

The first rubidium rare-earth(III) thiophosphates: $\text{Rb}_3M_3[\text{PS}_4]_4$ ($M = \text{Pr}, \text{Er}$)

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In memoriam of William T. Carnall

Abstract

The two *non*-isotypical rubidium rare-earth(III) thiophosphates $\text{Rb}_3M_3[\text{PS}_4]_4$ of praseodymium and erbium can easily be obtained by the stoichiometric reaction of the respective rare-earth metal, red phosphorus and sulfur with an excess of rubidium bromide (RbBr) as flux and rubidium source at 950°C for 14 days in evacuated silica tubes. The pale green platelet-shaped single crystals of $\text{Rb}_3\text{Pr}_3[\text{PS}_4]_4$ as well as the pink rods of $\text{Rb}_3\text{Er}_3[\text{PS}_4]_4$ are moisture sensitive. $\text{Rb}_3\text{Pr}_3[\text{PS}_4]_4$ crystallizes triclinically in the space group $P\bar{1}$ ($a = 926.79(5)$ pm, $b = 1050.83(5)$ pm, $c = 1453.28(7)$ pm, $\alpha = 84.329(4)^\circ$, $\beta = 88.008(4)^\circ$, $\gamma = 80.704(4)^\circ$; $Z = 2$), $\text{Rb}_3\text{Er}_3[\text{PS}_4]_4$ monoclinically in the space group $P2_1/n$ ($a = 915.97(5)$ pm, $b = 1575.86(7)$ pm, $c = 1843.32(9)$ pm, $\beta = 95.601(6)^\circ$; $Z = 4$). In both structures, there are three crystallographically different rare-earth cations present. $(M1)^{3+}$ is eightfold coordinated in the shape of a square antiprism, $(M2)^{3+}$ and $(M3)^{3+}$ are both surrounded by eight sulfur atoms as bicapped trigonal prisms each with a coordination number of eight as well as for the praseodymium, but better described as $\text{CN} = 7 + 1$ in the case of the erbium compound. These $[\text{MS}_8]^{13-}$ polyhedra form a layer according to $\infty\{[M_3[\text{PS}_4]_4]^{3-}\}$ by sharing edges with the isolated $[\text{PS}_4]^{3-}$ tetrahedra ($d(\text{P}-\text{S}) = 200\text{--}209$ pm, $\sphericalangle(\text{S}-\text{P}-\text{S}) = 102\text{--}116^\circ$). These layers are stacked with a repetition period of three in the case of the praseodymium compound, but of only two for the erbium analog. The rubidium cation $(\text{Rb}1)^+$ is located in cavities of these layers and tenfold coordinated in the shape of a tetracapped trigonal antiprism. The also tenfold but more irregularly coordinated rubidium cations $(\text{Rb}2)^+$ and $(\text{Rb}3)^+$ reside between the layers.

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1. Introduction

Since the simple ternary rare-earth *ortho*-thiophosphates $M[\text{PS}_4]$ ($M = \text{La-Nd}, \text{Sm}, \text{Gd-Lu}, \text{Y}, \text{Sc}$) [1–3] have been known for a long time, recent interests focus on their derivatives with the alkali metals ($A = \text{Li-Cs}$). To date, many new compounds have been found to exist not only with *ortho*-thiophosphate anions $[\text{PS}_4]^{3-}$, but also with ethane-like $[\text{P}_2\text{S}_6]^{4-}$ units (e.g., $\text{KLa}[\text{P}_2\text{S}_6]$ [4]) or even both (e.g., $\text{K}_4M_2[\text{PS}_4]_2[\text{P}_2\text{S}_6]$; $M = \text{La}$ [4], Nd [5]), as well as pyroanionic $[\text{P}_2\text{S}_7]^{4-}$ anions emerging in

$\text{KSm}[\text{P}_2\text{S}_7]$ [6]. What is remarkable about the *ortho*-thiophosphates containing alkali metals is that they are mostly derivatives of potassium so far. Only few are known with sodium, e.g., $\text{NaM}[\text{P}_2\text{S}_6]$ ($M = \text{Sm}, \text{Yb}$ [6]) or cesium, e.g., $\text{Cs}_3\text{Pr}_5[\text{PS}_4]_6$ [7] and $\text{Cs}_4\text{Pr}_2[\text{PS}_4]_2[\text{P}_2\text{S}_6]$ [8]. The aim of this work was to determine if rubidium-containing rare-earth(III) thiophosphates follow the concept of known compounds by building up isotypical structures with the potassium or cesium analogs or if they form new motifs. With the title compounds $\text{Rb}_3\text{Pr}_3[\text{PS}_4]_4$ (triclinic) and $\text{Rb}_3\text{Er}_3[\text{PS}_4]_4$ (monoclinic) the first synthesis of rubidium-containing rare-earth thiophosphates took place. The crystal structures of these new *ortho*-thiophosphates follow known patterns

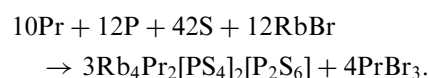
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in building up layers containing the rare-earth cations as well as discrete thiophosphate units and therefore constitute a new stoichiometry: $A_3M_3[PS_4]_4$.

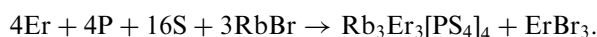
2. Experimental

The first basic approach was to synthesize $Rb_4Pr_2[P_2S_6][PS_4]_2$ in analogy to the *pseudo*-isotypical potassium [4,5] and cesium compounds [7,8] already known from the elements (praseodymium: ChemPur, 99.9%; red phosphorus: Knapsack, 99.999%; sulfur: ChemPur, 99.999%) with an excess of rubidium bromide (RbBr: ChemPur, 99.9%) as flux and rubidium source according to



The intended reaction did not take place but pale green platelet-shaped single crystals of $Rb_3Pr_3[PS_4]_4$ were obtained instead. Thereafter, it was possible to synthesize the erbium compound with the same chemical formula in stoichiometric reactions of the elements too, again with an excess of rubidium bromide (RbBr) as flux

and rubidium source according to



In both cases, the reactions were carried out in torch-sealed evacuated silica ampoules at 950°C for 14 days. The green platelets of $Rb_3Pr_3[PS_4]_4$ and the pink rods of $Rb_3Er_3[PS_4]_4$ turned out to be moisture sensitive. They were both examined by single crystal X-ray diffraction on a κ -CCD diffractometer (Nonius, Delft/NL). The results of the structure determinations as well as important internuclear distances and angles can be taken from Tables 1–3 (see [9–11]).

3. Results and discussion

$Rb_3Pr_3[PS_4]_4$ crystallizes triclinically in the space group $P\bar{1}$ ($a = 926.79(5)$ pm, $b = 1050.83(5)$ pm, $c = 1453.28(7)$ pm, $\alpha = 84.329(4)^\circ$, $\beta = 88.008(4)^\circ$, $\gamma = 80.704(4)^\circ$; $Z = 2$), but $Rb_3Er_3[PS_4]_4$ monoclinically in the space group $P2_1/n$ ($a = 915.97(5)$ pm, $b = 1575.86(7)$ pm, $c = 1843.32(9)$ pm, $\beta = 95.601(6)^\circ$; $Z = 4$) (see Table 1). Both structures are closely related, being built up of isolated $[PS_4]^{3-}$ tetrahedra which are

Table 1
Crystallographic data for the thiophosphates $Rb_3M_3[PS_4]_4$ ($M = Pr, Er$) and their determination

Formula	$Rb_3Pr_3[PS_4]_4$	$Rb_3Er_3[PS_4]_4$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
Lattice constants	$a = 926.79(5)$ pm $b = 1050.83(5)$ pm $c = 1453.28(7)$ pm $\alpha = 84.329(4)^\circ$ $\beta = 88.008(4)^\circ$ $\gamma = 80.704(4)^\circ$	$a = 915.97(5)$ pm $b = 1575.86(7)$ pm $c = 1843.32(9)$ pm $\alpha = 90^\circ$ $\beta = 95.601(6)^\circ$ $\gamma = 90^\circ$
Calculated density (D_x , g cm $^{-3}$)	3.145	3.499
Molar volume (V_m , cm 3 mol $^{-1}$)	418.44 ($Z = 2$)	398.67 ($Z = 4$)
$F(000)$	1208	2524
Diffractometer/wavelength	κ - CCD (Nonius)/MoK α : $\lambda = 71.07$ pm	
Index range	$\pm h = 12$, $\pm k = 13$, $\pm l = 18$	$\pm h = 11$, $\pm k = 20$, $\pm l = 23$
θ range	$1.0^\circ \leq \theta \leq 27.5^\circ$	$1.0^\circ \leq \theta \leq 27.5^\circ$
Absorption coefficient (μ , mm $^{-1}$)	11.82	16.40
Data corrections	Background, polarization and Lorentz factors; numerical absorption correction: program X-SHAPE [9]	
Collected reflections/unique ones	49181/6362	46498/6083
R_{int}/R_σ	0.096/0.055	0.098/0.076
Structure solution and refinement	Program package SHELX-93 and -97 [10]	
Scattering factors	International Tables, Vol. C [11]	
R_1 with $ F_o \geq 4\sigma(F_o)$	0.057 for 4712 reflections	0.064 for 4467 reflections
R_1/wR_2 /goodness of fit (GooF) (for all reflections)	0.086/0.141/1.017	0.094/0.148/1.070
Extinction (g)	0.00002(19)	0.00043(7)
Residual electron density ($\rho/e^- \times 10^{-6}$ pm $^{-3}$)	5.98 (max.) -5.17 (min.)	4.10 (max.) -3.52 (min.)

Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum (FIZ) Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: +49(0)7247/808-666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-414012 for $Rb_3Pr_3[PS_4]_4$ and CSD-414011 for $Rb_3Er_3[PS_4]_4$.

Table 2

Atomic coordinates and equivalent isotropic thermal displacement parameters (U_{eq}/pm^2)^a [23] for $\text{Rb}_3\text{Pr}_3[\text{PS}_4]_4$ and $\text{Rb}_3\text{Er}_3[\text{PS}_4]_4$

Atom	Wyckoff position	x/a	y/b	z/c	U_{eq}
Rb1	2i	0.26518(13)	0.57619(11)	0.35275(9)	412(3)
Rb2	2i	0.61227(16)	0.19857(15)	0.25314(9)	606(4)
Rb3	2i	0.20788(15)	0.07998(13)	0.07889(9)	521(4)
Pr1	2i	0.24465(6)	0.27957(5)	0.73572(3)	204(2)
Pr2	2i	0.23373(6)	0.01479(5)	0.47499(3)	201(2)
Pr3	2i	0.25317(6)	0.53127(5)	0.00273(3)	202(2)
P1	2i	0.4492(3)	0.2504(3)	0.5130(2)	217(5)
P2	2i	0.9923(3)	0.4316(3)	0.1820(2)	217(5)
P3	2i	0.0055(3)	0.9352(3)	0.3164(2)	205(5)
P4	2i	0.4697(3)	0.7204(3)	0.0969(2)	218(5)
S1	2i	0.3753(3)	0.4074(3)	0.5799(2)	306(6)
S2	2i	0.6568(3)	0.2506(3)	0.4677(2)	323(6)
S3	2i	0.3206(3)	0.2487(3)	0.4017(2)	279(6)
S4	2i	0.4418(3)	0.0861(3)	0.6039(2)	235(5)
S5	2i	0.9246(3)	0.4683(3)	0.3107(2)	306(6)
S6	2i	0.2116(3)	0.3731(3)	0.1715(2)	286(6)
S7	2i	0.8931(3)	0.2916(3)	0.1348(2)	300(6)
S8	2i	0.0563(3)	0.3973(3)	0.9049(2)	213(5)
S9	2i	0.2255(3)	0.9179(3)	0.2983(2)	271(6)
S10	2i	0.1078(3)	0.0582(3)	0.8028(2)	274(6)
S11	2i	0.0535(3)	0.2129(3)	0.5947(2)	221(5)
S12	2i	0.9473(3)	0.1020(3)	0.3816(2)	228(5)
S13	2i	0.2509(3)	0.7396(3)	0.1167(2)	297(6)
S14	2i	0.4381(3)	0.1252(3)	0.8751(2)	275(6)
S15	2i	0.4234(3)	0.4405(3)	0.8270(2)	236(5)
S16	2i	0.4963(3)	0.3180(3)	0.0390(2)	243(5)
Rb1	4e	0.21357(18)	0.10592(11)	0.93259(8)	395(4)
Rb2	4e	0.09221(19)	0.03409(11)	0.27100(9)	455(4)
Rb3	4e	0.20477(19)	0.49924(12)	0.92184(9)	495(4)
Er1	4e	0.19098(6)	0.27633(4)	0.41808(3)	252(2)
Er2	4e	0.21359(6)	0.27318(4)	0.16400(3)	220(2)
Er3	4e	0.18954(6)	0.26108(4)	0.68421(3)	227(2)
P1	4e	0.4197(4)	0.3597(2)	0.5816(2)	219(7)
P2	4e	0.4848(4)	0.1213(2)	0.7684(2)	230(7)
P3	4e	0.4365(4)	0.3104(2)	0.0304(2)	214(7)
P4	4e	0.4681(4)	0.2022(2)	0.3127(2)	213(7)
S1	4e	0.3608(4)	0.4049(2)	0.4801(2)	306(8)
S2	4e	0.1341(4)	0.1150(2)	0.1115(2)	268(7)
S3	4e	0.2959(4)	0.4150(2)	0.6552(2)	251(7)
S4	4e	0.3907(4)	0.2304(2)	0.5838(2)	312(8)
S5	4e	0.0547(4)	0.4237(2)	0.3678(2)	293(8)
S6	4e	0.2689(4)	0.1006(2)	0.7391(2)	259(7)
S7	4e	0.0998(4)	0.4282(2)	0.1887(2)	275(7)
S8	4e	0.0166(4)	0.2481(2)	0.2720(2)	266(7)
S9	4e	0.2151(4)	0.3119(2)	0.0173(2)	261(7)
S10	4e	0.0375(4)	0.1274(2)	0.4532(2)	272(7)
S11	4e	0.0248(4)	0.3082(2)	0.5371(2)	258(7)
S12	4e	0.4820(4)	0.3611(2)	0.1331(2)	235(7)
S13	4e	0.1888(4)	0.2978(2)	0.8301(2)	278(8)
S14	4e	0.3650(4)	0.1402(2)	0.3903(2)	267(7)
S15	4e	0.3763(4)	0.3219(2)	0.3062(2)	248(7)
S16	4e	0.4269(4)	0.1509(2)	0.2107(2)	242(7)

$$^a U_{eq} = \frac{1}{3} [U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^* \cos \gamma + 2U_{13}aca^*c^* \cos \beta + 2U_{23}bcb^*c^* \cos \alpha].$$

slightly distorted ($d(\text{P}-\text{S}) = 200-209$ pm, $\angle(\text{S}-\text{P}-\text{S}) = 102-116^\circ$) due to their anisotropic environment by rare-earth as well as rubidium cations. The cationic neighborhood of the $[(\text{P}1)\text{S}_4]^{3-}$ and the $[(\text{P}2)\text{S}_4]^{3-}$

tetrahedra is almost identical (see Fig. 1) in the praseodymium and the erbium compound with the slight difference that the individual metal to sulfur distances are influenced by the rare-earth trications of

Table 3

Important internuclear distances (d , pm) and angles (\angle , deg) in $\text{Rb}_3\text{Pr}_3[\text{PS}_4]_4$ and $\text{Rb}_3\text{Er}_3[\text{PS}_4]_4$

Rb1–S3	340.3	Rb2–S2	327.0	Rb3–S9	346.0		
Rb1–S2	348.4	Rb2–S7	329.6	Rb3–S6	348.7		
Rb1–S11	350.5	Rb2–S16	338.2	Rb3–S7	349.5		
Rb1–S1	354.1	Rb2–S3	340.7	Rb3–S13	352.4		
Rb1–S9	356.2	Rb2–S10	356.3	Rb3–S14	362.8		
Rb1–S5	361.2	Rb2–S4	356.4	Rb3–S14'	366.7		
Rb1–S6	364.5	Rb2–S12	362.9	Rb3–S10	376.2		
Rb1–S13	367.8	Rb2–S15	382.1	Rb3–S16	393.7		
Rb1–S1'	368.5	Rb2–S6	402.9	Rb3–S8	406.9		
Rb1–S15	381.9	Rb2–S14	413.4	Rb3–S10'	418.6		
Pr1–S1	285.2	Pr2–S3	280.8	Pr3–S7	281.7		
Pr1–S5	288.3	Pr2–S2	286.1	Pr3–S13	287.0		
Pr1–S10	289.6	Pr2–S9	286.2	Pr3–S6	287.4		
Pr1–S14	293.5	Pr2–S12	292.9	Pr3–S16	293.2		
Pr1–S11	296.1	Pr2–S4	296.4	Pr3–S8	295.6		
Pr1–S15	297.8	Pr2–S12'	299.1	Pr3–S16'	302.8		
Pr1–S8	319.8	Pr2–S11	308.9	Pr3–S15	310.4		
Pr1–S4	323.5	Pr2–S4	323.3	Pr3–S8'	313.5		
P1–S1	201.0	P2–S5	200.6	P3–S9	202.8	P4–S13	201.9
P1–S2	201.2	P2–S6	203.1	P3–S10	204.6	P4–S14	203.2
P1–S3	204.5	P2–S7	204.0	P3–S11	205.4	P4–S15	205.6
P1–S4	207.7	P2–S8	208.8	P3–S12	206.1	P4–S16	205.8
S1–P1–S2	111.3	S5–P2–S6	113.0	S9–P3–S10	114.6	S13–P4–S14	115.4
S1–P1–S3	109.4	S5–P2–S7	111.9	S9–P3–S11	111.9	S13–P4–S15	111.8
S1–P1–S4	108.6	S5–P2–S8	108.3	S9–P3–S12	104.8	S13–P4–S16	104.7
S2–P1–S3	108.6	S6–P2–S7	107.3	S10–P3–S11	107.3	S14–P4–S15	107.6
S2–P1–S4	108.7	S6–P2–S8	106.9	S10–P3–S12	111.6	S14–P4–S16	111.7
S3–P1–S4	110.2	S7–P2–S8	109.4	S11–P3–S12	106.4	S15–P4–S16	105.2
Rb1–S3	341.3	Rb2–S2	326.2	Rb3–S6	339.9		
Rb1–S1	343.4	Rb2–S7	329.9	Rb3–S9	343.3		
Rb1–S2	344.9	Rb2–S12	335.5	Rb3–S7	348.3		
Rb1–S5	348.4	Rb2–S3	338.2	Rb3–S13	359.3		
Rb1–S11	354.9	Rb2–S8	344.3	Rb3–S10	364.2		
Rb1–S13	356.1	Rb2–S14	357.8	Rb3–S10'	372.8		
Rb1–S9	360.1	Rb2–S15	365.6	Rb3–S4	374.5		
Rb1–S1'	364.7	Rb2–S10	374.5	Rb3–S14	380.8		
Rb1–S6	365.2	Rb2–S16	383.2	Rb3–S12	383.0		
Rb1–S15	385.5	Rb2–S6	391.9	Rb3–S14'	421.5		
Er1–S1	273.6	Er2–S7	271.2	Er3–S3	268.7		
Er1–S14	275.0	Er2–S2	274.6	Er3–S13	275.1		
Er1–S5	275.4	Er2–S9	277.3	Er3–S4	277.9		
Er1–S11	283.4	Er2–S16	281.8	Er3–S6	279.4		
Er1–S10	284.3	Er2–S8	284.2	Er3–S12	280.3		
Er1–S15	288.7	Er2–S12	292.6	Er3–S16	286.0		
Er1–S8	302.7	Er2–S15	298.6	Er3–S11	306.3		
Er1–S4	348.0	Er2–S4	317.5	Er3–S8	326.6		
P1–S1	202.5	P2–S5	201.0	P3–S9	201.9	P4–S13	201.6
P1–S2	202.7	–S6	202.5	P3–S10	202.5	P4–S14	203.9
P1–S3	204.6	–S7	204.4	P3–S11	203.5	P4–S15	206.4
P1–S4	205.6	–S8	207.9	P3–S12	206.0	P4–S16	204.8
S1–P1–S2	110.2	S5–P2–S6	113.7	S9–P3–S10	115.7	S13–P4–S14	114.5
S1–P1–S3	110.4	S5–P2–S7	112.3	S9–P3–S11	114.0	S13–P4–S15	113.9
S1–P1–S4	110.1	S5–P2–S8	106.8	S9–P3–S12	102.5	S13–P4–S16	103.8
S2–P1–S3	108.7	S6–P2–S7	107.8	S10–P3–S11	106.3	S14–P4–S15	105.4
S2–P1–S4	108.3	S6–P2–S8	107.4	S10–P3–S12	113.1	S14–P4–S16	113.5
S3–P1–S4	109.2	S7–P2–S8	108.7	S11–P3–S12	104.9	S15–P4–S16	105.7

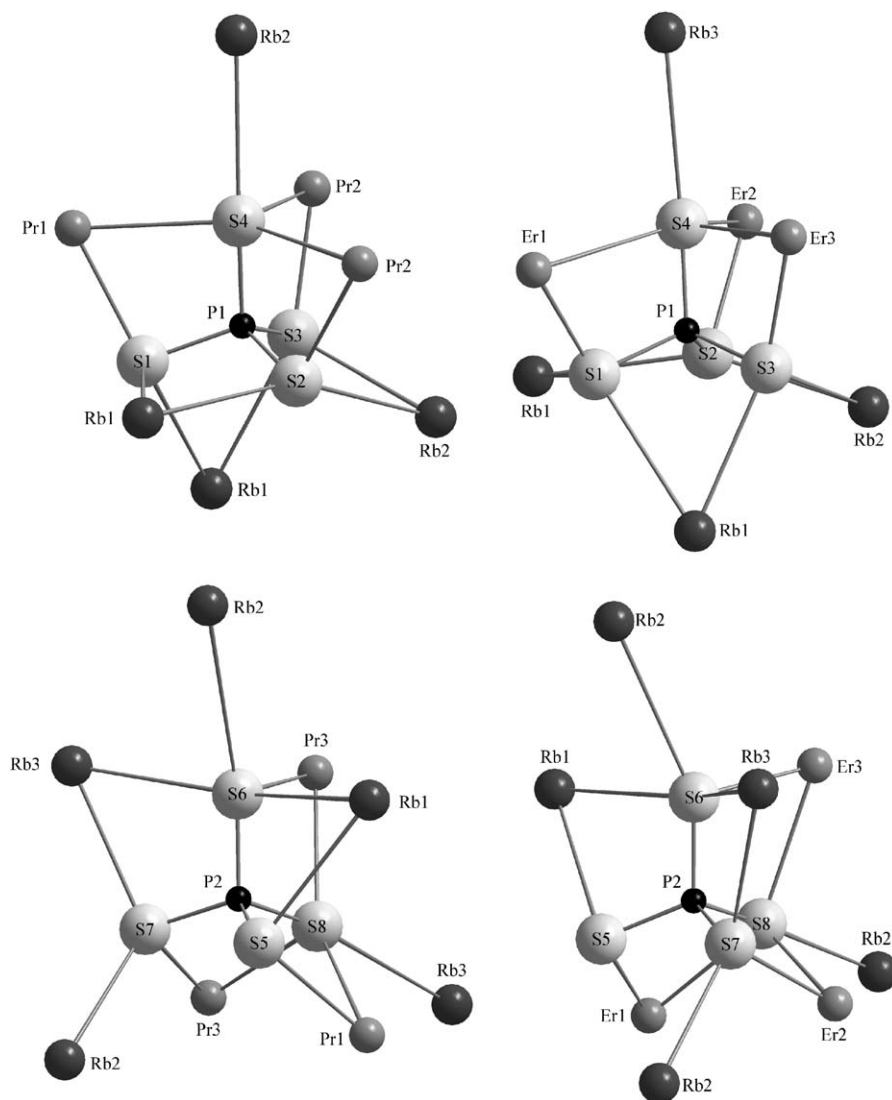


Fig. 1. Cationic surrounding of the isolated $[(P1)S_4]^{3-}$ and $[(P2)S_4]^{3-}$ tetrahedra in $Rb_3Pr_3[PS_4]_4$ (left) and $Rb_3Er_3[PS_4]_4$ (right).

course. Both share three edges with $[MS_8]^{13-}$ polyhedra about the rare-earth cations such that one sulfur atom is coordinated to all three M^{3+} cations plus a terminal rubidium atom. The other three edges of the $[PS_4]^{3-}$ tetrahedra are capped by three Rb^+ cations although in the $[(P2)S_4]^{3-}$ unit one of these rubidium atoms has a very large distance of about 450 pm to one of the sulfur atoms and can therefore not be termed as edge-sharing with the corresponding $[RbS_{10}]^{19-}$ polyhedron. The phosphorus-centered tetrahedra $[(P3)S_4]^{3-}$ and $[(P4)S_4]^{3-}$ are slightly different (Fig. 2), however. Even though both are coordinated by three rubidium and three rare-earth cations by sharing all edges with each cation polyhedron such that every sulfur atom has no more than two contacts to a rare-earth cation, the additional terminal rubidium cations behave differently. With the praseodymium compound, the $[(P3)S_4]^{3-}$

tetrahedra have one and the $[(P4)S_4]^{3-}$ tetrahedra even three terminal Rb^+ cations as compared to two for each $[PS_4]^{3-}$ tetrahedron about phosphorus P3 and P4 in the erbium compound. This phenomenon is caused by the different stacking of the $\infty\{[M_3[PS_4]_4]^{3-}\}$ layers bringing the $[PS_4]^{3-}$ tetrahedra to a different arrangement relative to one another as discussed later. These layers (Fig. 3) contain the afore-described $[PS_4]^{3-}$ tetrahedra and the three crystallographically different rare-earth cations (Fig. 4). The $(M1)^{3+}$ cation is surrounded by eight sulfur atoms, all part of edge-on coordinating $[PS_4]^{3-}$ tetrahedra, in the shape of a square antiprism as analogously found in $Cs_4Pr_2[PS_4]_2[P_2S_6]$ ($d(Pr-S) = 289-330$ pm) [8] or $NaEr_3S_3[SiS_4]$ ($d(Er-S) = 270-320$ pm) [12]. Both the $(M2)^{3+}$ and the $(M3)^{3+}$ cations are also eightfold coordinated by sulfur atoms as four edges of four attached different

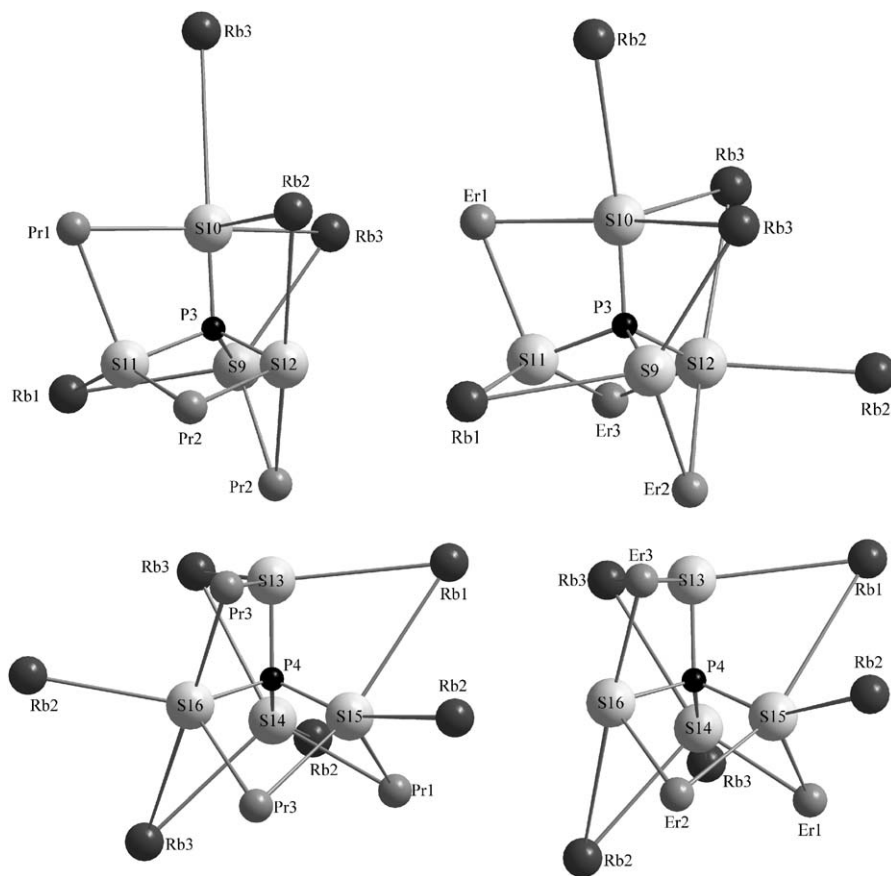


Fig. 2. Cationic surrounding of the isolated $[(P3)S_4]^{3-}$ and $[(P4)S_4]^{3-}$ tetrahedra in $Rb_3Pr_3[PS_4]_4$ (left) and $Rb_3Er_3[PS_4]_4$ (right).

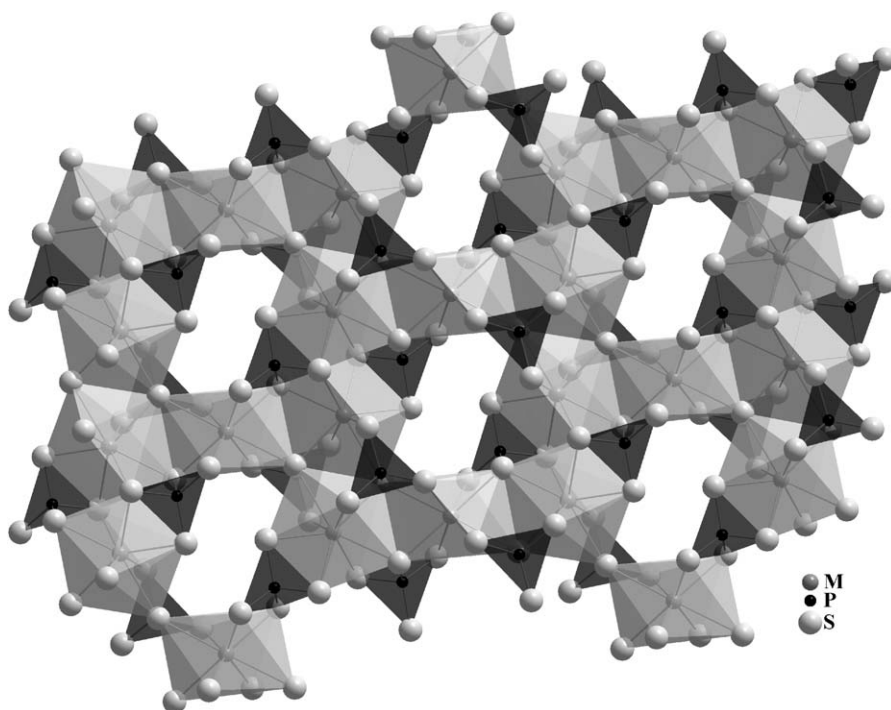


Fig. 3. Arrangement within the $2_{\infty} \{[M_3[PS_4]_4]^{3-}\}$ layers in $Rb_3M_3[PS_4]_4$ ($M=Pr, Er$).

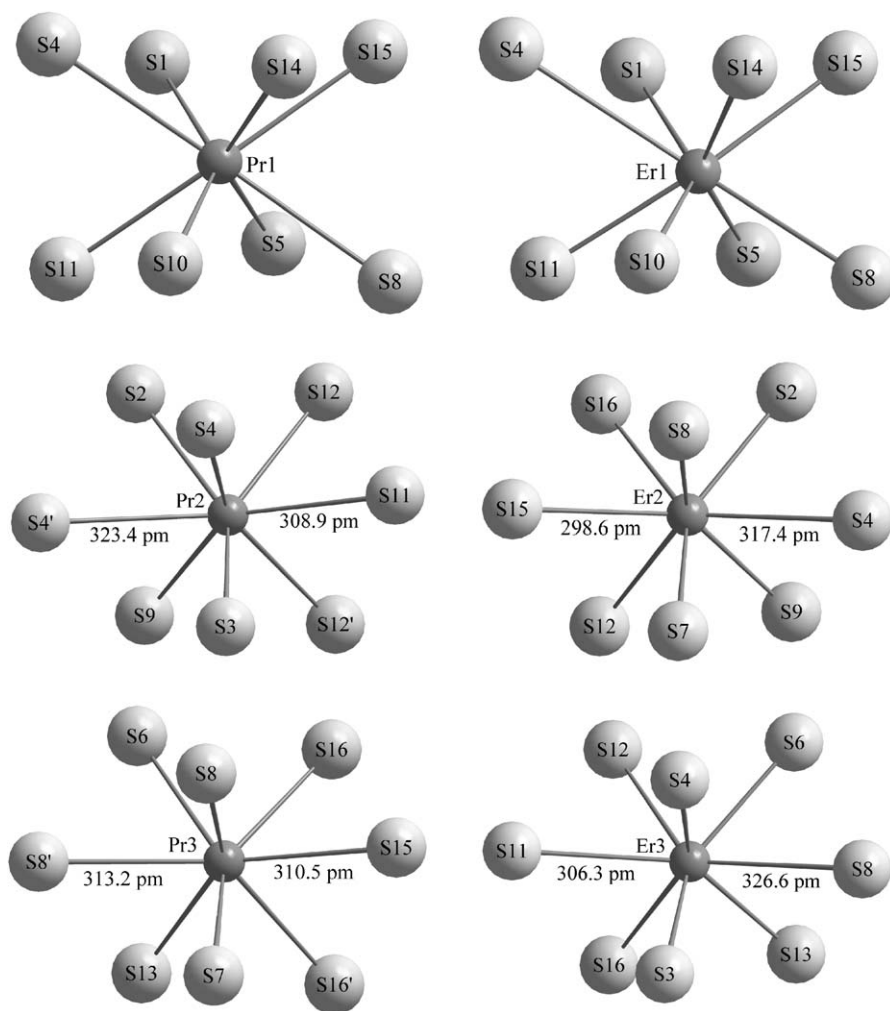


Fig. 4. Coordination environment about the rare-earth cations in $\text{Rb}_3\text{Pr}_3[\text{PS}_4]_4$ (left) and $\text{Rb}_3\text{Er}_3[\text{PS}_4]_4$ (right).

$[\text{PS}_4]^{3-}$ tetrahedra build up bicapped trigonal prisms. This is a well-known arrangement for rare-earth cations in sulfides as in the A-type $M_2\text{S}_3$ binaries [13,14] or in the oxygen-poor oxysulfides $M_{10}\text{OS}_{14}$ [15,16]; likewise the phenomena caused by the lanthanide contraction decrease the coordination number from 8 to $7+l$ with shrinking cationic radius just like in the U-type $M_2\text{S}_3$ binaries [17,18]. The same effect can be observed in the title compounds by shifting from praseodymium to erbium. A closer look at the distances within these polyhedra reveals values of 281–323 pm for $d(\text{Pr}^{3+}-\text{S}^{2-})$ and of 269–306 pm for $d(\text{Er}^{3+}-\text{S}^{2-})$ plus 317 pm for $d(\text{Er}2-\text{S}4)$ and 327 pm for $d(\text{Er}3-\text{S}8)$, respectively, for the distant caps of the two trigonal prisms. All these distances are in common ranges as compared, e.g., to the *pseudo*-binary $M[\text{PS}_4]$ -type *ortho*-thiophosphates ($d(\text{Pr}-\text{S}) = 289\text{--}305$ pm; $d(\text{Er}-\text{S}) = 287\text{--}289$ pm) [1–2,19] or C-type Pr_2S_3 ($d(\text{Pr}-\text{S}) = 287\text{--}307$ pm) [20] and D-type Er_2S_3 ($d(\text{Er}-\text{S}) = 261\text{--}294$ pm) [21], respectively. All rare-earth cations are surrounded ap-

proximately tetrahedrally by four $[\text{PS}_4]^{3-}$ units building up a layer of the composition ${}^2_{\infty}\{[M_3[\text{PS}_4]_4]^{3-}\}$ (Fig. 3), which offers empty sites where the rubidium cations ($\text{Rb}1$)⁺ are located. These ($\text{Rb}1$)⁺ cations reside in tenfold coordination (Fig. 5) in the shape of a tetracapped trigonal antiprism exhibiting rubidium to sulfur distances between 340 and 386 pm in both compounds, which are slightly larger than those in the RbMS_2 -type ternaries ($d(\text{Rb}-\text{S}) \approx 335$ pm, $6 \times$) [22] obviously due to the short S–S contacts (318–342 pm) as edges within the chelating complex $[\text{PS}_4]^{3-}$ anions. In both compounds the ($\text{Rb}2$)⁺ and ($\text{Rb}3$)⁺ cations are also tenfold coordinated, but in different and quite irregular shapes (Fig. 5). The rubidium–sulfur contacts are barely adequate and much like the $\text{Rb}1$ –S distances. They range from 326 up to 422 pm (see Table 3). These two Rb^+ cations are situated between the ${}^2_{\infty}\{[M_3[\text{PS}_4]_4]^{3-}\}$ layers, which explains their different and irregular surrounding. In the case of the praseodymium compound, these layers are arranged perpendi-

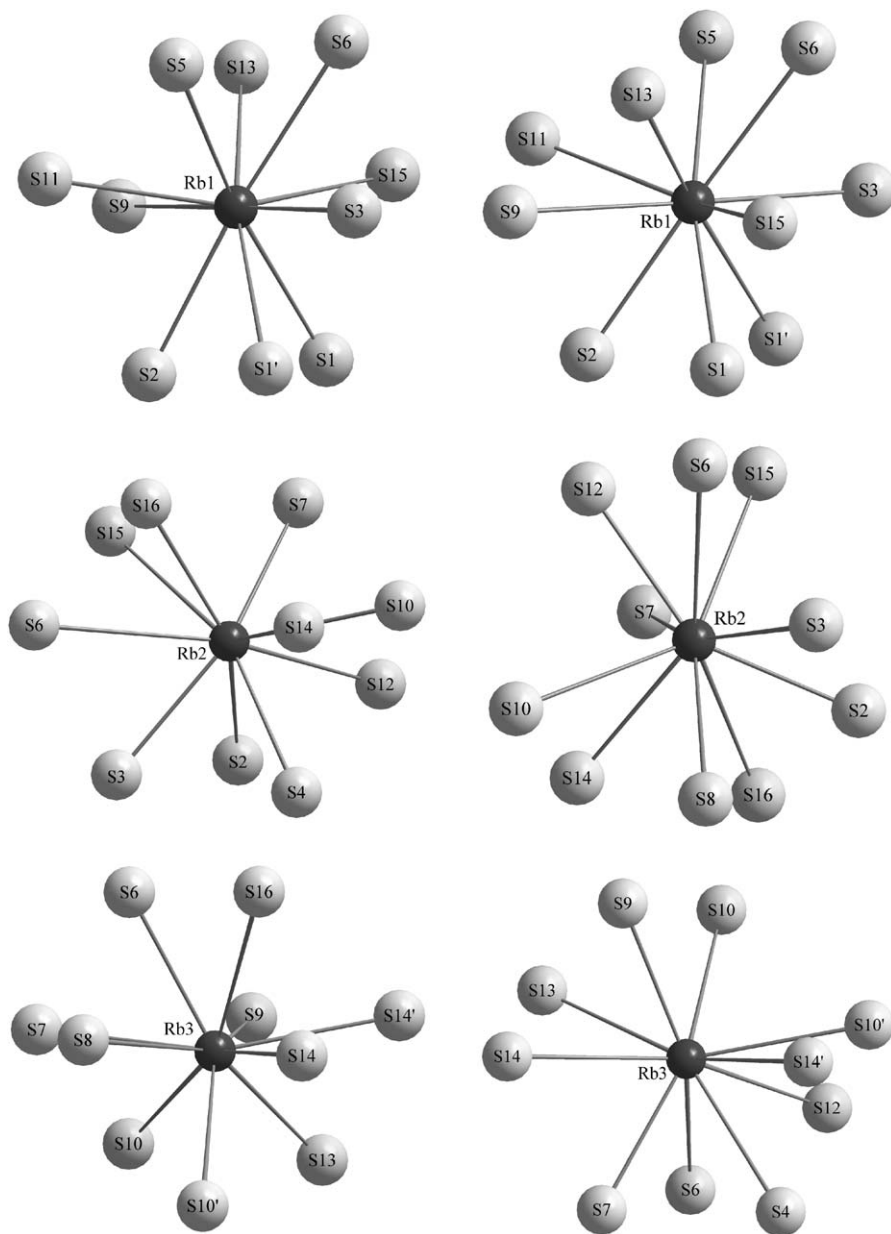


Fig. 5. Coordination environment about the rubidium cations in $\text{Rb}_3\text{Pr}_3[\text{PS}_4]_4$ (left) and $\text{Rb}_3\text{Er}_3[\text{PS}_4]_4$ (right).

cular to (100) and stacked with a repetition period of *three* (Fig. 6, above). For the erbium compound the layers are stacked parallel to (010) with a repetition period of only *two* (Fig. 6, below). Therefore, the title compounds fit well into the structure family of the *pseudo*-ternary rare-earth(III) *ortho*-thiophosphates(V) where the alkali to rare-earth metal ratio decides whether it is a layered structure or not. With its equal amounts of the two metal components (rubidium and rare-earth) they are situated on the layer-forming site of the equation, facing the compounds with lower (e.g., $\text{Cs}_3\text{Pr}_5[\text{PS}_4]_6$ [7]) or no amounts of alkali metals ($M[\text{PS}_4]$

[1–3]) at all forming three-dimensional networks with increasing cross-linkage.

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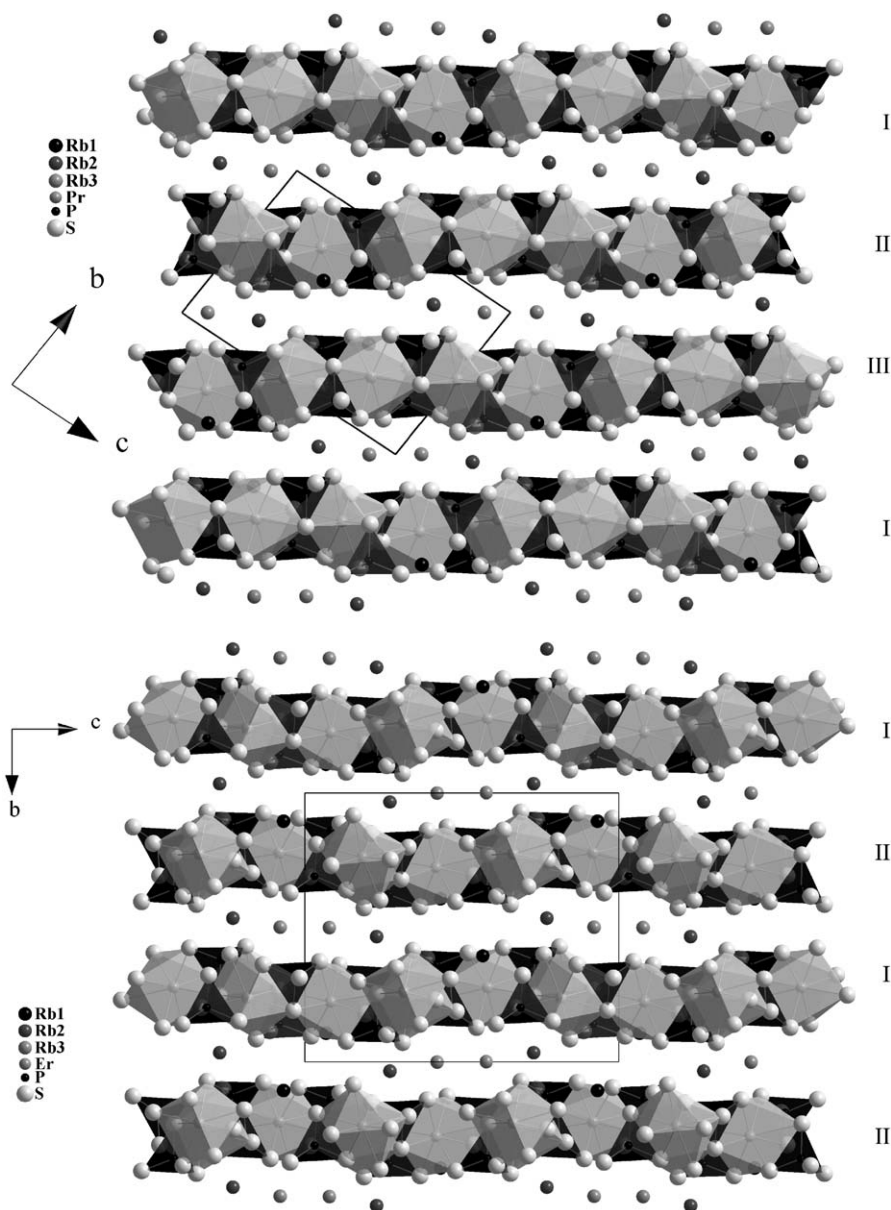


Fig. 6. Stacking of the $\infty^2\{[M_3[PS_4]_4]^{3-}\}$ layers and view at the crystal structures of $Rb_3Pr_3[PS_4]_4$ (above) and $Rb_3Er_3[PS_4]_4$ (below).

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