

Synthesis and Structure Determination of $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ and $\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$ by X-Ray Single Crystal and Neutron Powder Diffraction

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Two new compounds, $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ and $\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$, were synthesized from aqueous solutions of $\text{RbHSO}_4/\text{RbH}_2\text{PO}_4$. The compounds were characterized by X-ray single crystal analysis and neutron powder diffraction. For $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$, room temperature and a low temperature modification were found. According to X-ray crystal structure analysis, the compounds have the following crystal data: $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ ($T = 298$ K), monoclinic, space group $P2_1/n$, $a = 7.448(3)$ Å, $b = 7.552(2)$ Å, $c = 7.632(3)$ Å, $\beta = 100.47(3)^\circ$, $V = 422.1(3)$ Å³, $Z = 2$, $R_1 = 0.033$; $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ ($T = 160$ K), monoclinic, space group $P2_1/c$, $a = 11.555(3)$ Å, $b = 7.536(2)$ Å, $c = 9.593(2)$ Å, $\beta = 91.56(2)^\circ$, $V = 853.0(4)$ Å³, $Z = 4$, $R_1 = 0.041$; $\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$, orthorhombic, space group $P2_12_12_1$, $a = 7.612(6)$ Å, $b = 14.795(9)$ Å, $c = 7.446(4)$ Å, $V = 838.6(9)$ Å³, $Z = 2$, $R_1 = 0.045$. The compounds have different coordination numbers of rubidium, being 7, 8, 9, or 10 with Rb–O distances from 2.9 to 3.3 Å. In all cases there were difficulties in the allocation of sulfur and phosphorus due to the small differences in their radii and scattering factors. All structures are characterized by HSO_4^- and H_2PO_4^- , or disordered $\text{H}_x\text{S}/\text{PO}_4^-$ tetrahedra connected to zigzag chains via hydrogen bridges. These chains are linked by additional hydrogen bonds to a layer-like hydrogen bonding system. © 2000 Academic Press

INTRODUCTION

Metal hydrogen sulfates, selenates, and phosphates are potential candidates as proton conductors as well as ferroelectrics (1, 2). In the last few years, new mixed hydrogen sulfate phosphates (3) and hydrogen selenate phosphates (4) have been synthesized and structurally characterized. The physical properties mentioned above are strongly connected with phase transitions of the acidic oxosalts, which are of special interest. Recently, superprotonic phase transitions

were found for the compounds $\text{Cs}_3(\text{HSO}_4)_2(\text{H}_2\text{PO}_4)$ (5) and $\text{Cs}_3(\text{HSO}_4)_2(\text{H}_x\text{S}/\text{PO}_4)$ (6).

Systematic investigations in the system $M^+\text{HSO}_4^-/M^+\text{H}_2\text{PO}_4^-$ led to new mixed oxosalts with the general composition $M_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ and $M_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$ ($M = \text{K}, \text{Rb}$). In this article, the crystal structures of two new mixed rubidium hydrogen sulfate phosphates, $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ and $\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$, are presented. For $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$, a room temperature and a low temperature modification were found. In addition to the structure solution based on X-ray single crystal structure analysis, neutron powder diffraction experiments on powders were performed to determine the hydrogen bonding system.

EXPERIMENTAL

Synthesis

In a first step, RbHSO_4 and RbH_2PO_4 were synthesized by reaction of Rb_2CO_3 (Merck) with 96% sulfuric acid and 85% phosphoric acid, respectively (molar ratio of Rb to acid = 1). The separated and washed crystalline compounds were dissolved in warm water with varying molar ratios. Suitable crystals for single crystal structure analysis were obtained by slow crystallization at temperatures up to 80°C. Colorless plate-like crystals with the composition $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ were obtained from aqueous solutions with molar ratios $\text{RbHSO}_4:\text{RbH}_2\text{PO}_4$ of 1:2, 1:1, and 2:1. The compound $\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$ was crystallized from compositions between 2.3:1 to 3:1. For both compounds, the S to P ratios were confirmed by ion chromatography with coupled conductivity detection. For $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ and $\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$ the S:P ratios varied between 1.0 and 1.2 and 3.0 and 3.2, respectively. The purity of the phase of the compounds was verified by X-ray powder diffraction analysis. The compounds are stable in air.

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TABLE 1
Crystallographic Data

Radiation	Rb ₂ (HSO ₄)(H ₂ PO ₄) at 298 K		Rb ₂ (HSO ₄)(H ₂ PO ₄) at 160 K	Rb ₄ (HSO ₄) ₃ (H ₂ PO ₄) at 298 K	
	X-ray	Neutron	X-ray	X-ray	Neutron
F_w	364.99	364.99	364.99	735.11	735.11
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_12_12$	$P2_12_12_1$
a (Å)	7.448(3)	7.4409(2)	11.555(3)	7.612(6)	7.6152(5)
b (Å)	7.552(2)	7.5457(2)	7.536(2)	14.795(9)	14.7762(9)
c (Å)	7.632(3)	7.6205(2)	9.593(2)	7.446(4)	7.4410(4)
α (deg.)	90.00	90.00	90.00	90.00	90.00
β (deg.)	100.47(3)	100.488(1)	91.56(2)	90.00	90.00
γ (deg.)	90.00	90.00	90.00	90.00	90.00
V (Å ³)	422.1(3)	420.72(2)	853.0(4)	838.6(9)	837.3(9)
Z	2	2	4	2	2
μ (mm ⁻¹)	12.04		12.17	12.15	
ρ_{calcd} (g/cm ³)	2.872	2.881	2.903	2.911	2.900
Crystal size (mm)	0.4 × 0.3 × 0.1	powder	0.3 × 0.2 × 0.1	0.8 × 0.2 × 0.3	powder
θ_{min} (deg.)	3.5	5.0	3.9	2.7	5.0
θ_{max} (deg.)	30.0	80.0	30.3	28.0	80.0
Reflns., total	2466	827	1283	2387	914
Reflns., unique	1233		1194	2016	
Reflns., $I > 2\sigma(I)$	861		542	1020	
No. of parameters	66	79	109	112	71
wR_2^a	0.078		0.087	0.099	
R_1^a	0.033		0.041	0.045	
R_B		6.42			8.70
χ^2		3.42			5.52

^a R values are defined as $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$ and $R_1 = \sum |F_o - |F_c||/\sum |F_o|$.

X-Ray Structure Determination

Crystals suitable for X-ray structure analysis were selected under a polarization microscope. Data collections on single crystals at room temperature were performed on a four-circle diffractometer STADI-4 (Stoe). Additionally, data were collected at 160 K using an IPDS image plate diffractometer (Stoe) for Rb₂(HSO₄)(H₂PO₄). In both cases, MoK α -radiation ($\lambda = 0.7107$ Å) and a graphite monochromator were used (Table 1). Absorption corrections were performed for the room temperature measurements on the four-circle diffractometer using the psi-scan method with 7 and 8 reflections, respectively. The structures were solved by direct methods (SHELXS-86 (7)) and refined using SHELXL-93 (8). Due to similar scattering factors of sulfur and phosphorus, an exact calculation of the S to P ratio was not possible with X-ray diffraction analysis. Based on calculations using varying S:P ratios in the compounds Rb₂(HSO₄)(H₂PO₄) and Rb₄(HSO₄)₃(H₂PO₄), the structures were finally refined with S:P ratios of 1:1 and 3:1, respectively, in accord with quantitative chemical analysis. After cooling, the pattern of Rb₂(HSO₄)(H₂PO₄) shows numerous weak reflections, which indicates a superstructure. With warming up to room temperature, the low temperature modification is preserved. In both the room and

low temperature modifications of Rb₂(HSO₄)(H₂PO₄), statistically disordered sulfur and phosphorus atom positions are observed. Consequently, both types of atoms occupy the same positions in the crystal structure. This is due to their chemical similarity and the very small differences in their radii: $r_S^{+6} = 26$ pm, $r_P^{+5} = 31$ pm with CN = 4 (9). For the room temperature phase of Rb₂(HSO₄)(H₂PO₄), all hydrogen atoms were localized and refined with high standard deviations. Unfortunately, for the low temperature phase of Rb₂(HSO₄)(H₂PO₄) and for Rb₄(HSO₄)₃(H₂PO₄), the hydrogen atoms could not be localized.

Neutron Structure Determination

The neutron powder diffraction experiments were recorded at the Max von Laue-Paul Langevin institute in Grenoble (France) on a high-resolution 2-axis diffractometer (D 2B) using a germanium monochromator ($\lambda = 1.5941$ Å). The measurements of Rb₂(HSO₄)(H₂PO₄) were performed at temperatures of 5, 298, and 430 K. Rb₄(HSO₄)₃(H₂PO₄) was only measured at 298 K. The powder lines were analyzed by the Rietveld method using the program FULLPROF (10). The atomic coordinates of the heavy atoms and the S/P ratios from the former X-ray measurements were used as starting parameters for refinement. In several computing

cycles S/P positions and possible hydrogen positions were varied, refined, and compared with each other in relation to temperature factors, occupation factors, and bond distances. The final S/P ratio was smaller than 1.0 (S/P = 0.9/1.1). For $\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$, the calculations of the X-ray and neutron diffraction data with a S/P ratio of 3.0 led to the best results. In the final refinements, the occupation factors for H atoms were fixed at the values (1.0, 0.5, or 0.75) given in Table 2.

Due to higher scattering factors for hydrogen and oxygen in neutron diffraction experiments, their positions are determined with higher precision. Therefore, the neutron diffraction powder data are used to describe the O–H...O bonds of the hydrogen bonding system. The intensities of the superstructural reflections measured by the powder diffraction method were so small that an extended structural description is not possible for the low temperature modification of $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$. The neutron diffraction experiment at 430 K also did not indicate any significant change in the structure of this compound. The measurements at 5 and 430 K only revealed some changes of the lattice constants and bonding distances within the range of standard deviations. Therefore, exclusively the results of neutron diffraction experiments at room temperature will be discussed.

Due to the larger accuracy of single crystal structure data for the nonhydrogen atoms compared to powder data, Rb–O, S–O, and P–O distances from the X-ray single crystal structure experiments will be used in the following discussion.

The crystallographic data, as well as some more detailed experimental information, are summarized in Table 1. The atomic coordinates and the parameters for the equivalent isotropic temperature factors are given in Table 2. The struc-

TABLE 2
Atomic Coordinates and Equivalent Isotropic Thermal Parameters (\AA^2), X-Ray Data, and Neutron Data

Atom	x	y	z	U_{eq}
$\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ ($T = 289$ K)				
Rb	0.10886(5) <i>0.1105(5)</i>	0.31956(5) <i>0.3213(5)</i>	0.71977(5) <i>0.7215(5)</i>	0.0245(2) <i>0.0209(9)</i>
S/P	0.1009(1) <i>0.1023(8)</i>	0.1851(1) <i>0.1872(8)</i>	0.2529(1) <i>0.2549(7)</i>	0.0164(4) <i>0.013(1)</i>
O1	–0.0050(4) <i>–0.0035(6)</i>	0.3152(3) <i>0.3154(6)</i>	0.3345(4) <i>0.3370(6)</i>	0.0253(6) <i>0.024(1)</i>
O2	–0.0206(4) <i>–0.0214(6)</i>	0.0408(3) <i>0.0398(6)</i>	0.1569(4) <i>0.1575(6)</i>	0.0228(6) <i>0.019(1)</i>
O3	0.2020(4) <i>0.2052(6)</i>	0.2661(4) <i>0.2653(7)</i>	0.1180(4) <i>0.1189(6)</i>	0.0286(7) <i>0.024(1)</i>
O4	0.2398(5) <i>0.2408(8)</i>	0.0977(5) <i>0.0955(7)</i>	0.3980(5) <i>0.4021(6)</i>	0.0355(9) <i>0.031(1)</i>
H1*	0.22(2) <i>0.237(3)</i>	0.35(1) <i>0.404(3)</i>	0.11(2) <i>0.121(3)</i>	0.03(4) <i>0.049(3)</i>
H2*	0.25(1) <i>0.264(3)</i>	0.02(1) <i>–0.029(3)</i>	0.40(1) <i>0.377(3)</i>	0.02(3) <i>0.037(6)</i>
H3*	0 <i>0</i>	0 <i>0</i>	0 <i>0</i>	0.08(3) <i>0.027(5)</i>

TABLE 2—Continued

Atom	x	y	z	U_{eq}
$\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ ($T = 160$ K)				
Rb1	0.1954(1)	0.1823(2)	0.9137(2)	0.0248(3)
Rb2	–0.30458(8)	0.3179(2)	0.9139(2)	0.0108(3)
S/P1	0.4252(2)	0.1875(5)	0.1771(4)	0.0124(7)
S/P2	–0.0753(2)	0.1855(5)	0.6781(4)	0.0133(7)
O11	0.3304(7)	0.317(2)	0.164(1)	0.028(3)
O21	0.4122(5)	0.040(1)	0.069(1)	0.012(2)
O31	0.5434(5)	0.271(1)	0.156(1)	0.012(2)
O41	0.4244(7)	0.099(1)	0.322(1)	0.017(2)
O12	–0.1691(5)	0.318(1)	0.664(1)	0.009(2)
O22	–0.0898(8)	0.042(2)	0.569(1)	0.024(3)
O32	0.0449(7)	0.265(2)	0.665(2)	0.028(3)
O42	–0.0773(8)	0.103(2)	0.822(2)	0.028(3)
$\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$ ($T = 298$ K)				
Rb1	0 <i>0</i>	0 <i>0</i>	0.7789(2) <i>0.782(2)</i>	0.0272(5) <i>0.034(4)</i>
Rb2	0.1583(2) <i>0.157(1)</i>	–0.26588(8) <i>–0.2658(8)</i>	0.3650(2) <i>0.365(2)</i>	0.0320(4) <i>0.024(3)</i>
Rb3	–0.5000 <i>–0.5000</i>	0 <i>0</i>	0.0490(3) <i>0.050(3)</i>	0.0556(7) <i>0.046(5)</i>
S1	0.1528(4) <i>0.142(3)</i>	–0.2394(2) <i>–0.242(2)</i>	0.8528(4) <i>0.853(4)</i>	0.0268(7) <i>0.020(6)</i>
S2	0 <i>0</i>	–0.5 <i>–0.5</i>	0.4356(5) <i>0.422(5)</i>	0.0213(9) <i>0.017(8)</i>
P	0 <i>0</i>	0 <i>0</i>	0.2717(5) <i>0.272(3)</i>	0.0210(9) <i>0.018(4)</i>
O1	0.022(1) <i>0.016(2)</i>	–0.2033(5) <i>–0.2020(9)</i>	0.736(1) <i>0.743(2)</i>	0.033(2) <i>0.035(4)</i>
O2	0.240(1) <i>0.251(3)</i>	–0.1666(6) <i>–0.159(1)</i>	0.961(2) <i>0.954(3)</i>	0.056(3) <i>0.078(6)</i>
O3	0.079(1) <i>0.097(2)</i>	–0.3071(6) <i>–0.306(1)</i>	0.984(1) <i>0.978(2)</i>	0.046(3) <i>0.048(4)</i>
O4	0.290(1) <i>0.292(2)</i>	–0.2874(5) <i>–0.290(1)</i>	0.747(1) <i>0.740(2)</i>	0.033(2) <i>0.036(4)</i>
O5	0.362(1) <i>0.362(2)</i>	0.0399(5) <i>0.038(1)</i>	0.672(1) <i>0.676(2)</i>	0.034(2) <i>0.036(4)</i>
O6	–0.076(1) <i>–0.060(2)</i>	–0.4295(6) <i>–0.4243(9)</i>	0.557(1) <i>0.565(2)</i>	0.040(2) <i>0.037(4)</i>
O7	0.128(1) <i>0.140(2)</i>	0.0513(5) <i>0.051(1)</i>	0.153(1) <i>0.155(2)</i>	0.028(2) <i>0.045(5)</i>
O8	0.096(1) <i>0.091(2)</i>	–0.0675(5) <i>–0.0699(9)</i>	0.390(1) <i>0.389(2)</i>	0.032(2) <i>0.023(3)</i>
H1**	0.387(5)	–0.176(2)	0.993(4)	0.06(1)
H2***	0.146(6)	0.128(3)	0.205(6)	0.07(1)
H3***	0.248(3)	–0.062(2)	0.432(3)	0.035(5)

*Occupation factor 0.5.

**Occupation factor 1.0.

***Occupation factor 0.75.

tural results have been deposited at the FIZ (Karlsruhe, Germany) under CSD-numbers 410917 (room temp. phase) and 410918 (low temp. phase) for $[\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)]$ and 410919 for $[\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)]$.

RESULTS AND DISCUSSION

In the case of a statistical disorder in the crystal structure, the bond distances generally deviate from the values found

for bonds of nondisordered structures. In $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$, the S–O and P–O distances for the disordered sulfate/phosphate tetrahedra differ slightly from data given in the literature (11, 12). In the case of the $\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$, an S/P disorder was not found, although a statistical disorder of sulfur and phosphorus atoms is likely due to the small differences in the radii of both atoms.

$\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ (Room Temperature Phase)

$\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ crystallizes at room temperature in the monoclinic space group $P2_1/n$. In the structure, sulfur and phosphorus atoms are statistically disordered on one atomic position. The calculations in the noncentrosymmetric space group Pn also led to disordered atomic positions. According to quantitative analysis, the S/P atomic ratio is 0.80–1.00 (± 0.02). The rubidium atom is coordinated by nine oxygen atoms. The Rb–O distances range from 2.874 to 3.340 Å. The next oxygen atom is 3.605 Å further away from the rubidium atom and cannot be considered as belonging to the coordination sphere of Rb. These nine coordinating oxygen atoms belong to six different S/PO_4 tetrahedra. In comparison, the rubidium atoms in RbHSO_4 are coordinated by nine and ten oxygen atoms, respectively, with Rb–O distances 2.90–3.30 Å (13). In contrast, Rb is coordinated by eight oxygen atoms with bond lengths between 2.933 and 3.026 Å in RbH_2PO_4 (14). The mean S/P–O bond lengths in the tetrahedra in $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ amount to 1.505 Å. The bond lengths Rb–O and S/P–O are specified in Table 3. The distances in the hydrogen bonding system are given in Table 4. All hydrogen atom positions in the structure are half occupied. The hydrogen atom H2 has a special position. Two H-potential minima between the oxygen atoms O3 and O4 correspond to the atoms H1a and H1b. The hydrogen bond O3–H1a...H1b–O4 connect the $\text{H}_x\text{S/PO}_4$ tetrahedra to zigzag chains in the b -direction (Fig. 1a) with S/P–S/P–S/P angles of 119.2° . The O2–H2–O2' link these chains to a layer-like hydrogen bonding system parallel (1 0 $\bar{1}$) (Fig. 1b). The half donor and half acceptor functions of the oxygen atoms O2, O3, and O4 taking part in these hydrogen bridges explains their similar S/P–O bond lengths (S/P–O, 1.511–1.522 Å). In contrast, the S/P–O1 bond is shorter (1.468 Å) because O1 is not involved in a hydrogen bond. The O...O bridges with distances between 2.533 and 2.550 Å belong to the strong hydrogen bonds (15).

$\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ (Low Temperature Phase)

At a temperature below 180 K changes in the crystal structure of $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ were observed. The presence of superstructural reflections indicates a doubling of the unit cell volume (transformation matrix 1 0 $\bar{1}$, 0 1 0,

TABLE 3
Bond Distances (Å) from X-Ray Data

$\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ ($T = 298$ K)		$\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ ($T = 160$ K)		$\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$	
Rb–O1	2.874(3)	Rb1–O11	2.90(1)	Rb1–O1($\times 2$)	3.028(8)
Rb–O1a	2.909(3)	Rb1–O11a	3.00(1)	Rb1–O5($\times 2$)	2.925(9)
Rb–O1b	3.027(3)	Rb1–O21	3.072(9)	Rb1–O7($\times 2$)	3.047(9)
Rb–O2	2.991(3)	Rb1–O41	3.260(8)	Rb1–O8($\times 2$)	3.15(1)
Rb–O2a	3.073(3)	Rb1–O12	2.86(1)	Rb2–O1	2.903(9)
Rb–O3	3.019(4)	Rb1–O22	2.98(1)	Rb2–O1a	3.096(9)
Rb–O3a	3.058(3)	Rb1–O32	2.98(1)	Rb2–O3	2.97(1)
Rb–O4	3.265(4)	Rb1–O32a	3.03(1)	Rb2–O4	3.029(9)
Rb–O4a	3.340(4)	Rb1–O42	3.30(1)	Rb2–O4a	3.032(9)
		Rb2–O11	2.87(1)	Rb2–O5	2.890(8)
		Rb2–O21	2.975(8)	Rb2–O8	2.979(8)
		Rb2–O31	2.971(9)	Rb3–O2($\times 2$)	3.227(9)
		Rb2–O31a	3.07(1)	Rb3–O3($\times 2$)	2.93(1)
		Rb2–O41	3.29(1)	Rb3–O5($\times 2$)	3.06(1)
		Rb2–O12	2.899(8)	Rb3–O6($\times 2$)	3.17(1)
		Rb2–O12a	3.009(9)	Rb3–O7($\times 2$)	3.030(8)
		Rb2–O22	3.05(1)		
		Rb2–O42	3.23(1)		
S/P–O1	1.468(3)	S/P1–O11	1.47(1)	S1–O1	1.427(9)
S/P–O2	1.517(3)	S/P1–O21	1.53(1)	S1–O2	1.501(9)
S/P–O3	1.511(3)	S/P1–O31	1.521(7)	S1–O3	1.505(9)
S/P–O4	1.522(4)	S/P1–O41	1.54(1)	S1–O4	1.488(9)
		S/P2–O12	1.479(8)	S2–O5($\times 2$)	1.448(8)
		S/P2–O22	1.51(1)	S2–O6($\times 2$)	1.495(9)
		S/P2–O32	1.52(1)	P–O7($\times 2$)	1.521(7)
		S/P2–O42	1.51(1)	P–O8($\times 2$)	1.516(8)

1 0 1). In Fig. 2, the low temperature modification of $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ (space group $P2_1/c$) is shown. The comparison of the noncrystallographic equivalent pairs of S/P tetrahedra in the double volume cell has shown that

TABLE 4
Hydrogen Bonding Systems of $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ ($T = 298$ K, 160 K) and $\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$, Distances (Å) and Angles ($^\circ$) by Neutron Diffraction or X-Ray Diffraction

Bond	O...O	O–H	H...O	\angle O–H...O
$\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ ($T = 298$ K)				
O3–H1a...O4	2.533(7)	1.07(2)	1.47(2)	171(2)
O4–H1b...O3	2.533(7)	0.98(2)	1.57(2)	167(2)
O2–H2–O2'	2.550(6)	1.275(4)	1.275(4)	180.0
$\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ ($T = 160$ K)				
O31–H1...O41	2.49(1)			
O21–H2–O21'	2.52(1)			
O42–H3...O32	2.58(2)			
O22–H4–O22'	2.57(2)			
$\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$				
O2–H1...O3	2.73(3)	1.10(4)	1.63(4)	171(3)
O7...H2...O4	2.53(2)	1.20(5)	1.36(5)	162(4)
O8...H3...O6	2.69(2)	1.25(3)	1.48(3)	161(2)

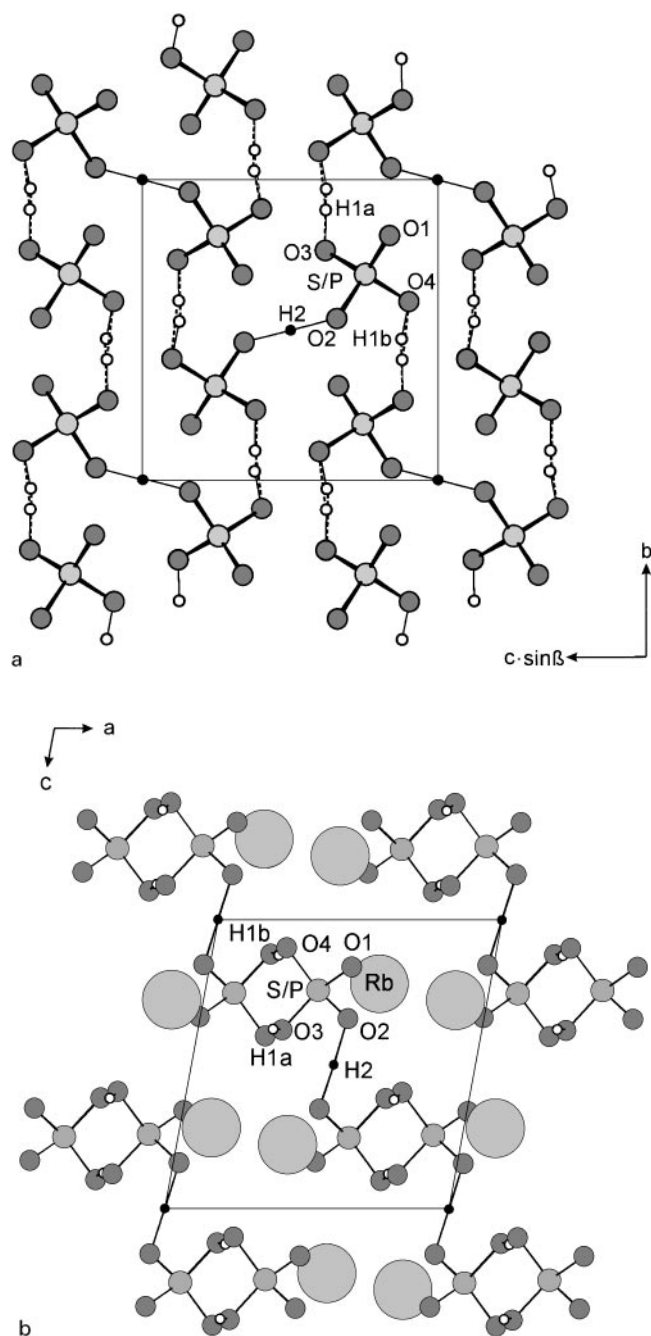


FIG. 1. Structure of $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ (room temperature phase). The half occupation for H1a and H1b is shown by open circles. (a) Layer-like hydrogen bonding system parallel $(1\ 0\ \bar{1})$ (Rb atoms are not shown). (b) Zigzag chains in the b -direction, produced by screw axis 2_1 .

there are small deviations in their positions from the calculated ones based on the matrix transformation. Such shifts of S/P tetrahedra are possibly due to a small modification in the hydrogen bonding system. However, this could not be proved using the data available. The unit cell of the room temperature phase is drawn in (broken lines). The two structures are very similar. Due to the doubling of the unit

cell two crystallographically different rubidium atoms are now present in the structure. The coordination of rubidium remains practically unchanged (distances Rb–O 2.86–3.30 Å). The position of sulfur and phosphorus is statistically disordered. For both crystallographically different S/P atom positions, the occupations by sulfur and phosphorus are equal. The S/P–O bond lengths in the S/P1 tetrahedra are situated between 1.47 and 1.54 Å. The S/P2–O distances are within the range 1.48 to 1.52 Å. The S/P1 tetrahedra are connected to zigzag chains in the b -direction via the hydrogen bonds $\text{O31} \cdots \text{O41}$ (2.49 Å), and the S/P2 tetrahedra are linked via $\text{O32} \cdots \text{O42}$ (2.58 Å). The S/P–S/P–S/P angles in both chains differ only slightly from those found in the room temperature modification (S/P1 chain 119.5° , S/P2 chain 119.7° , S/P chain 119.2°).

The hydrogen bonds $\text{O21} \cdots \text{O21}'$ (2.52 Å) connect the S/P1 chains to form layers parallel (100) . The S/P2 chains linked by $\text{O22} \cdots \text{O22}'$ (2.57 Å) bridges form layers of the same orientation shifted in the a -direction by approximately 0.5.

$\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$

$\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$ crystallizes in the noncentrosymmetric space group $P2_12_12$ (Fig. 3). In the unit cell, three crystallographically different rubidium atoms are present, as well as two crystallographically different S tetrahedra and one P tetrahedron. Rb1 is eightfold (Rb1–O: 2.925–3.157 Å), Rb2 is sevenfold (Rb2–O 2.89–3.100 Å), and Rb3 is tenfold (Rb3–O: 2.93–3.223 Å) coordinated by oxygen. S1 is surrounded by four oxygen atoms with a mean

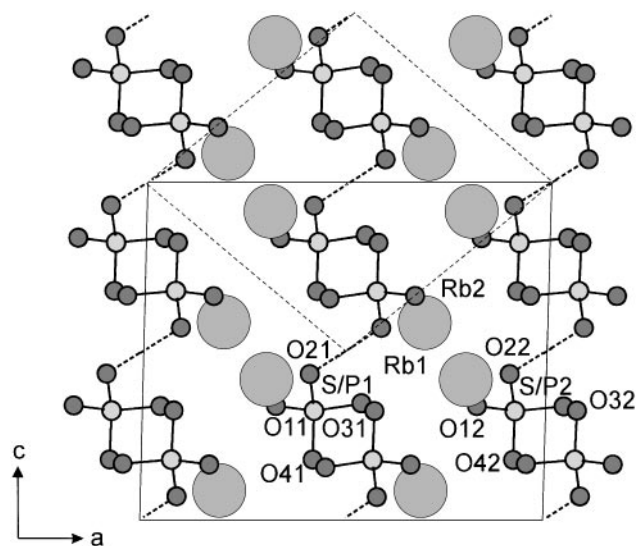


FIG. 2. Structure of $\text{Rb}(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ (low temperature phase). Projection in the b -direction; S/P chains are connected to layers parallel (100) ; the unit cell of the room temperature phase is drawn in broken lines.

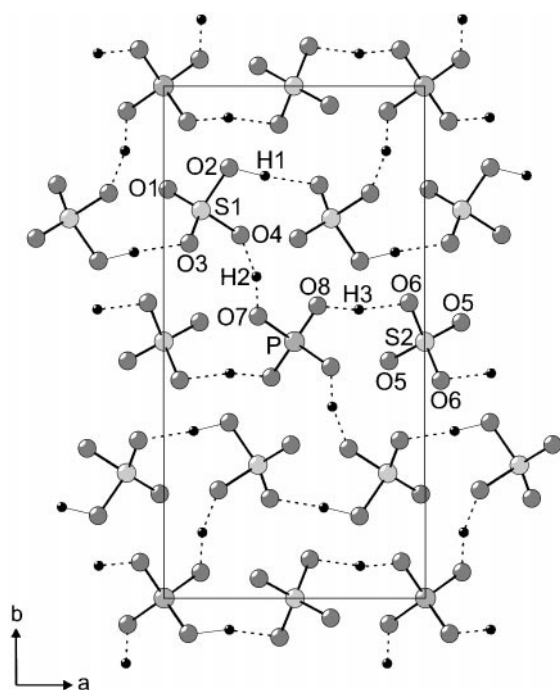


FIG. 3. Structure of $\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$. Projection in the c -direction; chains in the a -direction are linked over hydrogen bonds to wavelike layers parallel (001) (Rb atoms are not shown).

S–O distance of 1.48 Å. The bonds to the oxygen atoms O2, O3, and O4 are longer due to their additional participation in hydrogen bonds. The sulfur atom S2 is connected to O5 ($2\times$) and O6 ($2\times$) with distances of 1.448 and 1.495 Å, respectively. The phosphorus atom P is tetrahedrally surrounded by O7 (2×1.521 Å) and O8 (2×1.516 Å). The S2–O6, P–O7, and P–O8 distances are elongated due to additional donor/acceptor functions of the O atoms. An S/P disorder is not evident from a comparison of the S–O and P–O bonds. S1 and S2 with mean distances of 1.48 and 1.47 Å and phosphorus with a mean distance of 1.52 Å are in the range of typical S–O and P–O distances (mean S/P–O distance in $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)(\text{rt})$ 1.505 Å). An exact prediction of the donor and the acceptor functions of the oxygen atoms which take part in the O...O linkage is only possible in the case of the bond O2–H1...O3 (O...O distance 2.73 Å). The oxygen atom O2 in O2–H1...O3 acts as an 4-donor with a distance of 1.10 Å. In contrast, the hydrogen bonds O7...H2...O4 (O...O distance 2.53 Å) and O8...H3...O6 (O...O distance 2.69 Å) can be described as asymmetric, effectively centered H-bonds. In both cases, the hydrogen positions were found close to the bond center (O7–H2 1.20 Å, O4–H2 1.36 Å, O8–H3 1.25 Å, O6–H3 1.48 Å). The asymmetric H-bond environment is obviously due to the chemical differences between sulfur and phosphorus. Altogether 2.5 hydrogen atoms are distributed between three hydrogen bonds in the structure of $\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$. The final results of the neutron

diffraction experiments show that the hydrogen position of H1 is possibly fully occupied. This means H2 and H3 can only be occupied to 3/4. However, this assumption is in contrast to the length of the hydrogen bond O7...O4. The shorter bond suggests that H2 should be fully occupied and H1 and H3 have less than full occupancy. Unfortunately, this contradiction can not be solved on the basis of the data available.

In the crystal structure of $\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$, the hydrogen bond O2–H1...O3 links the S1 tetrahedra forming chains in the a -direction. The S2 and P tetrahedra are equally connected to chains in the a -direction by O8...H3...O6. Both types of chains are linked over O7...H2...O4 to wavelike layers parallel (0 0 1).

SUMMARY

The structure of $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)(\text{rt})$ is isotypic with $\text{K}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ (16) and $(\text{NH}_4)_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$, both known in the literature (17). In these structures, the S/P positions are also disordered and the ratio of sulfur:phosphorus is 1:1. Superstructural reflections characteristic for the low temperature modification of $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ were not found for these two structures. For an exact comparison of $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ with these compounds, they were reinvestigated by X-ray. In the structure of $\text{K}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$, superstructural reflections were even observed at room temperature. In $(\text{NH}_4)_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ when measured down to 160 K the same superstructural reflections were found. However, the data obtained for the low temperature phase did not give exact information on the type of changes occurring.

In $\text{Rb}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$, the S/P tetrahedra are connected to zigzag chains via hydrogen bonds. In $\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$ analogous chains are also formed by S and P tetrahedra. In both structures, these chains are linked by O...O bonds to a layer-like hydrogen bonding system. There are no compounds known to be isotypic with $\text{Rb}_4(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)$. The assignment of the sulfur and phosphorus positions in this structure was only possible by a comparison of the X–O distances. Two different types of tetrahedra chains are present. One chain is formed by S tetrahedra exclusively, the other one consists of both S and P tetrahedra. In contrast, only one type of chain is present in $\text{Cs}_3(\text{HSO}_4)_2(\text{H}_2\text{PO}_4)$ (3), whereby each third tetrahedron position in the chain is occupied by a P tetrahedron.

The difficulties in differentiating between the S and P atoms in the structure of compounds in the system $M'/\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ do not occur in mixed S/P compounds (4). Because of higher scattering factors, the position of selenium can be determined without doubt. Due to the larger differences in the atomic radii ($r(\text{Se}^{+6}, \text{CN } 4)$ 0.42 Å, $r(\text{P}^{+5}, \text{CN } 4)$ 0.31 Å) selenium and phosphorus tend to occupy different atomic positions.

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