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Synthesis and Structures of New One-Dimensional $KTiPS_5$ and $RbTiPS_5$

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Two new compounds $KTiPS_5$ and $RbTIPS_5$ have been synthesized through reactions of the elements with alkali metal halide fluxes. $KTiPS_5$ crystallizes in the space group $C_{2h}^3 - C2/m$ of the monoclinic system with four formula units in a cell of dimensions $a = 17.678(8)$, $b = 7.080(4)$, $c = 6.325(3)$ Å, $\beta = 97.99(4)°$. $RbTiPS_5$ crystallizes in the space group $C_{2h}^3 - C2/m$ of the monoclinic system with eight formula units in a cell of dimensions $a = 18.159(7)$, $b = 7.081(3)$, $c = 15.352(6)$ Å, $\beta = 124.07(2)°$. The structures of both compounds have been determined by single crystal X-ray techniques. Both structures consist of one-dimensional $_\infty^1[\mathrm{TiPS}_5^-]$ chains separated from one another by K^+ or Rb^+ cations. The linear chains are built up from the basic repeating unit, $[Ti_2(PS_4)_2S_2^{2-}]$, which is composed of two edge-shared TiS_6 octahedra and two PS_4 tetrahedra. There is no interchain bonding except the van der Waals interactions. The classical charge of the two compounds can be represented by $[A^+][Ti^{4+}][PS_4^{3-}][S^{2-}]$ (A = K or Rb).

INTRODUCTION

The transition metal chalcogenophosphates (chalcogen = S, Se) form a wide and interesting class of compounds that have attracted attention because of their various structural chemistry and their interesting properties. Although many ternary thiophosphates are now known (1), relatively few quaternary transition metal thiophosphates have been reported (2–5). Our efforts to prepare new quaternary thiophosphates are motivated by the desire to extend the chemistry of the ternary thiophosphates to the new quaternary compounds with novel anisotropic structures and properties.

Our synthetic approaches are based upon the knowledge of preferred coordination geometries of the transition metals and phosphorous. Two ternary titanium thiophosphates, TiP_2S_6 and $Ti_4P_8S_{29}$, have been structurally characterized (6, 7). The most prominent structural feature in these compounds is the presence of the titanium-centered octahedra and phosphorous-centered tetrahedra. In both structures, the TiS_6 octahedra are connected to form a

TABLE 1
Details of X-Ray Data Collection and Refinement

	$KTiPS_5$	$RbTiPS_5$
Formula mass, amu	278.27	324.64
Space group	$C_{2h}^3 - C2/m$	$C_{2h}^3 - C2/m$
a, Å	17.678(8)	18.159(7)
b, Å	7.080(4)	7.081(3)
c, Å	6.325(3)	15.352(6)
β[a], deg.	97.99(4)	124.07(2)
V, Å^3	783.9(7)	1635.1(1)
Z	4	8
T, K	293(2)	293(2)
Radiation	graphite monochromated Mo$K\alpha_1$ ($\lambda(K\alpha_1) = 0.7093$ Å)	
Linear absorption coefficient, cm^{-1}	30.51	83.32
Transmission factors[b]		0.635–0.705
Density, calc. g/cm^3	2.358	2.638
Crystal size, mm^3	$0.70 \times 0.06 \times 0.02$	$0.45 \times 0.05 \times 0.05$
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
Scan speed, deg. min^{-1}	5.0 in ω	4.0 in ω
Scan range, deg.	$1.5 + 0.35 \tan\theta$	$1.3 + 0.35 \tan\theta$
2θ limits, deg.	$3° \le 2\theta(\mathrm{Mo}K\alpha_1) \le 50°$	$3° \le 2\theta(\mathrm{Mo}K\alpha_1) \le 55°$
Data collected	$\pm h, -k, +l$	$\pm h, -k, +l$
No. of unique data with $F_o^2 > 0$	702	1464
No. of unique data with $F_o^2 > 2\sigma(F_o^2)$	609	1328
$wR2(F_o^2 > 0)$	0.1487	0.1076
R(on F_o for $F_o^2 > 2\sigma(F_o^2)$)	0.0549	0.0413
Goodness-of-fit on F^2	0.981	1.090
Minimum and maximum Residual electron density(e/Å^3)	min. = −0.95 max. = 1.21	min. = −1.26 max. = 0.93

[a] α and γ were constrained to be 90° in the refinement of cell constraints.

[b] The analytical method as employed in the Northwestern absorption program, AGNOST, was used for the absorption correction (15).

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TABLE 2
Atomic Coordinates (×10³) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for $KTiPS_5$ and $RbTiPS_5$

Atom	x	y	z	U_{eq} [a]
		$KTiPS_5$		
K	−2321(2)	0	2642(4)	38(1)
Ti	0	2225(2)	5000	20(1)
P	−1328(1)	5000	2885(4)	20(1)
S(1)	624(2)	0	3252(4)	24(1)
S(2)	849(1)	5000	3925(4)	18(1)
S(3)	−860(1)	−2667(2)	1667(3)	24(1)
S(4)	2539(1)	0	2451(4)	30(1)
		$RbTiPS_5$		
Rb(1)	1621(1)	5000	3634(1)	32(1)
Rb(2)	−6999(1)	10000	−8552(1)	35(1)
Ti(1)	0	2212(2)	0	20(1)
Ti(2)	0	−2763(2)	5000	21(1)
P(1)	744(2)	0	3977(2)	20(1)
P(2)	−1709(1)	5000	−975(2)	20(1)
S(1)	−2866(2)	5000	−1146(2)	31(1)
S(2)	−261(2)	0	882(2)	24(1)
S(3)	−588(1)	5000	574(2)	20(1)
S(4)	−1490(1)	7338(2)	−1595(1)	24(1)
S(5)	−55(1)	−2343(2)	3392(1)	24(1)
S(6)	−6104(1)	10000	−5874(2)	23(1)
S(7)	−3874(1)	5000	−4461(2)	20(1)
S(8)	1734(2)	0	3796(2)	27(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

three-dimensional network through various thiophosphate anions generated from the phosphorous-centered tetrahedra ($P_2S_6^{4-}$(TiP_2S_6), PS_4^{3-}, $P_2S_6^{2-}$, and $P_2S_7^{2-}$($Ti_4P_8S_{29}$)). From the known structures, titanium atoms coordinated to six S atoms are expected to be connected through sharing corners, edges, or faces with other TiS_6 octahedra and with tetrahedra centered by P atoms. The incorporation of alkali metals generally induces the decrease in dimensionality (8). As a result, infinite one-dimensional chains or two-dimensional layers can be generated as titanium thiophosphate polyanions. We anticipated that a new low-dimensional structure would be found if alkali metals were to successfully stabilize those polyanions through strong electrostatic interactions. To prepare new quaternary alkali metal titanium thiophosphates, eutectic alkali metal halide mixtures were used as reactive fluxes. This synthetic technique appears to be of general utility in preparing new multinary chalcogenides (e.g. KNb_2PS_{10} (9), $Rb_3Yb_7Se_{12}$, $CsEr_3Se_5$ (10), $CaYbInQ_4$ (Q = S, Se) (11), and $Ca_4(RE)_2In_4Q_{13}$(RE = La, Nd, Sm, Gd) (12)). Here we describe the synthesis and structural characterization of $KTiPS_5$, which is composed of infinite linear chains isolated by K^+ ions. We also describe the synthesis and structure of $RbTiPS_5$, which, although not isostructural with $KTiPS_5$, again comprises one-dimensional chains separated by Rb^+ ions.

EXPERIMENTAL

Synthesis. The compounds $KTiPS_5$ and $RbTiPS_5$ were prepared by the reactions of elemental Ti, P, and S with the use of the reactive halide flux technique. Stoichiometric combinations of the pure elements, Ti powder (CERAC 99.5%), P powder (CERAC 99.5%), and S powder (Aldrich 99.999%), were mixed in silica tubes with the addition of eutectic mixtures of KCl/LiCl or RbCl/LiCl. The mass ratios of reactants and fluxes were 1.0 : 9.1 for $KTiPS_5$ and 1.0 : 3.0 for $RbTiPS_5$.

For $KTiPS_5$, the tubes were evacuated ($\sim 10^{-2}$ Torr), sealed, and heated gradually to 650°C, where they were kept for 120 hr. The tubes were cooled to 250°C at 5°C/hr and then to room temperature at 50°C/hr. The excess halide flux was removed with distilled water and gold colored needle-shaped crystals up to 2 mm in length were found as a major product. As a minor phase, dark red polyhedral crystals were also isolated and were proved to be $K_3Ti_2P_5S_{18}$ by single crystal X-ray diffraction studies (13, 14). The $KTiPS_5$ is air and water stable. However, $K_3Ti_2P_5S_{18}$ decays slowly in the air. Analysis of these

TABLE 3
Anisotropic Displacement Parameters (Å² × 10³) for $KTiPS_5$ and $RbTiPS_5$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
			$KTiPS_5$			
K	49(2)	34(1)	32(1)	0	10(1)	0
Ti	26(1)	6(1)	28(1)	0	1(1)	0
P	24(1)	11(1)	23(1)	0	0(1)	0
S(1)	30(1)	7(1)	34(1)	0	9(1)	0
S(2)	23(1)	9(1)	21(1)	0	1(1)	0
S(3)	32(1)	14(1)	25(1)	−1(1)	−1(1)	5(1)
S(4)	23(1)	35(2)	29(1)	0	−1(1)	0
			$RbTiPS_5$			
Rb(1)	38(1)	28(1)	34(1)	0	22(1)	0
Rb(2)	44(1)	32(1)	34(1)	0	25(1)	0
Ti(1)	27(1)	10(1)	23(1)	0	14(1)	0
Ti(2)	30(1)	13(1)	24(1)	0	18(1)	0
P(1)	26(1)	14(1)	20(1)	0	14(1)	0
P(2)	23(1)	15(1)	21(1)	0	11(1)	0
S(1)	26(1)	31(1)	35(1)	0	17(1)	0
S(2)	37(1)	15(1)	27(1)	0	23(1)	0
S(3)	25(1)	16(1)	18(1)	0	11(1)	0
S(4)	30(1)	16(1)	22(1)	1(1)	13(1)	4(1)
S(5)	32(1)	18(1)	22(1)	−5(1)	15(1)	−4(1)
S(6)	25(1)	14(1)	29(1)	0	14(1)	0
S(7)	26(1)	14(1)	20(1)	0	14(1)	0
S(8)	30(1)	28(1)	31(1)	0	22(1)	0

Note. The anisotropic displacement factor exponent takes the form

$$-2\pi^2[h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23}].$$

TABLE 5
Bond Lengths [Å] and Angles [deg] for KTiPS$_5$ and RbTiPS$_5$

KTiPS$_5$		RbTiPS$_5$	
Ti–S(1)#1	2.294(2)	Ti(1)–S(2)#15	2.287(2)
Ti–S(1)	2.294(2)	Ti(1)–S(2)	2.287(2)
Ti–S(3)#1	2.441(2)	Ti(1)–S(4)#4	2.449(2)
Ti–S(3)#3	2.441(2)	Ti(1)–S(4)#16	2.449(2)
Ti–S(2)	2.618(2)	Ti(1)–S(3)#4	2.621(2)
Ti–S(2)#10	2.618*2)	Ti(1)–S(3)	2.621(2)
		Ti(2)–S(6)#17	2.305(2)
P–S(4)#5	1.983(4)	Ti(2)–S(6)#18	2.305(2)
P–S(3)#3	2.046(2)	Ti(2)–S(5)#19	2.433(2)
P–S(3)#14	2.046(2)	Ti(2)–S(5)	2.433(2)
P–S(2)#10	2.077(4)	Ti(2)–S(7)#20	2.607(2)
		Ti(2)–S(7)#18	2.607(2)
		P(1)–S(8)	1.966(3)
		P(1)–S(5)	2.050(2)
		P(1)–S(5)#2	2.050(2)
		P(1)–S(7)#20	2.091(3)
		P(2)–S(1)	1.965(3)
		P(2)–S(4)#16	2.056(2)
		P(2)–S(4)	2.056(2)
		P(2)–S(3)	2.091(3)
S(1)#1–Ti–S(1)	93.2(1)	S(2)#15–Ti(1)–S(2)	93.53(9)
S(1)#1–Ti–S(3)#1	87.44(9)	S(2)#15–Ti(1)–S(4)#4	101.62(8)
S(1)–Ti–S(3)#1	102.74(9)	S(2)–Ti(1)–S(4)#4	88.66(7)
S(1)#1–Ti–S(3)#3	102.74(9)	S(2)#15–Ti(1)–S(4)#16	88.66(7)
S(1)–Ti–S(3)#3	87.44(9)	S(2)–Ti(1)–S(4)#16	101.62(8)
S(3)#1–Ti–S(3)#3	165.3(1)	S(4)#4–Ti(1)–S(4)#16	165.1(1)
S(1)#1–Ti–S(2)	166.38(8)	S(2)#15–Ti(1)–S(3)#4	93.34(6)
S(1)–Ti–S(2)	93.36(7)	S(2)–Ti(1)–S(3)#4	166.80(7)
S(3)#1–Ti–S(2)	79.49(8)	S(4)#4–Ti(1)–S(3)#4	78.92(7)
S(3)#3–Ti–S(2)	89.44(8)	S(4)#16–Ti(1)–S(3)#4	89.78(7)
S(1)#1–Ti–S(2)#10	93.36(7)	S(2)#15–Ti(1)–S(3)	166.80(7)
S(1)–Ti–S(2)#10	166.38(8)	S(2)–Ti(1)–S(3)	93.34(6)
S(3)#1–Ti–S(2)#10	89.44(8)	S(4)#4–Ti(1)–S(3)	89.78(7)
S(3)#3–Ti–S(2)#10	79.49(8)	S(4)#16–Ti(1)–S(3)	78.92(7)
S(2)–Ti–S(2)#10	82.8(1)	S(3)#4–Ti(1)–S(3)	82.26(9)
S(4)#5–P–S(3)#3	113.7(1)	S(6)#17–Ti(2)–S(6)#18	93.2(1)
S(4)#5–P–S(3)#14	113.7(1)	S(6)#17–Ti(2)–S(5)#19	101.67(8)
S(3)#3–P–S(3)#14	107.7(2)	S(6)#18–Ti(2)–S(5)#19	88.03(7)
S(4)#5–P–S(2)#10	113.7(2)	S(6)#17–Ti(2)–S(5)	88.03(7)
S(3)#3–P–S(2)#10	103.5(1)	S(6)#18–Ti(2)–S(5)	101.67(8)
S(3)#14–P–S(2)#10	103.5(1)	S(5)#19–Ti(2)–S(5)	166.0(1)
		S(6)#17–Ti(2)–S(7)#20	166.41(7)
		S(6)#18–Ti(2)–S(7)#20	93.40(6)
		S(5)#19–Ti(2)–S(7)#20	90.42(7)
		S(5)–Ti(2)–S(7)#20	79.01(7)
		S(6)#17–Ti(2)–S(7)#18	93.40(6)
		S(6)#18–Ti(2)–S(7)#18	166.41(7)
		S(5)#19–Ti(2)–S(7)#18	79.01(7)
		S(5)–Ti(2)–S(7)#18	90.42(7)
		S(7)#20–Ti(2)–S(7)#18	82.74(9)
		S(8)–P(1)–S(5)	114.61(9)
		S(8)–P(1)–S(5)#2	114.61(9)
		S(5)–P(1)–S(5)#2	108.1(1)
		S(8)–P(1)–S(7)#20	114.8(1)
		S(5)–P(1)–S(7)#20	101.60(9)
		S(5)#2–P(1)–S(7)#20	101.60(9)
		S(1)–P(2)–S(4)#16	114.04(9)

TABLE 5—*Continued*

KTiPS$_5$	RbTiPS$_5$	
	S(1)–P(2)–S(4)	114.04(9)
	S(4)#16–P(2)–S(4)	107.2(1)
	S(1)–P(2)–S(3)	116.0(1)
	S(4)#16–P(2)–S(3)	102.06(9)
	S(4)–P(2)–S(3)	102.06(9)

Note. Symmetry transformations used to generate equivalent atoms:

#1 $-x, -y, -z + 1$
#2 $-x, -y, -z$
#3 $x, -y, z$
#4 $x - \frac{1}{2}, y - \frac{1}{2}, z$
#5 $x - \frac{1}{2}, y + \frac{1}{2}, z$
#6 $-x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$
#7 $-x - \frac{1}{2}, -y - \frac{1}{2}, -z + 1$
#8 $- x - \frac{1}{2}, -y - \frac{1}{2}, -z$
#9 $-x - \frac{1}{2}, -y + \frac{1}{2}, -z$
#10 $-x, -y + 1, -z + 1$
#11 $x + \frac{1}{2}, y + \frac{1}{2}, z$
#12 $x, y - 1, z$
#13 $x + \frac{1}{2}, y - \frac{1}{2}, z$
#14 $x, y + 1, z$

#1 $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$
#2 $x, -y, z$
#3 $x, y + 1, z$
#4 $-x, -y + 1, -z$
#5 $-x, y, -z$
#6 $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$
#7 $x - \frac{1}{2}, y + \frac{1}{2}, z - 1$
#8 $-x - 1, y, -z - 1$
#9 $-x - 1, -y + 2, -z - 1$
#10 $-x - 1, -y + 1, -z - 1$
#11 $x - \frac{1}{2}, y + \frac{3}{2}, z - 1$
#12 $x - \frac{1}{2}, -y + \frac{1}{2}, z - 1$
#13 $-x - \frac{3}{2}, -y + \frac{3}{2}, -z - 2$
#14 $-x - \frac{3}{2}, -y + \frac{5}{2}, -z - 2$
#15 $-x, -y, -z$
#16 $x, -y + 1, z$
#17 $x + \frac{1}{2}, y - \frac{3}{2}, z + 1$
#18 $-x - \frac{1}{2}, -y + \frac{1}{2}, -z$
#19 $-x, y, -z + 1$
#20 $x + \frac{1}{2}, y - \frac{1}{2}, z + 1$
#21 $-x, -y - 1, -z + 1$
#22 $x, y - 1, z$

compounds with the microprobe of an EDAX-equipped AMRAY 1200C scanning electron microscope indicated the presence of K, Ti, P, and S for both phases.

For RbTiPS$_5$, the tubes were evacuated (~10^{-2} Torr), sealed, and heated to 850°C, where they were kept for 48 hr. The tubes were cooled to 250°C at 5°C/hr and then to room temperature at 50°C/hr. The excess halide flux was removed with distilled water and gold colored needles up to 3 mm in length were isolated. These crystals are stable in air and water. The presence of all four elements (Rb, Ti, P, S) was confirmed with the electron microprobe analysis.

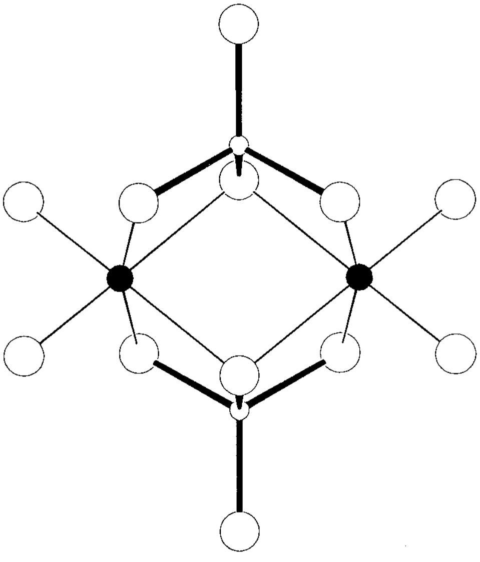

FIG. 1. Sketch of the basic repeating [$Ti_2(PS_4)S_2^{2-}$] unit in KTiPS$_5$ and RbTiPS$_5$. Filled circles are Ti atoms, small open circles are P atoms, and large open circles are S atoms.

Crystallographic studies. The crystal structures of KTiPS$_5$ and RbTiPS$_5$ were determined by single-crystal X-ray diffraction methods. Preliminary examination and data collection were performed with Mo$K\alpha_1$ radiation (λ = 0.7093 Å) on an MXC^3 diffractometer (Mac Science).

For KTiPS$_5$, the observed Laue symmetry and the systematic extinction (hkl: $h + k = 2n + 1$) were indicative of the monoclinic space groups $C^3_{2h} - C2/m$, $C^3_2 - C2$, and $C^3_s - Cm$. The centrosymmetric $C2/m$ was assumed and the satisfactory refinement confirmed the choice of this space group. The unit cell parameters and the orientation matrix for data collection were obtained from the least-squares refinement, using the setting angles of 24 reflections in the range $18° < 2\theta$ (Mo$K\alpha$) $< 26°$. The monoclinic cell parameters and calculated volume are a = 17.678(8), b = 7.080(4), c = 6.325(3) Å, β = 97.99(4)°, V = 783.9(7) Å^3. Additional crystallographic details are described in Table 1. Intensity data were collected with the $\omega - 2\theta$ scan technique. The intensities of two standard reflections,

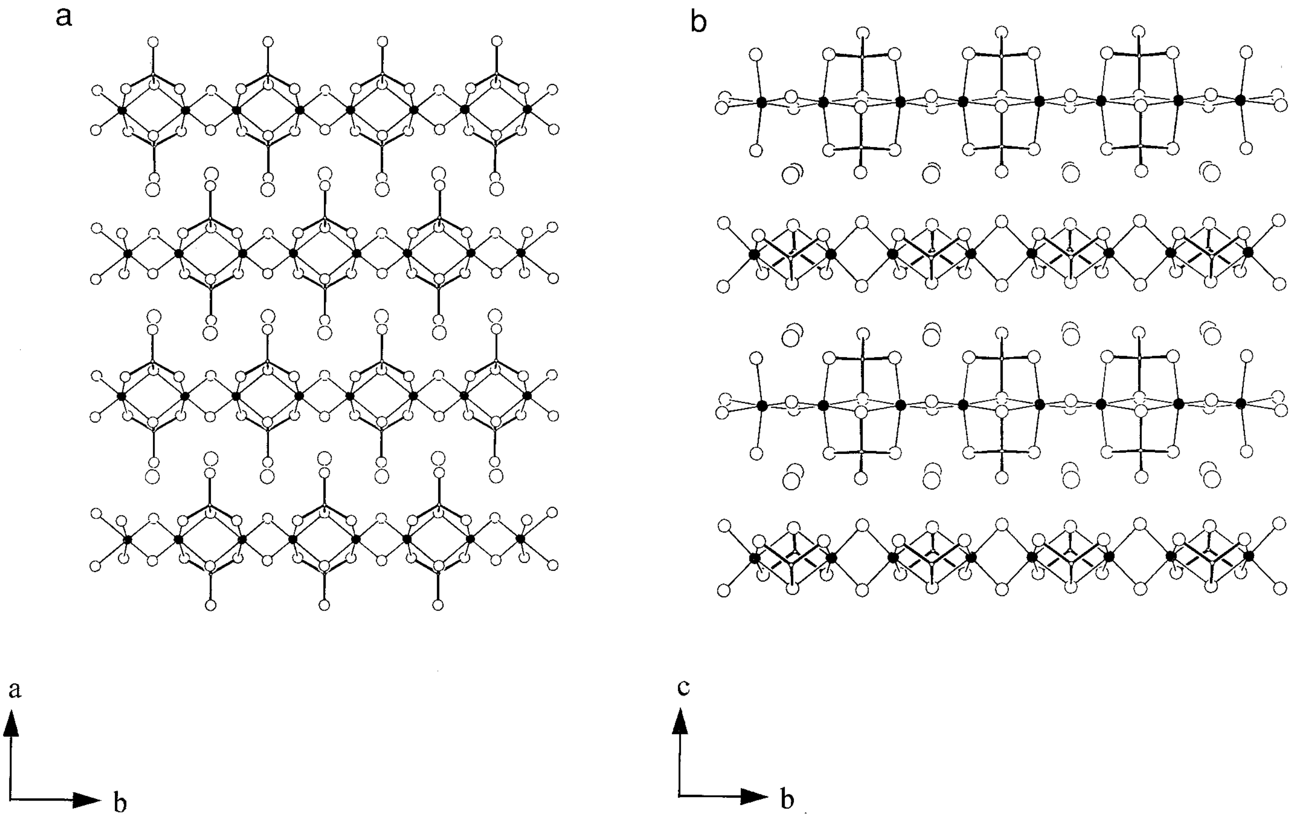

FIG. 2. View of the $^{1}_{\infty}[\mathrm{TiPS}_5^-]$ chains and alkali metals in (a) $\mathrm{KTiPS_5}$ and (b) $\mathrm{RbTiPS_5}$. The large open circles are the alkali metals; the medium open circles are the S atoms; the small open circles are the P atoms; the filled circles are the Ti atoms.

measured every hundred reflections, showed no significant deviations during the data collection. The scan rate was 5.0°/min. (in ω axis) and the variable scan repetitions allowed one time data collection for intense reflections and assured good counting statistics for weak reflections where two or three times data collections were made.

For $\mathrm{RbTiPS_5}$, the observed Laue symmetry and the systematic extinction (hkl: $h + k = 2n + 1$) were also indicative of the monoclinic space groups $C^3_{2h} - C2/m$, $C^3_2 - C2$, and $C^3_s - Cm$. The centrosymmetric $C2/m$ was assumed and the satisfactory refinement confirmed the choice of this space group. The unit cell parameters and the orientation matrix for data collection were obtained from the least-squares refinement, using the setting angles of 24 reflections in the range $20° < 2\theta\ (\mathrm{Mo}K\alpha) < 28°$. The monoclinic cell parameters and calculated volume are $a = 18.159(7)$, $b = 7.081(3)$, $c = 15.352(6)$ Å, $\beta = 124.07(2)°$, $V = 1635.1(1)$ Å^3. Intensity data were collected with the $\omega - 2\theta$ scan technique. The intensity of two standard reflections, measured every hundred reflections, showed no significant deviations during the data collection. The scan rate was 4.0°/min. (in ω axis) and the variable scan repetitions allowed one time data collection for intense reflections and assured good counting statistics for weak reflections where two or three times data collections were made. With the composition established the data for $\mathrm{RbTiPS_5}$ were corrected for absorption with the use of the analytical method of Tompa and de Meulenaer (15).

The initial positions for all atoms were obtained using direct methods of the SHELXS-86 program (16). The structure was refined by full matrix least squares techniques with the use of the SHELXL-93 program (17). For $\mathrm{KTiPS_5}$, the final cycle of refinement performed on F_o^2 with 702 unique reflections afforded residuals $wR2 = 0.1487$ and the conventional R index based on the reflections having $F_o^2 > 2\sigma(F_o^2)$ is 0.0549. A difference Fourier synthesis calculated with phase based on the final parameters shows no peaks of heights greater than 7.6% that of a S atom. For $\mathrm{RbTiPS_5}$, the final cycle of refinement performed on F_o^2 with 1464 unique reflections afforded residuals $wR2 = 0.1076$ and the conventional R index based on the reflections having $F_o^2 > 2\sigma(F_o^2)$ is 0.0413. A difference Fourier synthesis calculated with phase based on the final parameters shows no peak heights greater than 7.9% that of a S atom. In both phases, no unusual trends were found in the goodness of fit as a function of F_o, $\sin\theta/\lambda$, and Miller indices. Final values of the atomic parameters and equivalent isotropic displacement parameters are given in Table

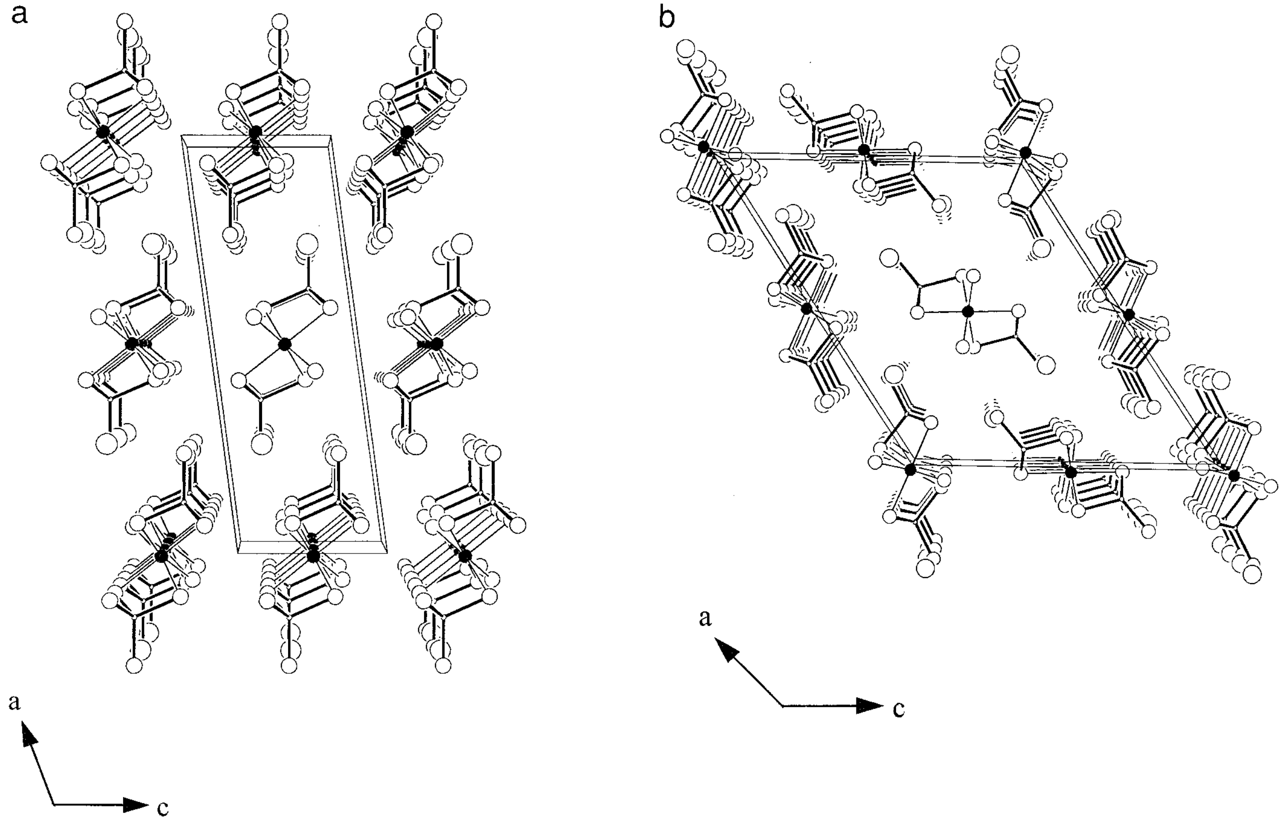

FIG. 3. View of the (a) $KTiPS_5$ and (b) $RbTiPS_5$ down the *b* axis showing the unit cell outline. Atoms are as marked in Fig. 2.

2. Anisotropic thermal parameters and structure amplitudes are given in Table 3 and Table 4,[2] respectively.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Selected bond distances and angles for $KTiPS_5$ and $RbTiPS_5$ are listed in Table 5. The structures of both compounds are made up of one-dimensional $^{1}_{\infty}[TiPS_5^-]$ chains. These chains are isolated by alkali metal cations. The coordination about Ti and P atoms in both structures are slightly distorted from ideal geometries (Table 5). Ti–S and P–S distances are in good agreement with those calculated from crystal radii typical for these atoms in titanium thiophosphate structures (6, 7).

There is only one crystallographically distinct Ti atom in $KTiPS_5$. The Ti atom is octahedrally coordinated by six S atoms. The TiS_6 groups have crystallographically imposed two-fold symmetry but show approximate octahedral $m\bar{3}m$ molecular symmetry. Two TiS_6 units combine together by sharing edges and Ti atoms are bridged by two PS_4 tetrahedra to form the basic repeating unit, $[Ti_2(PS_4)_2S_2^{2-}]$ (Fig. 1). These repeating units are linked together by sharing two μ-S atoms to form the one-dimensional $^{1}_{\infty}[TiPS_5^-]$ chain. Along the chain, Ti $\cdots$ Ti interactions alternate in the sequence of one short (3.151(4) Å) and one long (3.929(4) Å) distances (Fig. 2a). There is no intermetallic bonding interaction between the Ti atoms. These chains are extended along the [010] direction. The K^+ cations that separate these chains exhibit coordination number eight. K $\cdots$ S distances range from 3.180(4) to 3.685(4) Å (Fig. 3a). The charge balance can be described by $[K^+][Ti^{4+}][PS_4^{3-}][S^{2-}]$.

Although two crystallographically distinct Ti atoms are found in $RbTiPS_5$, the second Ti atom can be generated by translation of $(\mathbf{b} + \mathbf{c})/2$ from the first Ti atom. Therefore the arrangement of Ti atoms in $RbTiPS_5$ is exactly same as that of $KTiPS_5$. The $^{1}_{\infty}[TiPS_5^-]$ chain is still retained and identical *b* spacings (7.080(4) Å for $KTiPS_5$; 7.081(3) Å for $RbTiPS_5$) indicate the resemblance of the basic re-

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[2] See NAPS document No. 05313 for 9 pages of supplementary material (including Table 4). Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 up to 20 pages plus \$.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling, for the first 20 pages, and \$1.00 for additional 10 pages of material, \$1.50 for postage of any microfiche orders.

peating unit [$Ti_2(PS_4)_2S_2^{2-}$] in both compounds. The most significant structural deviation of $RbTiPS_5$ from $KTiPS_5$ is in the orientation of the thiophosphate ligands in the chains (Fig. 2b, Fig. 3b). The unit cell contains two crystallographically independent chains with different orientations. Consequently, the unit cell expands twice in the *a*–*c* plane. This modification is probably due to the size effect of the larger Rb^+ ions (18). The ionic radius ratio of Rb^+/S^{2-} is 0.88, which is much larger than $K^+/S^{2-} = 0.82$. After the completion of these determinations we discovered the report on the structure of isostructural $KTiPSe_5$ and $RbTiPSe_5$ prepared from molten alkali metal polyselenophosphate fluxes (19). Our results clearly show that $KTiPS_5$ is isostructural with them but $RbTiPS_5$ is not. This is not surprising because the ionic radius ratios in Se compounds ($K^+/Se^{2-} = 0.76$; $Rb^+/Se^{2-} = 0.81$) are comparable with that of $KTiPS_5$. One of the Rb atoms (Rb(1)) is surrounded by eight S atoms (3.360(3)–3.547(1) Å) and the other Rb atom (Rb(2)) is coordinated by nine S atoms (3.363(3)–3.620(2) Å). Again the classical charge balance of the compound can be represented by [Rb^+][Ti^{4+}][PS_4^{3-}][S^{2-}]. This assignment is consistent with the fact that $RbTiPS_5$ is an insulator at room temperature along the needle axis (20).

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