# New Layered Quaternary Tantalum Thiophosphates Containing Binuclear $[Ta_2S_{10}]$ Units: Synthesis and Crystal Structures of the Two New Compounds $K_{0.42}TaPS_5$ and $Rb_{0.42}TaPS_5$

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Dedicated to Professor Arndt Simon on the Occasion of his 65th Birthday

**Abstract.** The reactions of Ta with an in situ formed polythiophosphate melt of  $A_2S_3$  (A = K, Rb),  $P_2S_5$ , and S at 500 °C yield the two new quaternary tantalum thiophosphates  $A_{0.42(2)}TaPS_5$ (A = K (I) and Rb (II)). The compounds are isostructural and crystallize in the orthorhombic space group Fddd with Z = 16. Compound I has lattice parameters a = 9.6983(6) Å, b = 14.373(2) Å, c = 21.642(2) Å, and compound II a = 9.878(2) Å, b = 14.288(2) Å, c = 21.687(2) Å. Each Ta atom is surrounded by six S atoms in an octahedral environment. Two [TaS<sub>6</sub>] octahedra share a common edge to form the dimeric [Ta<sub>2</sub>S<sub>10</sub>] unit. These units are linked by sharing common edges with four tetradentate [PS<sub>4</sub>] groups yielding a two-dimensional layered structure. The connection scheme leads to the formation of one type of cavities within the layers which are occupied by the alkali metal cations. The layers are stacked onto each other in a …ABAB… fashion and channels run along [011], [0-11], [01-1], and [0-1-1] with approximate dimensions of 4.1  $\cdot$  7.9 Å. The electron transfer from the alkali metals to the host material yields a short Ta-Ta distance within the [Ta<sub>2</sub>S<sub>10</sub>] units. The compounds were characterized by energy dispersive Xray analysis and infrared spectroscopy in the MIR region.

**Keywords:** Tantalum; Thiophosphates; Crystal structure; Flux reaction; Vibrational properties

# Neue schichtartige quaternäre Tantalthiophosphate mit binuklearen $[Ta_2S_{10}]$ -Einheiten: Synthese and Kristallstrukturen der beiden neuen Verbindungen $K_{0.42}TaPS_5$ and $Rb_{0.42}TaPS_5$

Inhaltsübersicht. Die Reaktion von Tantal mit einer in-situ gebildeten Polythiophosphatschmelze aus  $A_2S_3$  (A = K, Rb),  $P_2S_5$  und Schwefel führte bei 500 °C zur Bildung der beiden neuen quaternären Tantalthiophosphate  $A_{0.42(2)}TaPS_5$  (A = K (I) und Rb (II)). Die Verbindungen sind isostrukturell und kristallisieren in der orthorhombischen Raumgruppe Fddd mit Z = 16. Verbindung I: a = 9.6983(6) Å, b = 14.373(2) Å, c = 21.642(2) Å, Verbindung II: a = 9.878(2) Å, b = 14.288(2) Å, c = 21.687(2) Å. Jedes Tantalatom ist oktaedrisch von sechs Schwefelatomen umgeben. Zwei TaS<sub>6</sub>-Oktaeder sind über eine gemeinsame Kante zur dimeren Ta<sub>2</sub>S<sub>10</sub>-Einheit verbunden. Die Verknüpfung dieser Einheiten mit vier tetra-

#### Introduction

In the last few years we investigated the A-M-P-S family (A = alkali metal, M = group IV or V metal) and demonstrated that the use of the alkali metal polythiosphate flux method is a suitable synthetic tool for the synthesis of new

dentat agierenden PS<sub>4</sub>-Tetraedern über gemeinsame Kanten führt zur zweidimensionalen Schichtstruktur. In den Schichten werden durch dieses Verknüpfungsschema Löcher gebildet, welche von den Alkalimetallkationen besetzt sind. Die Schichten sind in der Abfolge …ABAB… übereinander gestapelt. Kanäle mit einer ungefähren Abmessung von 4.1 · 7.9 Å verlaufen entlang [011], [0-11], [01-1] und [0-1-1]. Der Elektronentransfer von den Alkalimetallen auf das Wirtsgitter führt zu recht kurzen Ta-Ta-Abständen in den Ta<sub>2</sub>S<sub>10</sub>-Einheiten. Die Verbindungen wurden mit energiedispersiver Röntgenfloureszenzanalyse und Infrarotspektroskopie im MIR-Bereich charakterisiert.

quaternary thiophosphates [1-7]. We have shown that a systematic variation of the reaction parameters leads to the formation of new thiophosphates with interesting structural features. The known ternary thiophosphates with group 5 metals [8–16] have long been of interest as potential host materials for alkali metal intercalation with possible technological applications as cathode materials in batteries, like the well known lithium intercalated derivatives of the layered MPX<sub>3</sub> family (M = transition metal; X = S, Se) [17–19]. Despite the favorable structural features of the ternary thiophosphates only a few attempts were carried out to incorporate alkali metals. The first experiments were started with the compounds  $M_2PS_{10}$  (M = V, Nb) and  $V_2P_4S_{13}$  [20, 21], but neither an electrochemical process nor

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the reaction in an eutectic alkali metal halide flux led to the desired products. Very recently we synthesized the new quaternary thiophosphates K<sub>0.38</sub>TaPS<sub>6</sub> and Rb<sub>0.46</sub>TaPS<sub>6</sub> [7]. These compounds are the first structurally characterized alkali metal intercalated derivatives of the known ternary  $TaPS_6$  phase [14] and demonstrate that the low-dimensional host structures of group 5 thiophosphates are stable during the intercalation process. A structure closely related to TaPS<sub>6</sub> is observed in the quaternary niobium thiophosphates  $ANb_2P_2S_{12}$  (A = K, Rb, Cs) [22]. In all these compounds the electron transfer from the alkali metals to the host material leads to a significant shortening of the M-M distances within the biprismatic  $[M_2S_{12}]$  units (M = Nb, Ta). These results confirms the assumption that the lowlying acceptor levels of the highly oxidized metals in the bimetallic building blocks are responsible for the alkali metal intercalation of the ternary M-P-S phases [20].

The successful synthesis of intercalated phases mentioned above pointed out the high synthetic potential of the chemistry in alkali metal polythiosphate fluxes, and the formation of new interesting solid-state materials can be expected which cannot be obtained by traditional methods.

Interestingly, analyzing the structures of the ternary and quaternary tantalum thiophosphates only  $[Ta_2S_{11}]$  or  $[Ta_2S_{12}]$  units and tetrahedral  $[PS_4]$  groups are found as the general structural motifs [2, 6, 7, 14, 15, 16, 23]. In our ongoing investigations of the A-Ta-P-S system we have obtained the quaternary tantalum thiophosphates  $A_{0.42(2)}TaPS_5$  (A = K and Rb) in which a  $[Ta_2S_{10}]$  unit is observed for the first time. This unit is composed of two  $TaS_6$  octahedra sharing a common edge. In the present contribution the syntheses, crystal structures and vibrational properties of these new compounds are reported.

#### **Results and Discussion**

#### Crystal structures

The two compounds  $K_{0.42(2)}TaPS_5$  (I) and  $Rb_{0.42(2)}TaPS_5$ (II) are isostructural and crystallize in the orthombic space group Fddd with 16 formula units in the cell. In the cell there are each one unique alkali metal, Ta, and P atom and three crystallographically independent S atoms. A section of one layer of the novel two-dimensional crystal structure is shown in Figure 1. The main feature of this new structure type is the presence of binuclear [Ta<sub>2</sub>S<sub>10</sub>] units which are interconnected via tetrahedral [PS<sub>4</sub>] groups into a layered structure.

The Ta atom is surrounded by two  $\mu_2$ -S<sup>2-</sup> ions and four S<sup>2-</sup> anions in a distorted octahedral environment (Fig. 2, Table 1 and 2). Two [TaS<sub>6</sub>] octahedra share a common edge to form dimeric [Ta<sub>2</sub>S<sub>10</sub>] units with an average Ta-S distance of 2.469 Å for both compounds (Table 1 and Fig. 2). The average Ta-S distances in the title compounds are comparable with those found for the [TaS<sub>6</sub>] octahedra in CsTa<sub>4</sub>P<sub>3</sub>S<sub>19</sub> [23] and in TaS<sub>2</sub> [25]. The shortest Ta-S bonds of 2.336(3) Å (I) and 2.341(3) Å (II) are observed to the  $\mu_2$ -



Fig. 1 Crystal structure of  $K_{0.42}$ TaPS<sub>5</sub> and Rb<sub>0.42</sub>TaPS<sub>5</sub> with view approximately along the crystallographic c axis.



Fig. 2 Environment of the  $[Ta_2S_{10}]$  units in the crystal structure of  $K_{0.42}TaPS_5$  and  $Rb_{0.42}TaPS_5$ .

Table 1 Selected bond distances/Å for  $K_{0.42}TaPS_5$  (I) and  $Rb_{0.42}TaPS_5$  (II). Estimated standards deviations are given in parentheses.

	Ι	II
Ta - S(1)	2.467(3) (x2)	2.463(3) (x2)
Ta - S(2)	2.603(2) (x2)	2.603(3) (x2)
Ta - S(3)	2.336(3) (x2)	2.341(3) (x2)
Ta - Ta	3.1194(6)	3.127(2)
<b>-</b> S(1)	2.057(2) (x2)	2.059(4) (x2)
- S(2)	2.028(2) (x2)	2.029(4) (x2)
A - S(1)	3.156(2) (x2)	3.228(3) (x2)
A - S(1)	3.429(4) (x2)	3.445(4) (x2)
A - S(2)	3.460(9) (x2)	3.641(6) (x2)
A - S(2)	3.949(3) (x2)	3.946(4) (x2)

 $S^{2-}$  anions bridging the two Ta atoms, whereas the longest Ta-S distances are in *trans* position to the short Ta-S bonds (Table 1 and Fig. 2). The [TaS<sub>6</sub>] octahedra in the two compounds are severely distorted as is evidenced by the S-Ta-S angles (Table 2).

	Ι	П
S(1) - Ta - S(1)	162.38(7)	163.1(2)
S(1) - Ta - S(2)	77.83(5) (x2)	77.64(9) (x2)
S(1) - Ta - S(2)	89.54(6) (x2)	90.2(2) (x2)
S(2) - Ta - S(2)	88.83(8)	88.5(2)
S(3) - Ta - S(1)	85.25(4) (x2)	84.42(7) (x2)
S(3) - Ta - S(1)	106.69(4) (x2)	107.04(7) (x2)
S(3) - Ta - S(2)	163.04(4) (x2)	162.02(7) (x2)
S(3) - Ta - S(2)	89.83(5) (x2)	90.31(9) (x2)
S(3) - Ta - S(3)	96.26(7)	96.2(2)
S(1) - P - S(1)	107.3(2)	106.7(2)
S(2) - P - S(1)	114.11(7) (x2)	114.9(2) (x2)
S(2) - P - S(1)	102.56(6) (x2)	102.0(2) (x2)
S(2) - P - S(2)	116.2(2)	116.4(3)

Table 2 Selected angles/° for K<sub>0.42</sub>TaPS<sub>5</sub> (I) and Rb<sub>0.42</sub>TaPS<sub>5</sub> (II). Estimated standard deviations are given in parentheses.



Fig. 3 Interconnection of the  $[Ta_2S_{10}]$  units by  $[PS_4]$  tetrahedra in the crystal structure of  $K_{0.42}TaPS_5$  and  $Rb_{0.42}TaPS_5$  with atomic labeling. The dashed lines highlight the rectangular tunnel mentioned in the text and the numbers are the distances between the atoms in Å measured from coordinate to coordinate.

The  $[Ta_2S_{10}]$  units share common edges with four tetradentate [PS<sub>4</sub>] groups (Fig. 3). The arrangement of the [PS<sub>4</sub>] groups with respect to the line joining two neighbored Ta atoms leads to the formation of layers with one type of cavities. The wall of the cavities is formed by the S(1) atoms yielding a nearly rectangular opening. The dimensions of the openings measure about 4.07  $\cdot$  5.1 Å for I and 4.06  $\cdot$ 5.3 Å for II (measured from coordinate to coordinate) (Fig. 3).

The average P-S bond lengths in the tetradentate  $[PS_4]$ tetrahedra amount to 2.043 Å for compound I and 2.044 Å for compound II (Table 1). The average P-S distances are in good agreement with values reported for [PS<sub>4</sub>] tetrahedra in  $Cs_2Ta_2P_2S_{12}$  and in the intercalated  $TaPS_6$  phases [6, 7]. The [PS<sub>4</sub>] tetrahedra are significantly distorted as is evidenced by the S-P-S angles (102.56(6) to 116.2(2)° in I and 102.0(2) to 116.4(3)° in II) (Table 2).



Fig. 4 View of the channels along [011] in the crystal structure of K<sub>0.42</sub>TaPS<sub>5</sub> and Rb<sub>0.42</sub>TaPS<sub>5</sub>.



Fig. 5 Crystal structure of K<sub>0.42</sub>TaPS<sub>5</sub> and Rb<sub>0.42</sub>TaPS<sub>5</sub> with view along the crystallographic a axis showing the stacking sequence ...ABAB... perpendicular to [001].

The individual  $[TaPS_5]$  layers extending in the (001) plane are separated by about 3.72 (I) and 3.81 Å (II) (measured from coordinate to coordinate) and are stacked along [001] in a sequence ... ABAB... (Fig. 5). Consequently, the cavities of neighboring layers are not located directly above each other. But nearly rectangular channels are formed running along [011], [0-11], [01-1], and [0-1-1] with approximate dimensions of  $4.1 \cdot 7.9$  Å (Fig. 4).

The two new compounds represent the first tantalum thiophosphates containing  $[Ta_2S_{10}]$  units formed by edge-sharing of two  $[TaS_6]$  octahedra. We note that  $[TaS_6]$  octahedra were also observed in the quaternary compound  $CsTa_4P_3S_{19}$  [23]. But in contrast to the title compounds two  $[TaS_6]$  groups are linked to a central  $[Ta_2S_{11}]$  unit yielding a  $[Ta_4S_{17}(S_2)]$  fragment.

An interesting feature of the structure is the location of the alkali metal cations. The inter-layer separation is too small to accommodate the large cations  $[r(K^+) = 1.51 \text{ Å}, r(Rb^+) = 1.61 \text{ Å} (CN = 8)]$  [26]. Hence, they are situated approximately in the middle of the rectangular openings within the layers. The cations are surrounded by eight S atoms forming irregular polyhedra. Two of the S atoms are from one neighboring layer. The K-S bonds range from 3.157 to 3.945 Å (average K-S distance: 3.499 Å; Table 1) and Rb-S distances from 3.228 to 3.946 Å (average Rb-S distance: 3.565 Å; Table 1). The average A-S distances (A = K, Rb) match well with the sum of the ionic radii [26]. Within the channels (see above) the cations are disordered, and unusual short distances occur between neighbored symmetry equivalent cations (see exp. Part). Obviously, fully occupied sites for the A<sup>+</sup> ions would lead to a different cation arrangement.

It is surprising that the b axis of the Rb compound is shorter than that of the K compound. This contraction is the result of the space requirements of the larger Rb<sup>+</sup> ion and the response of the thiophosphate network. The Rb-S(1) distances (3.228 and 3.445 Å) are longer than the analogous K-S(1) bonds (3.157 and 3.434 Å) which leads to a lengthening of the S(1)...S(1) separation along the a-axis from 5.124 in I to 5.339 Å in II. The expansion is accompanied by a significant contraction of the S(2)...S(2)separation along the b axis (8.245 vs. 8.135 Å) (see Fig. 3). It is interesting to note that the replacement of  $K^+$  by the larger Rb<sup>+</sup> not simply leads to an expansion of the inorganic network, i.e. a lengthening of all axes. This observation implies that the strong covalent Ta-S and P-S bonds are responsible for the rigidity of the network and the flexibility is due to variable angles around Ta and P.

Another interesting feature of the compounds is an electron transfer from the alkali metal atoms to the host material. In the host lattice only the Ta<sup>5+</sup> cations can be reduced by the electron transfer. Hence, the low-lying acceptor levels (*d*-block bands) of the highly oxidized metals in the  $[Ta_2S_{10}]$ building blocks are responsible for the alkali metal intercalation. The electron transfer leads to relatively short interatomic Ta-Ta distances within the [Ta<sub>2</sub>S<sub>10</sub>] groups which amount to 3.1194(6) Å for compound I and 3.127(2) Å for compound II (Table 1). These distances are significantly shorter than in compounds containing neighbored Ta<sup>5+</sup> (d<sup>0</sup>) atoms [2, 6, 14, 15, 16, 23] and are comparable with those found in the intercalated phases K<sub>0.38</sub>TaPS<sub>6</sub> (3.142(2) Å) and Rb<sub>0.46</sub>TaPS<sub>6</sub> (3.1011(5) Å) [7]. The electronic situation in the title compounds may be described as  $A_x^+Ta^{(5-x)+}P^{5+}S_5^{2-}$  (A = K, Rb; x = 0.42(2)).

In view of the present results, further investigations are indispensable concerning the physical properties, the deintercalation behavior of the compounds and the homogeneity range with respect to the alkali metal content. The deintercalation could be an elegant synthetic route to design new materials which could serve as hosts for further intercalation experiments.



Fig. 6 MIR spectra of K<sub>0.42</sub>TaPS<sub>5</sub>(top) and Rb<sub>0.42</sub>TaPS<sub>5</sub> (bottom).

## Vibrational properties

The MIR spectra of  $K_{0.42}$ TaPS<sub>5</sub> and Rb<sub>0.42</sub>TaPS<sub>5</sub> are shown in Figure 6. According to the results of the X-ray structure determination the spectroscopic relevant units are tetrahedral [PS<sub>4</sub>] groups. The spectrum of compound I displays three strong absorption bands at 601, 574 and 545 cm<sup>-1</sup>, which may be assigned to P-S stretching vibrations. Analogous bands are observed for II.

# Experimental

# Syntheses

The compounds  $K_{0.42}$ TaPS<sub>5</sub> (I) and  $Rb_{0.42}$ TaPS<sub>5</sub> (II) were prepared by reacting a mixture of  $A_2S_3$  (A = K, Rb), Ta,  $P_2S_5$ , and S in a 1:8:3:10 molar ratio (Ta, 99.97 %, Fluka;  $P_2S_5$ , 99.99 % purity, Alfa; S, 99.99 %, Heraeus).  $A_2S_3$  (A = K, Rb) was synthesized by the reaction of stoichiometric amounts of the elements (K, Rb > 99 %, Chempur) in liquid ammonia under argon atmosphere. The reaction mixtures were thoroughly mixed in a N<sub>2</sub>-filled glove box

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and loaded into glass ampoules. After evacuation to  $10^{-3}$  mbar the ampoule was flame-sealed and placed in a computer-controlled furnace.

## Synthesis of $K_{0.42}$ TaPS<sub>5</sub> (I)

Compound I was prepared from a reaction mixture of  $K_2S_3$ (0.15 mmol), Ta (1.2 mmol),  $P_2S_5$  (0.45 mmol) and S (1.5 mmol). The mixture was heated to 500 °C within 18 h. This temperature was kept for 4 days before the sample was cooled down to 250 °C with 2 °C h<sup>-1</sup> followed by cooling to room temperature within 10 h. The residual  $K_xP_yS_z$  flux was removed with dry DMF and after washing with ether black crystals were obtained (yield: ~85 % based on Ta). Scanning electron micrographs of the product revealed black crystals with a multi-faced polyhedra-like morphology. The X-ray powder pattern of the product is dominated by reflections of compound I and only very weak reflections of a second phase were present which could not be identified until now. An EDX analysis of several selected crystals indicated the presence of all four elements (K, Ta, P, S) and for all crystals the atomic ratio was identical amounting to (~1):2:2:10.

# Synthesis of Rb<sub>0.42</sub>TaPS<sub>5</sub> (II)

Single crystals of the isostructural compound **II** were prepared from a reaction mixture of  $Rb_2S_3$  (0.09 mmol), Ta (0.72 mmol),  $P_2S_5$  (0.27 mmol) and S (0.9 mmol). The sample was heated to 500 °C within 18 hours and kept at this temperature for 4 days. Afterwards the sample was cooled to 150 °C with 3 °C h<sup>-1</sup> and then in 6 hours to room temperature. The residual  $Rb_xP_yS_z$  flux was removed with dry DMF and after washing with ether black polyhedra-like crystals were obtained (yield: ~70 % based on Ta). The X-ray powder pattern of the product is dominated by reflections of compound **I** and weak reflections of a second phase were present which could not be identified until now. An EDX analysis of several selected single crystals always yields the same ratio for the elements, i.e. within the margin of error and the limits of the method the crystals have an identical chemical composition.

#### Single crystal X-Ray diffraction

Single crystal X-ray work was performed using a STOE Imaging Plate Diffraction System (IPDS) (MoK $\alpha$  radiation;  $\lambda =$ 0.71073 Å). The raw intensities were treated in the usual way applying a Lorentz, polarization and a numerical absorption correction. Structure solution was performed with SHELXS-97 [24]. Refinement was done against F<sup>2</sup> using SHELXL-97 [24]. All atoms were refined with anisotropic displacement parameters. For compound I an extinction correction was performed. The K and Rb content in the two compounds was refined yielding K<sub>0.42(1)</sub>TaPS<sub>5</sub> and Rb<sub>0.42(1)</sub>TaPS<sub>5</sub>. Within the accuracy of the method and 3 esd's the composition of the two compounds is identical. Concerning the disorder of the alkaline metal cations long exposed images of the crystals were made. From these investigations there are no hints for a superstructure or diffuse intensities.

Technical details of the data acquisition as well as some refinement results for compounds I and II are summarized in Table 3, atomic coordinates and equivalent isotropic displacement parameters are given in Table 4 for compound I and in Table 5 for compound II. Table 3 Technical details of data acquisition and some refinement results for  $K_{0.42}TaPS_5$  (I) and  $Rb_{0.42}TaPS_5$  (II).

Compound	I	II
Crystal system	orthorhombic	orthorhombic
a / Å	9.6983(6)	9.879(2)
b / Å	14.373(2)	14.288(2)
c / Å	21.642(2)	21.687(2)
V / Å <sup>3</sup>	3016.8(3)	3061.2(5)
Space group	Fddd (no. 70)	Fddd (no. 70)
Z	16	16
Calc. density / $g \text{ cm}^{-3}$	3.418	3.546
Crystal color	black	black
$\mu / \text{mm}^{-1}$	16.33	18.45
F(000)	2811	2940
Scan range	$5^\circ \le 2\theta \le 56^\circ$	$5^{\circ} \le 2\theta \le 51^{\circ}$
Index range	$-12 \le h \le 12$	$-11 \le h \le 11$
	$-18 \le k \le 18$	$-17 \le k \le 17$
	$-28 \le 1 \le 28$	$-25 \le l \le 25$
Reflections collected	7360	5525
Independent reflections	914	674
Temperature / K	293	293
R <sub>int</sub>	0.0519	0.0736
Min./max. transm.	0.0955/ 0.1613	0.0713/0.1290
refl. with $F_o > 4\sigma(F_o)$	745	509
Number of parameters	41	40
x <sup>a)</sup>	0.0528	0.0531
$R_1$ for $F_o > 4\sigma(F_o)$	0.0285	0.0352
wR <sub>2</sub> for all reflections	0.0757	0.0866
GOOF	1.034	1.057
$\Delta \rho / e \dot{A}^{-3}$	1.29 / -1.68	1.35 / -2.36

<sup>a)</sup> w = 1/[ $\sigma^2(F_o^2)$  + (x · P)<sup>2</sup>; P = (Max (F<sub>o</sub><sup>2</sup>,0) + 2 · F<sub>c</sub><sup>2</sup>) / 3

**Table 4** Atomic coordinates and equivalent isotropic displacement parameters  $U_{eq}$  (Å<sup>2</sup>) for K<sub>0.42</sub>TaPS<sub>5</sub>. Estimated standards deviations are given in parentheses. The  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor (s.o.f. of K1 = 0.42(2)).

	<i>Wyckoff</i> position	x	у	Z	$\mathbf{U}_{eq}$
K(1)	16g	1/8	5/8	0.1588(5)	69(3)
Ta(1)	16f	5/8	0.5165(1)	1/8	23(1)
P(1)	16g	3/8	3/8	0.1530(1)	25(1)
S(1)	32h	0.3816(2)	0.4902(1)	0.0967(1)	30(1)
S(2)	32h	0.5516(2)	0.3871(1)	0.2025(1)	32(1)
S(3)	16g	5/8	5/8	0.2054(1)	30(1)

**Table 5** Atomic coordinates and equivalent isotropic displacement parameters  $U_{eq}$  (Å<sup>2</sup>) for Rb<sub>0.42</sub>TaPS<sub>5</sub>. Estimated standards deviations are given in parentheses. The  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor (s.o.f. of Rb1 = 0.42(2)).

	<i>Wyckoff</i> position	x	у	Z	U <sub>eq</sub>
Rb(1)	16g	1/8	5/8	0.1509(3)	70(2)
Ta(1)	16f	5/8	0.5156(1)	1/8	30(1)
P(1)	16g	3/8	3/8	0.1519(2)	34(1)
S(1)	32h	0.3872(3)	0.4903(2)	0.0952(1)	37(1)
S(2)	32h	0.5489(3)	0.3851(2)	0.2012(1)	41(1)
S(3)	16g	5/8	5/8	0.2054(2)	37(1)

#### Physical property measurements

MIR spectra (4000-400 cm<sup>-1</sup>, 2 cm<sup>-1</sup> resolution) were collected on a Genesis FT-spectrometer (ATI Mattson). The compounds were ground together with KBr in a N<sub>2</sub>-filled glove box and pressed into a transparent pellet.

EDX analysis was performed with a Philips ESEM XL 30 scanning electron microscope equipped with an EDAX analyzer.

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