

Rb₂P₂S₆ – A New Alkali Thiophosphate: Crystal Structure and Vibrational Spectra of Rubidium Hexathiodiphosphate(V)

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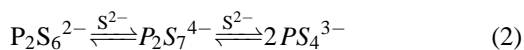
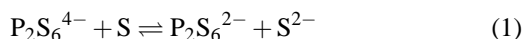
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Single crystals of rubidium hexathiodiphosphate(V), Rb₂P₂S₆, have been obtained and investigated by single crystal X-ray diffraction, and IR/FIR and Raman spectroscopy. The title compound crystallizes isotypically to the potassium, caesium and thallium analogues in the orthorhombic space group *Immm* (no. 71) with $a = 8.485(3)$, $b = 6.953(3)$, $c = 9.259(3)$ Å, and $Z = 2$, final $R1 = 0.0579$ and $wR2 = 0.0987$. The crystal structure is characterized by discrete [P₂S₆]²⁻ anions (edge-sharing double-tetrahedra) with D_{2h} symmetry. Rubidium is coordinated by ten sulfur atoms forming a slightly distorted two-capped tetragonal prism with a coordination number CN_{Rb} 10. The FT-Raman and FT-IR/FIR spectra have been recorded and a factor group analysis was carried out.

Key words: Thiophosphate, Rb₂P₂S₆, Crystal Structure, Raman, IR

Introduction

The four known types of alkali thiophosphates, Me₄P₂S₆, Me₂P₂S₆, Me₄P₂S₇ and Me₃PS₄, belong to the group of ionic thiophosphates. They may be prepared by high-temperature element syntheses dependent on stoichiometric and preparative conditions [1–3]. At higher temperature these thiophosphates are connected by coupled Lewis acid-base and redox equilibria:



The hexathiometadiphosphates (= hexathiodiphosphates(V)), Me₂P₂S₆, are of special interest because in the crystal structure there are discrete P₂S₆²⁻ anions contrary to the polymeric structures of the oxo analogues, (MPO₃)_n. Only a few compounds, Me₂P₂S₆ with Me = Na, K, Cs, Tl and Ag have been described.

The thiophosphates of stoichiometry MePS₃ with Me = Na, Ag and Tl were first described by Thilo and Ladwig [4] who proposed a chain structure for these compounds in analogy to the corresponding metaphosphates. Crystal structure determinations of the silver [5], thallium [6], potassium and caesium [7] thiophosphates showed the [P₂S₆]²⁻ ion as the structural unit therein. Na₂P₂S₆ and Rb₂P₂S₆ were synthesized

and characterized first by Menzel [8], but no single crystals could be obtained for structure determination.

Very recently, the crown-ether derivatives of Na₂P₂S₆ and K₂P₂S₆: [K(18-crown-6)]₂ [P₂S₆] · 2CH₃CN [9, 10] and [Na(12-crown-4)]₂ [P₂S₆] · CH₃CN [11] have been synthesized and characterized by crystal structure determination and vibrational spectra.

Experimental Section

Synthesis

The light-yellow title compound was prepared by high-temperature synthesis from stoichiometric amounts of the elements (4 g charge) in evacuated and sealed quartz tubes [6, 8]. To prevent a violent exothermic reaction it was important to have the Rb metal in an extra open quartz tube separated from the P and S components and to run a slow pre-reaction (50 °C/h) at < 180 °C so that sulfide formation could take place *via* the gas phase. Thereafter the reaction mixture was heated up to 800 °C (50 °C/h) and kept at this temperature for 8 h. Cooling with 50 °C/h yielded crystalline Rb₂P₂S₆ (Fp: 462 °C [8]). As Rb₂P₂S₆ is quickly hydrolyzed, all handling had to be done under a strictly inert atmosphere (glovebox, argon).

Determination of the crystal structure

A suitable single crystal of the title compound was selected under a polarization microscope and mounted in a

Table 1. Crystallographic data and details of the structure determination and refinement for Rb₂P₂S₆.

Empirical formula	Rb ₂ P ₂ S ₆
Crystal system	orthorhombic
Space group / Z	<i>Immm</i> (No. 71) / 2
<i>a</i> [Å]	8.485(3)
<i>b</i> [Å]	6.953(3)
<i>c</i> [Å]	9.259(3)
<i>V</i> [Å ³]	546.2(3)
Calculated density [g/cm ³]	2.59
Measured temperature [K]	223
μ (Mo-K α) [mm ⁻¹]	10.2
Crystal size [mm ³]	0.25 × 0.22 × 0.20
Crystal colour	yellow
Diffractometer, scan mode	Stoe-IPDS 2, rotation at $\varphi = 0$ and 45°, $\omega = 2$, 150 frames, IP distance 75 mm
Radiation Mo-K α [Å]	0.71073, Graphite monochromator
θ [°]	2.0–26.0
$h_{\min}, h_{\max}, k_{\min}, k_{\max}, l_{\min}, l_{\max}$	–10, 10; –8, 8; –11, 11
<i>F</i> (000)	400
Absorption correction	empirical
Independent reflections / $R_{\text{int}}/R_{\text{sigma int.}}$	3366 / 0.0997 / 0.0560
Reflections / parameters	899 / 78
Extinction coefficient	0.00125(2)
Goodness-of-Fit	1.124
$R(I > 2\sigma(I))$	$R1 = 0.0566, wR2 = 0.0876$
R (all data)	$R1 = 0.0579, wR2 = 0.0987$
Structure solution and refinement	SHELXS-97 and SHELXL-97 [13]
Largest difference peaks and hole	2.462 / –1.903

glass capillary ($d = 0.3$ mm, oil protection). Single crystal X-ray diffraction studies were performed on a Stoe IPDS II diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 223 K. Crystal data and experimental conditions are given in Table 1. Intensity data were collected in the φ -scan mode. With the help of direct methods [12, 13] the atomic positions could be determined by successive refinement with Fourier syntheses including anisotropic displacement parameters (Table 2). For the structure drawings the programs DIAMOND [14] and POV-RayTM [15] were used. Selected distances and angles are listed in the Table 3.

Raman and IR spectrum

The FT-Raman spectrum of the crystalline title compound was recorded with a Raman module FRA 106 (Nd:YAG laser, 1064 nm, > 200 mW) attached to a Bruker IFS 66v interferometer. The FT-IR/FIR spectra were obtained from KBr and PE pellets, respectively, with the same interferometer. All sample handling was done under strictly inert conditions in a dry nitrogen atmosphere.

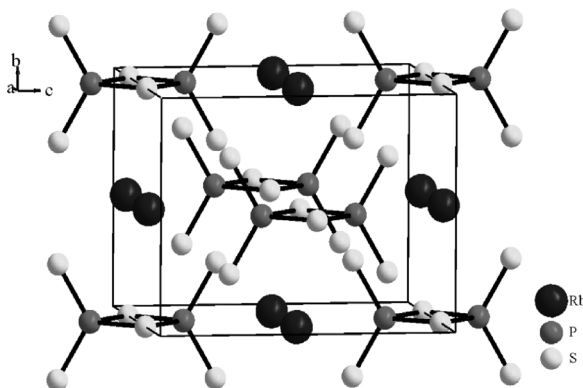
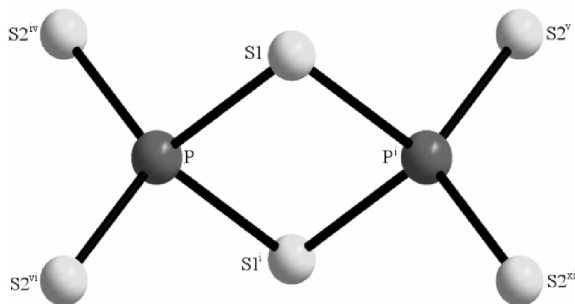
Table 2. Atomic coordinates and equivalent isotropic displacement parameters / Å² for Rb₂P₂S₆.

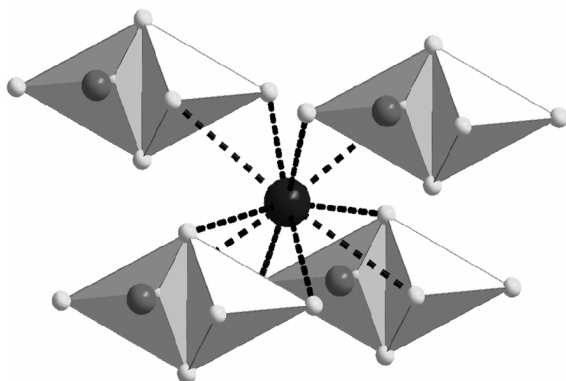
Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Rb	4 <i>f</i>	0.2388(1)	0	1/2	0.0292(5)
P	4 <i>j</i>	1/2	0	0.1588(3)	0.0220(7)
S1	4 <i>e</i>	0.3168(3)	0	0	0.0267(7)
S2	8 <i>l</i>	0	0.2565(2)	0.2319(6)	0.0291(6)

Table 3. Selected bond lengths [Å] and angles [°] for Rb₂P₂S₆.

<i>[P₂S₆]²⁻ Anion:</i>			
P - S1, S1 ⁱ	2.139(2)	⟨ S1 - P - S2 ^{iv} ⟩	110.65(5)
P - S2 ^{iv} , S2 ^v , S2 ^{vi} , S2 ^{xii}	1.973(2)	⟨ S2 ^{iv} - P - S2 ^{vi} ⟩	118.24(2)
P - P ⁱⁱ	2.937(1)	S1 - S2 ^{iv}	3.381(1)
⟨ S2 - P - S2 ⁱ ⟩	91.13(4)	S2 ^{iv} - S2 ^{vi}	3.386(1)
<i>Rb⁺ Coordination:</i>			
Rb - S1, S1 ^{ix}			3.509(1)
Rb - S2 ⁱⁱⁱ , S2 ^v , S2 ^{vii} , S2 ^{viii}			3.521(2)
Rb - S2, S2 ^{iv} , S2 ^x , S2 ^{xi}			3.666(2)

ⁱ $-x+1, -y, z$; ⁱⁱ $x, -y, -z$; ⁱⁱⁱ $x+1/2, y+1/2, z-1/2$; ^{iv} $x+1/2, -y+1/2, -z+1/2$; ^v $-x+1/2, -y+1/2, z-1/2$; ^{vi} $-x+1/2, y-1/2, -z+1/2$; ^{vii} $-x, y, -z$; ^{viii} $x, -y+1, -z$; ^{ix} $x, y+1, z$; ^x $-x, -y+1, z$; ^{xi} $-x+1/2, -y+1/2, -z+1/2$; ^{xii} $x+1/2, y-1/2, z-1/2$.

Fig. 1. Unit cell contents for Rb₂P₂S₆.Fig. 2. [P₂S₆]²⁻ anion in Rb₂P₂S₆.

Fig. 3. Coordination of Rb^+ in $\text{Rb}_2\text{P}_2\text{S}_6$.

Results and Discussion

Description of the crystal structure

The title compound crystallizes in the orthorhombic space group *Immm* with the lattice parameters: $a = 8.485(3)$, $b = 6.953(2)$, $c = 9.259(3)$ Å, and $Z = 2$ (Fig. 1). The structure is isotypic to $\text{Me}_2\text{P}_2\text{S}_6$ ($\text{Me} = \text{K}, \text{Cs}, \text{Tl}$) [6–7].

The crystal structure is characterized by discrete $[\text{P}_2\text{S}_6]^{2-}$ anions with D_{2h} symmetry. Two PS_4 tetrahedra are connected by a common edge. The P-S bond lengths range from 1.973(2) to 2.139(2) Å (Fig. 2). These values are very similar to those found in related structures [6–7, 9–11].

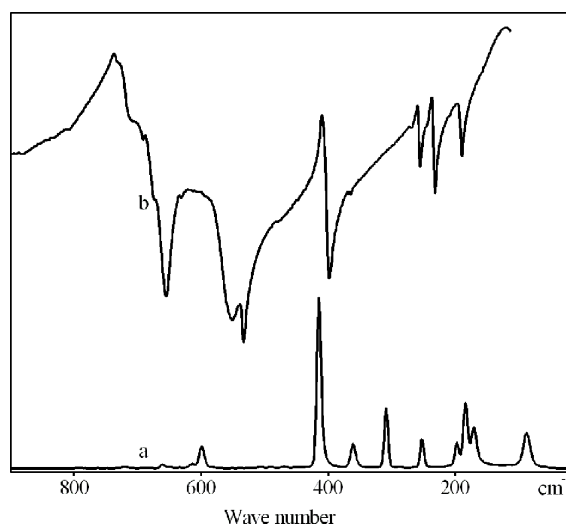
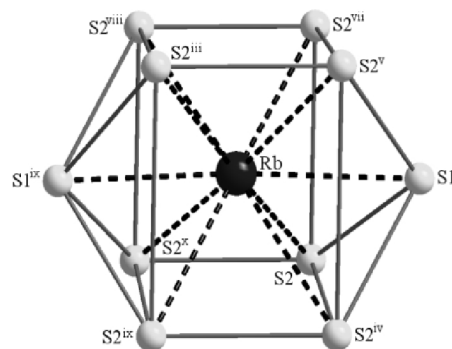
Rubidium is coordinated by ten sulfur atoms, of which eight are located at the corners of a slightly distorted tetragonal prism with Rb-S bonds of 3.521(2) and 3.666(2) Å, and two additional ones form caps with Rb-S distances of 3.509(1) Å.

Vibrational spectrum and assignment

Vibrational modes of the $[\text{P}_2\text{S}_6]^{2-}$ anion

The Raman and IR spectra of crystalline $\text{Rb}_2\text{P}_2\text{S}_6$ (Fig. 4) are dominated by the vibrational modes of the $[\text{P}_2\text{S}_6]^{2-}$ unit situated in the frequency region below 800 cm^{-1} . Therefore and due to the quite similar molecular parameters of the $[\text{P}_2\text{S}_6]^{2-}$ unit in $\text{K}_2\text{P}_2\text{S}_6$ and $\text{Cs}_2\text{P}_2\text{S}_6$ [7], $[\text{K}(18\text{-crown-6})]_2[\text{P}_2\text{S}_6] \cdot 2\text{CH}_3\text{CN}$ [10] and $[\text{Na}(12\text{-crown-4})_2]_2[\text{P}_2\text{S}_6] \cdot \text{CH}_3\text{CN}$ [11] the spectra have been interpreted only with respect to $[\text{P}_2\text{S}_6]^{2-}$ with D_{2h} symmetry.

A vibrational analysis of the $[\text{P}_2\text{S}_6]$ unit with D_{2h} symmetry [16] results in

Fig. 4. FT-Raman (a, $\lambda_{\text{exc.}} = 1064\text{ nm}$) and FT-IR (b) spectra of crystalline $\text{Rb}_2\text{P}_2\text{S}_6$ at room temperature. (Raman, intensity in arbitrary units; IR, transmittance).

$$\Gamma_{\text{vib}}(D_{2h}) = 4A_g + A_u + 2B_{1g} + 3B_{1u} + 2B_{2g} + 2B_{2u} + B_{3g} + 3B_{3u},$$

with the *gerade* species being Raman active and the *ungerade* species, except A_u , infrared active. The rule of mutual exclusion is valid.

Based on vibrational analyses and *ab initio* calculations [16, 17] the vibrational frequencies of $\text{P}_2\text{S}_6^{2-}$ have been assigned. This P_2S_6 assignment may be transferred here for the title compound for the sake of comparability with that of other investigated $\text{P}_2\text{S}_6^{2-}$ salts. The vibrational frequencies of $\text{Rb}_2\text{P}_2\text{S}_6$ are in best agreement with those measured by Menzel [8]. The data are given in Table 4 along

Raman this work	Raman Rb ₂ P ₂ S ₆ [8]	IR this work	IR Rb ₂ P ₂ S ₆ [8]	Assignment / mode description (<i>D</i> _{2h}) [8, 17]
		711 vvw		
		693, 674 vw	716, 692 m	Combination?
		656 vs	659 m,br	$\nu_8 / B_{1u}, \nu_{as} PS_2$
662 vw	663 vw,br			$\nu_{11} / B_{2g}, \nu_{as} PS_2$
613 vvw	634 vw			Combination?
599 w-m	600 m			$\nu_1 / A_g, \nu_s PS_2$
		551 s,br	551 m,br	$\nu_{16} / B_{3u}, \nu_{as} PS_2$
		533 m	534 vw	$\nu_{13} / B_{2u}, \nu_{ring}$
490 vw				Combination?
415 vvs	415 vs			$\nu_2 / A_g, \nu_{ring}$
		398 vs	397 m,br	$\nu_{17} / B_{3u}, \nu_{ring}$
361 m	362 m	367, 364 vw		$\nu_6 / B_{1g}, \nu_{ring}$
309 s	309 s			$\nu_3 / A_g, \delta_{ring}$
281 vvw		271 vvw		
		258 m	258 m	$\nu_{18} / B_{3u}, ring\ torsion$
252 m	253 m	248 vvw		$\nu_7 / B_{1g}, \delta PS_2$
		235 s	235 s	$\nu_9 / B_{1u}, \delta PS_t S_b$
205 vvw		213 vvw		
197 w-m	198 w			$\nu_{12} / B_{2g}, \delta PS_2$
		194 m	194 m	ν_{14} / B_{2u}
184 vs	185 m			$\nu_{15} / B_{3g}, \delta PS_2$
171 s	172 m			$\nu_4 / A_g, \delta_{ring}$
			84 vs,br	$\nu_5 / A_u // \nu_{10} / B_{1g} ?$
<i>Lattice vibrations</i>				
87 vs	88 m, br			[A _g ?]
			84 vs,br	[B _u species]
50 vvw				[B _g species]
37 vvw				[B _g species]

Table 4. Vibrational frequencies (cm⁻¹) of crystalline Rb₂P₂S₆ along with their estimated intensities and proposed assignments.

Estimated intensities: s: strong, m: medium, w: weak, v: very, sh: shoulder, br: broad.

with their estimated intensities and their proposed assignment.

Vibrational modes of crystalline Rb₂P₂S₆, factor group analysis

Based on the determined crystal structure and the site symmetry of the atoms the total irreducible representation for crystalline Rb₂P₂S₆ may be obtained disregarding the presence of a covalently bonded [P₂S₆]²⁻ anion [18, 19]. The title compound as well as K₂P₂S₆ and Cs₂P₂S₆ [7] crystallize in space group *Immm* (*D*_{2h}²⁵, no. 71) with *Z* = 2 and *Z*^B = 1, respectively. The site symmetry / Wyckoff sites for the elements are: Rb on 4*f*/*C*_{2v}; P on 4*j*/*C*_{2v}; S₁ (S_{bridge}) on 4*e*/*C*_{2v}, and S₂ (S_{terminal}) on 8*l*/*C*_s [20, 21]. The A₁(T_z), B₁(T_y) and B₂(T_x) – *C*_{2v} site-group species for Rb, P and S₁ atoms as well as the A'(T_x, T_y) and A''(T_z) – *C*_s site-group have to be correlated to the *D*_{2h} factor-group species. The lattice vibrations involving Rb⁺, $\Gamma_{Rb}^{cyst.}$, inclusive the acoustical vibrations, result in

$$\Gamma_{Rb}^{cyst.} = 1 A_g + 1 B_{2g} + 1 B_{3g} + 1 B_{1u} + 1 B_{2u} + 1 B_{3u},$$

with

$$\Gamma_{Rb}^{acoust.} = 1 B_{1u}(T_z) + 1 B_{2u}(T_y) + 1 B_{3u}(T_x).$$

The total irreducible representation for the Rb₂P₂S₆ crystal, $\Gamma^{crist.}$, is obtained as the sum of the mentioned correlated factor-group species in *D*_{2h} derived for Rb, P and S₁ (all in *C*_{2v}) and S₂ (*C*_s)

$$\begin{aligned} \Gamma^{crist.} = & 5 A_g + 3 B_{1g} + 4 B_{2g} + 3 B_{3g} \\ & + 1 A_u + 5 B_{1u} + 5 B_{2u} + 4 B_{3u}, \end{aligned}$$

with the *gerade* species being Raman active and the *ungerade* species, except A_u (inactive), being IR active. The mutual exclusion rule is valid.

Since Rb₂P₂S₆ is built up from Rb⁺ and P₂S₆²⁻ ions the total irreducible representation of the crystalline compound, $\Gamma^{crist.}$, can also be obtained from the internal P₂S₆²⁻ vibrations, $\Gamma_{P_2S_6}^{int.}$, the lattice vibrations $\Gamma_{Rb}^{crist.}$ and $\Gamma_{P_2S_6}^{crist.}$ and the P₂S₆²⁻ librations, $\Gamma_{P_2S_6}^{lib}$ [18, 19] (*c.f.* Table 5). The number of species in B_{1g} – B_{3g} and B_{1u} – B_{3u} can be interchanged with the axis settings for the P₂S₆²⁻ unit.

The lattice vibrations of the title compound as well as those of isotypic K₂P₂S₆ / Cs₂P₂S₆ [7] and Tl₂P₂S₆

Species D_{2h}	Number of modes						Spectral activity	
	N_{total}	$N_{\text{acoust.}}$	$N_{\text{Rb/trans.}}$	$N_{\text{P}_2\text{S}_6/\text{tr.}}$	$N_{\text{lib.}}$	$N_{\text{vib/P}_2\text{S}_6}$	Raman	IR
A _g	5		1			4	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$	
B _{1g}	3				1	2	α_{xy}	
B _{2g}	4		1		1	2	α_{xz}	
B _{3g}	3		1		1	1	α_{yz}	
A _u	1					1	inactive	
B _{1u}	5	1		1		3		E // z
B _{2u}	5	1		1		3		E // y
B _{3u}	4	1		1		2		E // x
Σ	30	3	3	3	3	18		

[6] are not pronounced, and they could not be assigned in detail (*c.f.* Table 4 and 5).

Conclusion

With the receipt of single crystals of the title compound its crystal structure could be determined. As expected, but now verified, Rb₂P₂S₆ is isotypic to K₂P₂S₆ and Cs₂P₂S₆. Only the crystal structures of Na₂P₂S₆ and Li₂P₂S₆ have been left undetermined in the exclusive group of the alkali hexathiodiphosphates(V). The vibrational spectrum of the crys-

talline compound was investigated by a factor group analysis.

Supporting information available

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (Fax: (49) 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD_416176.

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