. 62), $a = 9.277(1)$ Å, $b = 10.935(1)$ Å, $c = 9.251(1)$ Å, $V = 938.5$ Å^3, $Z = 4$, $R_{gt}(F) = 0.027$, $wR_{ref}(F^2) = 0.046$, $T = 153$ K.

Source of material

Rb_3PS_4 was synthesized by the reaction of 1.0 mmol phosphorus (Alfa, 99.999%), 2.0 mmol sulfur (Sinoreag., 99.999%), and 1.5 mmol prepared Rb_2S_3 [1]. The reaction mixture was loaded in a evacuated silica tube under argon atmosphere in a glove box. The tube was sealed under a 10^{-2} Pa atmosphere and then placed in a computer-controlled furnace. The sample was heated to 773 K in 8 h, kept at 773 K for 72 h, cooled at 3 K/h to 373 K, and then the furnace was turned off. The reaction mixture was washed with *N,N*-dimethylformamide. The reaction product consisted of white grey plate crystals which were modestly stable in air.

Discussion

As confirmed by STRUCTURE TIDY [2], Rb_3PS_4 is isotypic with Li_3PS_4 [3], K_3PS_4 [4], K_3PSe_4 [5], Tl_3PSe_4 [6], and Tl_3AsS_4 [6]. The structure contains $[PS_4]^{3-}$ anions separated by Rb^+ cations. Each unit cell comprises four equivalent $[PS_4]^{3-}$ anions. The P atom is tetrahedrally coordinated by S atoms with P—S distances ranging from 2.043(1) Å to 2.055(1) Å and S–P–S angles ranging from 108.82(4)° to 111.48(6)°, consistent with those in Li_3PS_4 [3] and K_3PS_4 [4]. The Rb atoms in the structure are both coordinated by seven S atoms in distorted pentagonal bipyramidal configurations. The Rb—S distances range from 3.271(1) Å to 3.469(1) Å for Rb1 and from 3.273(1) Å to 3.980 (1) Å for Rb2, well comparable to those in $Rb_4In_2S_5$ (3.203(1) Å – 3.954(1) Å) [7].

Table 1. Data collection and handling.

Crystal:	white-gray plate, size 0.05 × 0.10 × 0.24 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	165.54 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ω/φ
$2\theta_{max}$:	57.84°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7513, 1235
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1091
$N(param)_{refined}$:	44
Program:	SHELXTL [8]

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}
Rb(1)	8*d*	0.04077(3)	0.54111(2)	0.29421(3)	0.0144(1)	0.0086(1)	0.0143(1)	0.0004(1)	−0.0006(1)	0.0000(1)
Rb(2)	4*c*	0.15553(4)	¼	0.08945(4)	0.0149(2)	0.0309(2)	0.0145(1)	0	0.0027(1)	0
S(1)	4*c*	0.02031(1)	¼	0.43031(9)	0.0093(5)	0.0114(4)	0.0114(4)	0	−0.0013(3)	0
S(2)	8*d*	0.32921(7)	0.09538(6)	0.45449(7)	0.0134(4)	0.0136(3)	0.0166(3)	−0.0047(2)	0.0003(3)	0.0037(3)
S(3)	4*c*	0.20929(1)	¼	0.73980(9)	0.0131(5)	0.0113(4)	0.0096(4)	0	0.0000(3)	0
P	4*c*	0.22326(1)	¼	0.51937(9)	0.0080(5)	0.0092(4)	0.0088(4)	0	0.0005(3)	0

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