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$RbPbPS_4$

Jiyong Yao and James A. Ibers*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, USA

Correspondence e-mail: ibers@chem.northwestern.edu

Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(S–P) = 0.002 Å
R factor = 0.020
wR factor = 0.049
Data-to-parameter ratio = 27.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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Rubidium lead phosphorus tetrasulfide, $RbPbPS_4$, possesses the $CsSmGeS_4$ structure type, crystallizing in space group $P2_12_12_1$ of the orthorhombic system. The structure consists of two-dimensional [$PbPS_4$] layers built from PbS_7 monocapped trigonal prisms and PS_4 tetrahedra. The layers are separated by Rb atoms.

Comment

In an effort to expand the range of $ABiMS_4$ (A = Rb and Cs, and M = Si and Ge; Yao *et al.*, 2002) compounds by substitution chemistry, the new compound $RbPbPS_4$ was obtained by the simultaneous substitution of Pb^{2+} for Bi^{3+} and P^{5+} for M^{4+}. The compound crystallizes in the non-centrosymmetric space group $P2_12_12_1$ and is isostructural with $CsSmGeS_4$ (Bucher & Hwu, 1994), which was refined with a different cell setting. The two unit cells become similar by cyclic permutation of the axes of the latter [$a_{old} = b_{new}$; $b_{old} = c_{new}$; $c_{old} = a_{new}$].

The structure of $RbPbPS_4$ (Fig. 1) consists of two-dimensional [$PbPS_4$] layers separated by Rb atoms. Each Rb atom is coordinated by a distorted bicapped trigonal prism of eight S atoms. The Rb—S bond lengths range from 3.368 (2) to 3.789 (1) Å, comparable with those of 3.323 (1)–3.577 (1) Å in $RbBiSiS_4$ (Yao *et al.*, 2002). Each P atom is coordinated by a tetrahedron of four S atoms. The P—S bond lengths range from 2.032 (2) to 2.064 (2) Å, consistent with those of 2.004 (2)–2.056 (2) Å in $ScPS_4$ (Lee & Hilt, 1992). Each Pb atom is coordinated by a monocapped trigonal prism of seven S atoms. The Pb—S distances range from 2.920 (1) to 3.282 (2) Å, comparable with those of 3.066 (3)–3.188 (3) Å in Li_2PbGeS_4 (Aitken *et al.*, 2001). The largest difference in Pb—S bond lengths within the PbS_7 polyhedron is 0.362 (2) Å. The

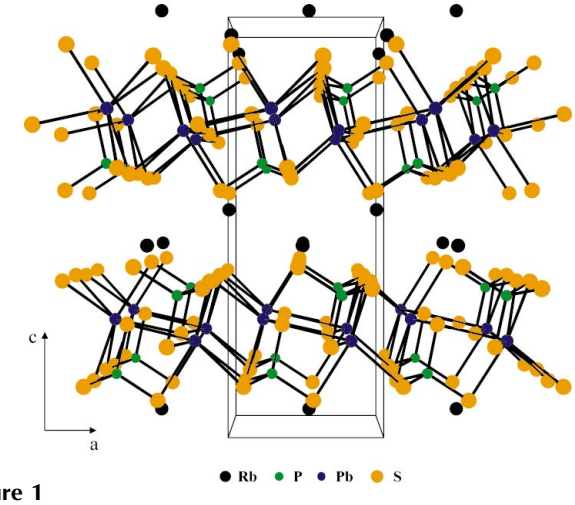

Figure 1
The structure of $RbPbPS_4$, viewed down [010].

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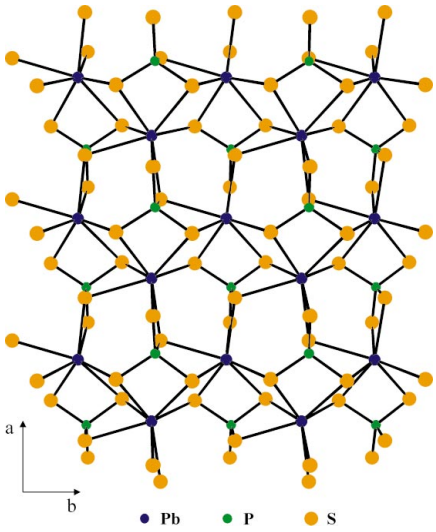

Figure 2
The structure of the two-dimensional [$PbPS_4$] layer in $RbPbPS_4$.

structure of the two-dimensional [$PbPS_4$] layer is shown in Fig. 2. The neighboring PbS_7 polyhedra share opposite edges of the rectangular planes of the prisms to form zigzag chains along the *b* direction. Two parallel polyhedral chains are connected by the sharing of opposite edges of the PS_4 tetrahedra. Each PS_4 tetrahedron is arranged in such a way that one of the S atoms becomes the cap of an adjacent PbS_7 polyhedron. The two [$PbPS_4$] slabs in the unit cell of $RbPbPS_4$ are related by a 2_1 screw axis along *a*.

Experimental

Yellow plates of $RbPbPS_4$ were obtained from a solid-state reaction of Rb_2S_3 (0.5 mmol), Pb (Alfa, 99.5%, 1.0 mmol), P_2S_5 (Aldrich, 99.5%, 0.5 mmol), and S (Aldrich, 99.5%, 1.0 mmol). The reactive flux Rb_2S_3 (Sunshine *et al.*, 1987) was prepared by the stoichiometric reaction of Rb (Aldrich, 98+%) and S in liquid NH_3. The reactants were loaded into a fused-silica tube under an Ar atmosphere in a glove box. The tube was sealed under a 10^{-4} Torr atmosphere (1 Torr = 133.322 Pa) and then placed in a computer-controlled furnace. The sample was heated to 1073 K over a period of 20 h, kept at 1073 K for 84 h, cooled at 6 K h^{-1} to 373 K and then cooled rapidly to room temperature.

Crystal data

$RbPbPS_4$
M_r = 451.87
Orthorhombic, $P2_12_12_1$
a = 6.3987 (7) Å
b = 6.6899 (7) Å
c = 17.2975 (19) Å
V = 740.45 (14) Å^3
Z = 4
D_x = 4.053 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7200 reflections
θ = 2.4–28.8°
μ = 30.54 mm^{-1}
T = 153 (2) K
Plate, yellow
0.18 × 0.16 × 0.016 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: numerical face indexed (*SHELXTL*; Sheldrick, 2003)
T_{min} = 0.047, T_{max} = 0.603
8784 measured reflections
1807 independent reflections
1759 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 28.8°
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -23 \rightarrow 23$

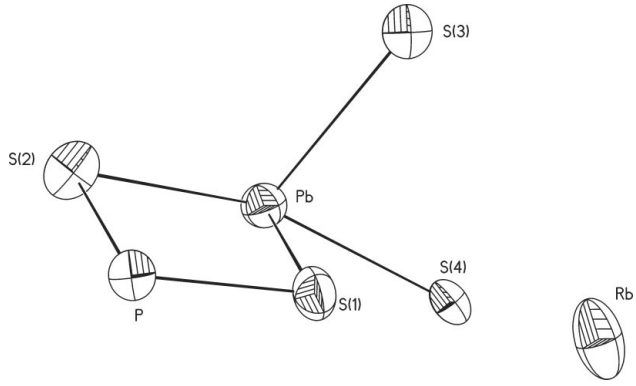

Figure 3
The asymmetric unit of $RbPbPS_4$, showing displacement ellipsoids at the 90% probability level.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.049
S = 1.39
1807 reflections
65 parameters
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 2.11 e Å^{-3}
$\Delta\rho_{min}$ = −1.57 e Å^{-3}
Absolute structure: Flack (1983), 704 Friedel pairs
Flack parameter = 0.550 (7)

Table 1
Selected geometric parameters (Å, °).

Rb—S1	3.3680 (15)	Pb—S2	2.9945 (16)
Rb—S2^{i}	3.4075 (17)	Pb—S3	3.0430 (16)
Rb—S4^{ii}	3.4345 (16)	Pb—S1	3.0900 (14)
Rb—S4	3.4412 (16)	Pb—S3^{vii}	3.1116 (16)
Rb—S3^{iii}	3.4639 (17)	Pb—S2^{vii}	3.2823 (16)
Rb—S2^{iv}	3.4734 (17)	P—S4^{iv}	2.0320 (18)
Rb—S3^{v}	3.4898 (17)	P—S2	2.038 (2)
Rb—S4^{iii}	3.7887 (14)	P—S3^{viii}	2.0381 (19)
Pb—S4	2.9204 (14)	P—S1	2.0644 (19)
Pb—S1^{vi}	2.9290 (14)		
S4^{iv}—P—S2	111.36 (9)	S4^{iv}—P—S1	111.30 (8)
S4^{iv}—P—S3^{viii}	109.75 (8)	S2—P—S1	106.65 (8)
S2—P—S3^{viii}	108.05 (8)	S3^{viii}—P—S1	109.62 (8)

Symmetry codes: (i) $\frac{1}{2}-x, -y, z-\frac{1}{2}$; (ii) $x, y-1, z$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, -z$; (iv) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $x-1, y, z$; (vi) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$.

The value of the Flack (1983) parameter suggests an enantiomeric twin. Examination of the resultant atomic coordinates with the program *ADDSYM* in the *PLATON* suite of programs (Spek, 2003) did not reveal additional symmetry. The structure was thus refined as a twin. The resultant twin ratio is 0.550 (7):0.450 (7). The displacement ellipsoids are reasonable (Fig. 3). The highest residual electron density is 0.06 Å from the Pb site. The deepest hole is 0.75 Å from this same site.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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