New Rubidium Zinc Hydrogen Phosphate, $Rb_2Zn_2(HPO_4)_3$: Synthesis, Crystal Structure, and ^{31}P Single-Crystal NMR

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A new rubidium zinc hydrogen phosphate, $Rb_2Zn_2(HPO_4)_3$, is prepared by an unusual method utilizing long nucleation times. This material is crystallized from a gel with an initial composition of 1.0 ZnO/0.94 P_2O_5/0.96 Rb_2O/0.04 Li_2O/41 H_2O, while the phosphate concentration equals 1.6 M and pH = 3.5. The gel is placed in a sealed Pyrex flask at 52 °C, and after 4.5 months crystallization of $Rb_2Zn_2(HPO_4)_3$ is noticed. This new crystalline compound has a three-dimensional framework structure built from spiral chains of alternating PO_4 and ZnO_4 tetrahedra connected pairwise and assembled by other PO_4 tetrahedra, rubidium ions, and hydrogen bonds. The two rubidium ions, Rb(1) and Rb(2), have an exceptionally low number of oxygen contacts in the first coordination sphere, five and seven, respectively. Crystal data: monoclinic, $P2_1/c$ (no. 14), $a = 12.5880(4)$, $b = 12.7170(8)$, $c = 7.5827(8)$ Å, $\beta = 96.100(1)°$, $Z = 4$. A single-crystal ^{31}P NMR investigation of $Rb_2Zn_2(HPO_4)_3$ was performed employing a two-axis goniometer probe and reveals the presence of three chemically and six magnetically nonequivalent phosphorus sites, in accordance with the crystal structure. ^{31}P chemical shielding anisotropies and isotropic chemical shifts (−3.3(3), −2.6(3), and 2.0(3) ppm) have been determined for the three phosphorus sites.

Introduction

An extraordinarily large number of orthophosphates have been characterized in the past 2 decades, e.g., the discovery of open framework aluminum phosphates (1982),[1] beryllium phosphates (1989),[2] and zinc phosphates (1991),[3] which in many cases have interesting framework crystal structures. Transition metal substituted aluminum phosphates with open framework structures are of considerable interest for a vide variety of purposes, e.g., catalysis.[4] Poor thermal stability of these materials often limits their utilization. This has prompted investigation of fully substituted aluminum phosphate materials, i.e., $Al^{3+} \rightarrow Zn^{2+} + M^+$ where M = alkali metal, and exploration of new strategies for their synthesis in our laboratory.

Open framework materials are generally prepared under mild conditions because they are topologically metastable.[5] Synthesis at moderate temperatures is of increasing importance, and in some cases crystallization of new materials is facilitated by slow nucleation in silica gel[6] or utilization of successive conversion of materials.[7] It is well established that the nucleation time increases upon lowering the temperature of the synthesis.[8,9] In some cases the nucleation time can be several months.[10,11]

The chemistry of synthesized zinc orthophosphates shows a variety of compounds, and recent research has expanded the $ZnO-P_2O_5-H_2O$−amine family of synthetic materials considerably. The first members were discovered in 1992 and today ca. 20 have been reported.[12] Apparently, only one templated alkali metal zinc orthophosphate is known, $LiZn(HPO_4)(PO_4)\cdot enH_2\cdot H_2O$.[10] An analogue to zeolite X, reported as $Na_{67}((CH_4)_4N)_{12}Zn_8(ZnPO_4)_{96}\cdot 192H_2O$, is partly templated by hydrated sodium ions and partly by the ammonium ions.[13]

A number of new members in the system, $M_2O-ZnO-P_2O_5-H_2O$ where M = alkali metal, have been synthesized recently.[3,11,14−20] We present here the synthesis of a new

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rubidium zinc hydrogen orthophosphate, $Rb_2Zn_2(HPO_4)_3$, which has an unusually long nucleation time. A detailed structural characterization combining X-ray diffraction and NMR spectroscopic measurements on single-crystal samples reveals an exceptional coordination for the rubidium atoms.

Experimental Section

Synthesis and Initial Phase Identification. A white gel was prepared in the following way. The powdered solids $LiOH{\cdot}H_2O$ (0.158 g), RbCl (5.260 g), and $Zn(CH_3COO)_2{\cdot}2H_2O$ (10.072 g) were mixed together. H_2O (26.0 g) was added, and then 50% RbOH (9.181 g) followed by 85% H_3PO_4 (9.961 g) were added slowly under stirring. The molar composition of the thick milky gel was $1.0ZnO/0.94P_2O_5/0.96Rb_2O/0.04Li_2O/41H_2O$. The concentration of phosphate was ca. 1.6 M, and the pH of the gel was 3.5. This batch was divided into three portions denoted A, B, and C.

A portion of the gel, A, was heated in a Teflon lined steel autoclave at 120 °C for 6 days, giving a needle-shaped crystalline product of $RbZn_2(HPO_4)(PO_4)$.[20] The clear solution (A) in equilibrium with the crystalline material was decanted and placed in a beaker, allowing evaporation of the solvent at room temperature. After 12 days a crystalline material was isolated and identified as a recently described new material, $RbZn(H_2PO_4)(HPO_4){\cdot}H_2O$.[19] This procedure was repeated by again removing the solution from the crystalline material and allowing evaporation of the liquid, leaving crystals of RbH_2PO_4 and a mixture of RbH_2PO_4, RbCl, and possibly Rb_2ZnCl_4.[21,22]

Another portion, B, was placed in a sealed Pyrex flask at 52 °C for 4.5 months when transparent crystals were noticed, and after 6 months three crystals with dimensions up to 7 mm and a total mass of 0.252 g were separated from the gel. Fragments of a crystal were used for structural investigation, combining information from single-crystal X-ray diffraction and ^{31}P NMR, and a new material with composition $Rb_2Zn_2(HPO_4)_3$ was identified as discussed in the following. The remaining gel B was placed at 21 °C for 14 days in a sealed flask, and then another rubidium zinc phosphate formed, $RbZn(H_2PO_4)(HPO_4){\cdot}H_2O$.[19]

A portion of the gel, C, was left to stand at room temperature for 6 months in a sealed Pyrex flask in order to prevent evaporation. The polycrystalline product (white powder) was a mixture of $RbZn(H_2PO_4)(HPO_4){\cdot}H_2O$, RbH_2PO_4, and possibly an unidentified impurity.[19,21]

The commercial chemicals were 85% H_3PO_4 (Fluka, extra pure >98%), $LiOH{\cdot}H_2O$ (Fluka, puriss p.a. >99%), RbCl (Chempur, >99%), 50% RbOH aqueous solution (Aldrich, 99%), and $Zn(CH_3COO)_2{\cdot}2H_2O$ (Fluka, purum p.a. >99.0%).

Powder X-ray diffraction data for phase identification and refinement of unit cell parameters were obtained using a Siemens D5000 diffractometer equipped with a primary beam germanium monochromator (Cu Kα_1 radiation, $\lambda = 1.5406$ Å). The data were collected from 5° to 90° in 2θ with a step length of 0.02° and counting time of 2−15 s per step, mounting ca. 20 mg of powdered sample on a glass plate. The program CELLKANT[23] was used to refine the unit cell parameters from the observed *d* spacings. The indexed powder pattern of $Rb_2Zn_2(HPO_4)_3$ (37 reflections) is provided in Table 1 using the refined unit cell dimensions of $Rb_2Zn_2(HPO_4)_3$: monoclinic, $a = 12.576(5)$, $b = 12.729(4)$, $c = 7.592(3)$ Å, $\beta = 96.13(4)°$, and $V = 1208.4(8)$ Å^3.

Table 1. Indexed Powder Diffraction Pattern of $Rb_2Zn_2(HPO_4)_3$ Based on the Unit Cell Parameteres $a = 12.576(5)$, $b = 12.729(4)$, $c = 7.592(3)$ Å, $\beta = 96.13(4)°$, $V = 1208.4(8)$ Å^3

h	*k*	*l*	d_{calc}	d_{obs}	I/I_o
1	0	0	12.5039	12.4341	2
1	1	0	8.9200	8.9232	2
0	1	1	6.4927	6.4984	2
0	2	0	6.3644	6.3598	8
−1	1	1	5.9916	5.9923	2
2	1	0	5.6118	5.6045	2
1	1	1	5.5574	5.5469	7
−2	1	1	4.7255	4.7237	1
−1	2	1	4.6438	4.6470	3
2	1	1	4.3103	4.3114	3
2	2	1	3.7180	3.7095	4
0	1	2	3.6185	3.6223	100
−1	3	1	3.5983	3.5986	12
2	3	0	3.5108	3.5125	9
3	2	0	3.4869	3.4876	3
3	1	1	3.3698	3.3689	7
−2	1	2	3.2807	3.2833	11
0	4	0	3.1822	3.1878	45
4	0	0	3.1261	3.1290	14
2	0	2	3.0886	3.0907	53
3	2	1	3.0631	3.0618	4
4	1	0	3.0359	3.0348	6
2	1	2	3.0015	2.9995	3
−3	0	2	2.9592	2.9606	4
−3	3	1	2.8413	2.8452	5
1	4	1	2.8289	2.8240	32
3	3	1	2.6974	2.6979	9
0	5	0	2.5458	2.5460	9
−1	0	3	2.5193	2.5182	4
5	0	0	2.5009	2.4983	3
−1	5	1	2.3838	2.3857	10
2	5	0	2.3578	2.3573	4
4	2	2	2.1551	2.1570	3
−2	3	3	2.1058	2.1044	3
1	5	2	2.0610	2.0594	3
5	0	2	1.9893	1.9908	3
6	3	0	1.8706	1.8700	6

Table 2. Crystallographic Data for $Rb_2Zn_2(HPO_4)_3$

chemical formula, $Rb_2Zn_2(HPO_4)_3$	fw = 589.63 g mol^{-1}
$a = 12.5880(4)$ Å	space group $P2_1/c$ (No. 14)
$b = 12.7170(8)$ Å	$T = -153$ °C
$c = 7.5827(8)$ Å	$\lambda = 0.710\ 73$ Å
$\beta = 96.100(1)°$	$\rho_{calcd} = 3.27$ g cm^{-3}
$V = 1207.0(1)$ Å^3	$\mu = 123.2$ cm^{-1}
$Z = 4$	$R(F_o)^a = 0.036$
	$R_w(F_o)^b = 0.045$

^{a} $R(F_o) = \sum(||F_o| - |F_c||)/(\sum|F_o|)$. ^{b} $R_w(F_o) = [\sum(w||F_o| - |F_c||)^2/(\sum w|F_o|)^2]^{1/2}$. Weighting scheme: $w = \{[\sigma_{cs}(F^2) + F^2]^{1/2} - |F|^2\}^{-2}$.

A thermal investigation was performed by combining information from thermogravimetric (TG) and differential scanning calorimetric (DSC) measurements between 20 and 700 °C using a heating and cooling rate of 5 °C min^{-1}. TG was performed using a SETARAM 92-12 instrument, nitrogen atmosphere, and an open Al_2O_3 crucible for the sample. DSC was performed using a SETARAM 92-16.18 instrument, argon atmosphere, and open platinum crucibles for the sample and the reference, Al_2O_3. The temperature and enthalpy change calibrations of the DSC measurements were performed using the low to high quartz transition.

Single-Crystal X-ray Diffraction. A clear, colorless crystal fragment of $Rb_2Zn_2(HPO_4)_3$ (0.20 × 0.10 × 0.04 mm^3) was used for the data collection performed on a Siemens SMART diffractometer equipped with a CCD detector and graphite-monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å, using the SMART program.[24] Approximately one hemisphere of data was collected in frames covering 0.3° in ω in three sets at different φ angles using a detector to crystal distance of 40.0

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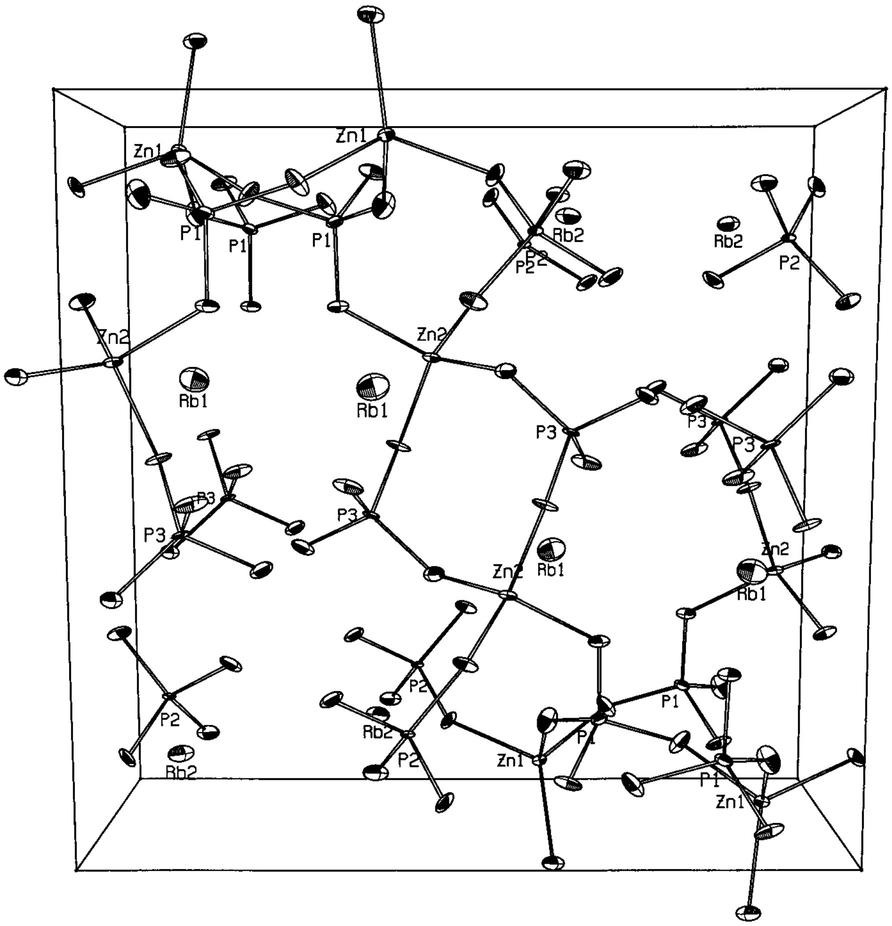

Figure 1. Unit cell content of $Rb_2Zn_2(HPO_4)_3$ shown as 50% thermal ellipsoids and giving the atom-labeling scheme. The crystal structure is shown as an *ab* projection with the *a* axis horizontal.

mm, giving a total of 14 836 reflections ($R_{\mathrm{int}} = 0.083$). Data were corrected for Lorentz polarization effects and for absorption using an empirical method (program SADABS)[24] [transmission (max/min) 0.69/0.30], giving 3698 unique reflections of which 2691 were observed, $I > 3\sigma(I)$. The crystallographic details are given in Table 2.

A structural model was found using direct methods and the program SIR97 in space group $P2_1/c$.[25] Programs from the KRYSTAL software package were used for structure refinement.[26] Hydrogen atoms were placed one-third of the distance between the oxygens: O(4)−O(3), 2.610 Å; O(8)−O(11), 2.566 Å; O(12)−O(11), 2.561 Å. The H atom positions were not refined. All atoms were refined with anisotropic displacement parameters except H atoms, which were kept isotropic. Scattering factors of neutral atoms were applied throughout this work. The refinement converged at $R(F_o) = 0.036$ and $R_w(F_o) = 0.045$, with 176 parameters refined using full matrix least squares based on all F and a weighting scheme of $w = \{[\sigma_{\mathrm{CS}}(F^2) + F^2]^{1/2} - |F|\}^{-2}$. Residual electron density was located close to the heavy atoms, Rb [$\Delta\rho$ (max/min), 2.0(2)/(−1.6(2)) e Å^{-3}]. Atomic coordinates and equivalent thermal displacement parameters are shown in Table 3. Figure 1 shows the atom-labeling scheme and 50% thermal ellipsoids of the unit cell contents. Figure 1 was prepared using the program OrtepIII, and the program Atoms, version 4.0, was used for preparation of the polyhedra drawings (Figures 2 and 3).[27,28]

Additional crystallographic results are given in Supporting Information.

Table 3. Atomic Coordinates and Isotropic Thermal Parameters of $Rb_2Zn_2(HPO_4)_3$

	x	*y*	*z*	U_{iso}
Rb1	−0.36941(4)	0.12050(4)	0.62488(7)	0.0222(3)
Rb2	0.14458(3)	0.12898(4)	0.10389(6)	0.0132(2)
Zn1	−0.04815(4)	0.10354(4)	0.65436(7)	0.0076(2)
Zn2	−0.33763(4)	0.05181(4)	0.13292(7)	0.0088(3)
P1	−0.14946(9)	0.17971(9)	0.01186(15)	0.0074(5)
O1	−0.2654(2)	0.1773(2)	0.0516(4)	0.013(2)
O2	−0.1312(3)	0.1112(3)	0.8556(4)	0.016(2)
O3	−0.1132(3)	0.2926(2)	0.9831(4)	0.015(2)
O4	−0.0767(3)	0.1329(3)	0.1744(4)	0.015(2)
P2	0.17346(9)	0.07887(8)	0.5788(1)	0.0061(5)
O5	0.2594(2)	0.0049(2)	0.6552(4)	0.015(2)
O6	0.1011(2)	0.0310(2)	0.4264(4)	0.012(2)
O7	0.1050(3)	0.1234(2)	0.7165(4)	0.013(2)
O8	0.2293(3)	0.1723(2)	0.4878(4)	0.014(2)
P3	0.43721(9)	0.13548(9)	0.0982(2)	0.0078(5)
O9	0.5321(3)	0.0996(2)	0.2257(4)	0.013(2)
O10	0.3536(2)	0.0485(2)	0.0619(4)	0.013(2)
O11	0.3861(2)	0.2336(3)	0.1655(4)	0.016(2)
O12	0.4862(3)	0.1617(3)	−0.0804(5)	0.017(2)
H4	−0.0888	0.1575	0.2768	0.028(17)
H8	0.2807	0.1909	0.5232	0.066(28)
H12	0.4526	0.1967	−0.1654	0.142(47)

Spectroscopic Investigation. Single-crystal ^{31}P NMR experiments were performed at 14.1 T (242.9 MHz) on a Varian Unity-INOVA 600 spectrometer employing a new goniometer design described elsewhere.[29] This probe is particularly designed for studies of small crystals and has only two axes of rotation (*a* and *b*). Rotation of the

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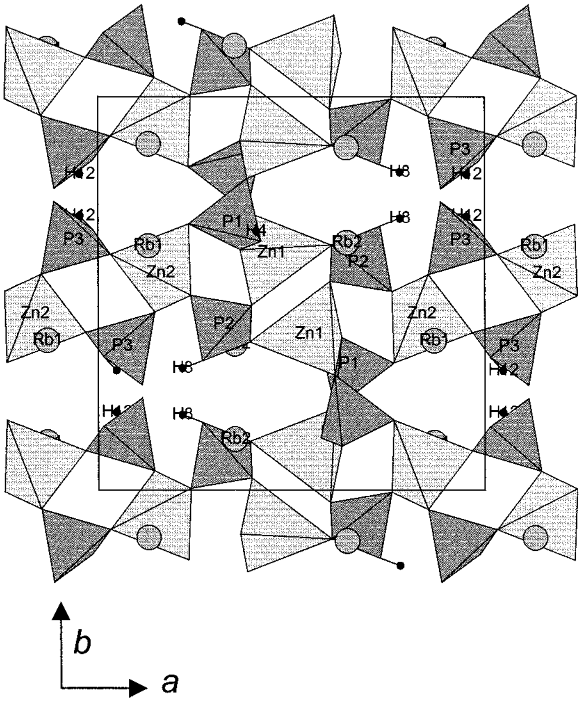

Figure 2. Crystal structure of $Rb_2Zn_2(HPO_4)_3$ shown as an *ab* projection. Tetrahedra of PO_4 are dark, and ZnO_4 are light. Hydrogen atoms are shown as small-size black circles, Rb atoms as larger circles.

crystal is fully automated and computer controlled, which yields a high degree of precision for the angle setting (±0.3°).[30] For each axis of rotation 25 spectra were recorded following an increment of 15° for the rotation angle. Each spectrum is the sum of 16 transients measured with a spectral width of 100 kHz, single-pulse excitation ($\tau_p = 3.5$ μs), and a repetition delay of 128 s. The crystal of $Rb_2Zn_2(HPO_4)_3$ used for the single-crystal NMR investigation was approximately 1 × 1 × 2 mm^3. The analysis of the single-crystal NMR spectra was performed by the software package ASICS.[30] The CSA parameters are defined by $\delta_\sigma = \delta_{zz} - \delta_{iso}$ and $\eta_\sigma = (\delta_{xx} - \delta_{yy})/\delta_\sigma$, where the principal elements are defined in the order $|\delta_{zz} - \delta_{iso}| > |\delta_{xx} - \delta_{iso}| > |\delta_{yy} - \delta_{iso}|$. All principal elements and isotropic chemical shifts are in ppm relative to 85% H_3PO_4.

Results and Discussion

Synthesis. The new material $Rb_2Zn_2(HPO_4)_3$ is prepared using moderate temperature (52 °C) solvothermal synthesis, and crystallization is noticed after ca. 4.5 months.[31] Long nucleation times have also been found in the initial preparation of β-$LiZnPO_4 \cdot H_2O$ and $LiZn(HPO_4)(PO_4) \cdot \mathit{en}H_2 \cdot H_2O$, ca. 3 months at 21 °C.[10,11] The nucleation time of the β-phase is found to depend on the composition of the reaction mixture,[11] which suggests that a faster synthetic route might be developed for the preparation of $Rb_2Zn_2(HPO_4)_3$. The synthesis presented here reveals the diversity of solvothermal synthesis and phosphate chemistry; one gel gives three different rubidium zinc orthophosphates and at least three other phases.[32]

Thermal Investigation. Thermogravimetric measurements showed a total mass loss of 4.4% in the temperature range 255−415 °C, with a significant mass loss of 3.2% in the range 280−305 °C. This observation is in accordance with loss of water ($1.5H_2O$) from $Rb_2Zn_2(HPO_4)_3$, with a calculated mass loss of 4.58%. Differential scanning calorimetry of $Rb_2Zn_2(HPO_4)_3$ revealed three thermal events on the heating curve and one on the cooling curve. An endothermic event in the temperature range 298−329 °C (peak value at 320 °C) with an enthalpy change of $\Delta H = 82 \pm 22$ kJ/mol is equivalent to the mass loss detected by TG. The obtained material is metastable and gives an exothermic DSC effect in the range 452−473 °C (peak value at 463 °C), $\Delta H = -5.6 \pm 1.5$ kJ/mol. An endothermic signal at 647−668 °C (peak value at 658 °C), $\Delta H = 4.5 \pm 1.2$ kJ/mol, corresponds to a reversible change in the sample because an exothermic event was visible on the cooling curve at 612−575 °C (peak value at 603 °C), $\Delta H = -5.2 \pm 1.4$ kJ/mol. The thermal decomposition product has not yet been identified but might be a mixture containing $RbZnPO_4$ and other phases.

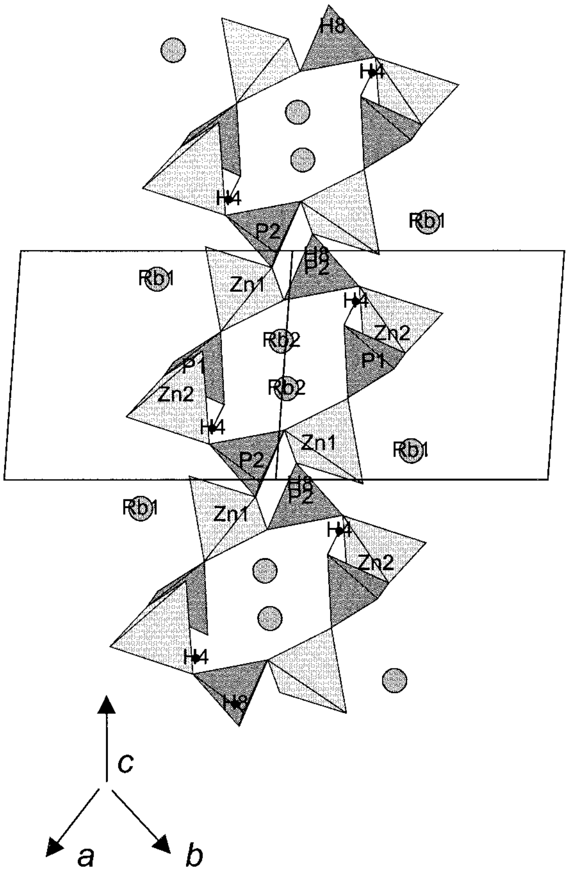

Figure 3. Crystal structure of $Rb_2Zn_2(HPO_4)_3$, viewed along the (110) direction showing ladders of alternating four- and eight-rings running along the *c* direction. Hydrogen atoms are shown as small-size dark circles and Rb as larger circles. PO_4 is represented as dark tetrahedra and ZnO_4 as light tetrahedra.

Description of the Crystal Structure. The crystal structure of $Rb_2Zn_2(HPO_4)_3$ is illustrated in Figure 2 as an *ab* projection and can be seen as a framework built from three crystallographically distinct tetrahedra of PO_4 all having one longer P−O bond with hydrogen on O(4), O(8), and O(12). The framework is interrupted by the hydroxyl groups O(4), O(8), and O(12)

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(32) Preparation of crystalline materials by evaporation of a solvent is a method that has been known for a very long time. The residue from a solvothermal synthesis in equilibrium with solid material has a unique composition. Such solutions can in some cases be useful for preparation of other materials.

Table 4. Selected Bond Lengths and Angles for the Crystal Structure of $Rb_2Zn_2(HPO_4)_3$[a]

P1−O2	1.508(3)	Zn1−O6^{iii}	1.913(3)
P1−O1	1.521(3)	Zn1−O2	1.941(3)
P1−O3	1.529(3)	Zn1−O7	1.952(3)
P1−O4	1.572(3)	Zn1−O3^{i}	1.969(3)
P2−O5	1.503(3)	Zn2−O5^{iii}	1.932(3)
P2−O6	1.521(3)	Zn2−O10^{viii}	1.946(3)
P2−O7	1.531(3)	Zn2−O9^{iv}	1.949(3)
P2−O8	1.576(3)	Zn2−O1^{ix}	1.967(3)
P3−O11	1.517(3)	P3−O10	1.531(3)
P3−O9	1.525(3)	P3−O12	1.582(3)
O4−H4	0.865	H4−O3	1.745
O8−H8	0.714	H8−O11	1.883
O12−H12	0.857	H12−O11	1.703
Rb1−O1^{i}	2.965(3)	Rb2−O10^{v}	2.872(3)
Rb1−O12^{ii}	3.071(3)	Rb2−O4	2.892(3)
Rb1−O5^{iii}	3.098(3)	Rb2−O8^{vi}	2.915(3)
Rb1−O9^{iv}	3.158(3)	Rb2−O7	2.928(3)
Rb1−O10	3.194(3)	Rb2−O8^{v}	3.042(3)
Rb2−O6^{v}	2.849(3)	Rb2−O2^{vii}	3.076(3)
O1−P1−O2	111.9(2)	O2−Zn1−O6^{iii}	95.6(1)
O2−P1−O3	111.0(2)	O6^{iii}-Zn1−O7	119.6(1)
O2−P1−O4	105.8(2)	O3^{i}−Zn1−O6^{iii}	106.4(1)
O1−P1−O3	110.8(2)	O2−Zn1−O7	113.8(1)
O1−P1−O4	109.1(2)	O2−Zn1−O3^{i}	105.3(1)
O3−P1−O4	108.0(2)	O3^{i}−Zn1−O7	113.8(1)
O5−P2−O6	113.0(2)	O5^{iii}−Zn2−O10^{viii}	112.9(1)
O5−P2−O7	113.8(2)	O5^{iii}−Zn2−O9^{iv}	101.0(1)
O5−P2−O8	107.7(2)	O1^{ix}−Zn2−O5^{iii}	110.6(1)
O6−P2−O7	109.3(2)	O9^{iv}−Zn2−O10^{viii}	117.1(1)
O6−P2−O8	103.2(2)	O1^{ix}−Zn2−O10^{viii}	107.9(1)
O7−P2−O8	109.2(2)	O1^{ix}−Zn2−O9^{iv}	107.2(1)
O9−P3−O11	111.3(2)	O9−P3−O10	112.0(2)
O10−P3−O11	110.3(2)	O9−P3−O12	104.8(2)
O11−P3−O12	109.4(2)	O10−P3−O12	108.8(2)
P1−O4−H4	115.0(3)	P1−O3−H4^{i}	123.6(2)
P2−O8−H8	120.9(3)	P3−O11−H8^{i}	121.6(2)
P3−O12−H12	123.1(3)	P3−O11−H12^{vi}	119.3(2)
O1^{i}−Rb1−O12^{ii}	107.20(9)	O9^{iv}−Rb1−O12^{ii}	120.63(9)
O1^{i}−Rb1−O5^{iii}	94.56(8)	O10^{iii}−Rb1−O12^{iii}	64.44(8)
O1^{i}−Rb1−O9^{iv}	91.69(9)	O5^{iii}−Rb1−O9^{iv}	57.17(8)
O1^{i}−Rb1−O10^{iii}	136.82(9)	O5^{iii}−Rb1−O10^{iii}	99.58(8)
O5^{iii}-Rb1−O12^{ii}	158.25(9)	O9^{iv}−Rb1−O10^{iii}	130.04(8)
O6^{v}−Rb2−O10^{v}	101.61(9)	O4−Rb2−O8^{vi}	115.55(9)
O4−Rb2−O6^{v}	64.66(9)	O4−Rb2−O7	96.99(9)
O6^{v}−Rb2−O8^{vi}	138.42(9)	O4−Rb2−O8^{v}	93.81(9)
O6^{v}−Rb2−O7	145.40(9)	O2^{vii}−Rb2−O4	86.25(9)
O6^{v}−Rb2−O8^{v}	48.51(8)	O7−Rb2−O8^{vi}	75.31(9)
O2^{vii}-Rb2−O6^{v}	57.50(9)	O8^{vi}−Rb2−O8^{v}	91.71(8)
O4−Rb2−O10^{v}	159.77(9)	O2^{vii}−Rb2−O8^{vi}	156.44(9)
O8^{vi}−Rb2−O10^{v}	84.64(9)	O7−Rb2−O8^{v}	165.79(8)
O7−Rb2−O10^{v}	86.58(9)	O2^{vii}−Rb2−O7	94.07(9)
O8^{v}−Rb2−O10^{v}	86.47(9)	O2^{vii}−Rb2−O8^{v}	95.83(9)
O2^{vii}−Rb2−O10^{v}	73.62(9)	O2^{vii}−Rb2−O8^{v}	95.83(9)

[a] Symmetry codes: (*i*) *x*, 0.5 − *y*, *z* − 0.5; (*ii*) *x* − 1, *y*, 1 + *z*; (*iii*) −*x*, −*y*, 1 − *z*; (*iv*) *x* − 1, *y*, *z*; (*v*) *x*, *y*, 1 + *z*; (*vi*) *x*, 0.5 − *y*, 0.5 + *z*; (*vii*) −*x*, −*y*, 2 − *z*; (*viii*) −*x*, −*y*, −*z*; (*ix*) *x*, *y*, *z* − 1; (*x*) 1 + *x*, *y*, *z*.

and by O(11), which is pendant and acceptor for two hydrogen bonds [from H(8) and H(12)]; O(3) is acceptor for H(4). Selected bond lengths and angles are shown in Table 4.

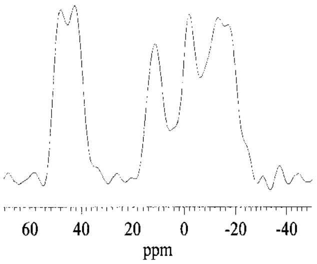

Figure 4. Selected single-crystal ^{31}P NMR spectrum of $Rb_2Zn_2(HPO_4)_3$ revealing six ^{31}P resonances.

Table 5. Calculated Oxidation States, V_i, for the Structure of $Rb_2Zn_2(HPO_4)_3$, Using Ref 33 and the Bond Lengths Given in Table 4 Excluding the H Atoms

	no.	V_i	CN
cation			
phosphorus	1	5.04	4
	2	5.04	4
	3	4.95	4
zinc	1	2.10	4
	2	2.07	4
rubidium	1	0.54	5
	2	1.15	7
oxygen			
framework	1	1.94	3
	2	1.98	3
	5	2.01	3
	6	2.07	3
	7	1.94	3
	9	1.89	3
	10	2.05	4
H-bond donor	4	1.31	2
	8	1.41	2
	12	1.21	2
H-bond acceptor	11	1.31	1
	3	1.76	2

The apparent "triple four-ring units" visible in Figure 2 formed by the Zn, P(1), and P(2) tetrahedra are interconnected by P(3) to form chains along the *a* axis. These parallel chains are related by the *c* glide planes and the screw axes. Figure 3 shows apparent "triple four-ring units" viewed along the (110) direction and reveals that they are in fact ladders of alternating four- and eight-rings running along the *c* direction. These ladders, built from two spiral chains of alternating $P(1,2)O_4$ and ZnO_4 tetrahedra, are assembled by $P(3)O_4$, rubidium ions, and hydrogen bonds to form a three-dimensional framework structure. Figure 3 shows that Rb(2) is placed in the openings of the eight-rings.

Oxidation states, V_i, were calculated as a sum of bond valencies using the bond lengths shown in Table 4 not including the H atoms, and the results are given in Table 5.[33] Framework oxygen atoms (nos. 1, 2, 5, 6, 7, and 9) coordinated to one Rb, Zn, and P each have V_i in the range 1.89−2.07 and O(10) coordinated to two Rb, one Zn, and P have V_i of 2.05, in agreement with the expected (numerical) value of 2.0. The hydroxyl oxygens O(4), O(8), and O(12) have V_i of 1.31, 1.41, and 1.20, and O(3) and O(11) have calculated oxidation states of 1.76 and 1.30, since they are all participating in hydrogen bonding (the sum of V_i for these five oxygens is 7, in accordance with the missing bond valence from three H atoms). The cations P, Zn, and Rb(2) have calculated oxidation states in agreement with the expected values. The low value of 0.54 for Rb(1) is caused by an unusually low number of oxygen contacts, five, in the first coordination sphere, but Rb(1) has some longer oxygen contacts. The calculated oxidation state for Rb(1) is $V_i = 0.75$, including oxygen contacts in the range 3.31−3.87 Å to O(2), O(1)*, O(12)*, O(11), O(3), O(9)*, and O(9)**. A similar calculation for Rb(2) gives $V_i = 1.30$, including oxygen contacts up to 3.88 Å to O(11), O(7)*, O(2)*, and O(3) (the atoms marked with an asterisk are symmetry-related to atoms shown in Table 4).

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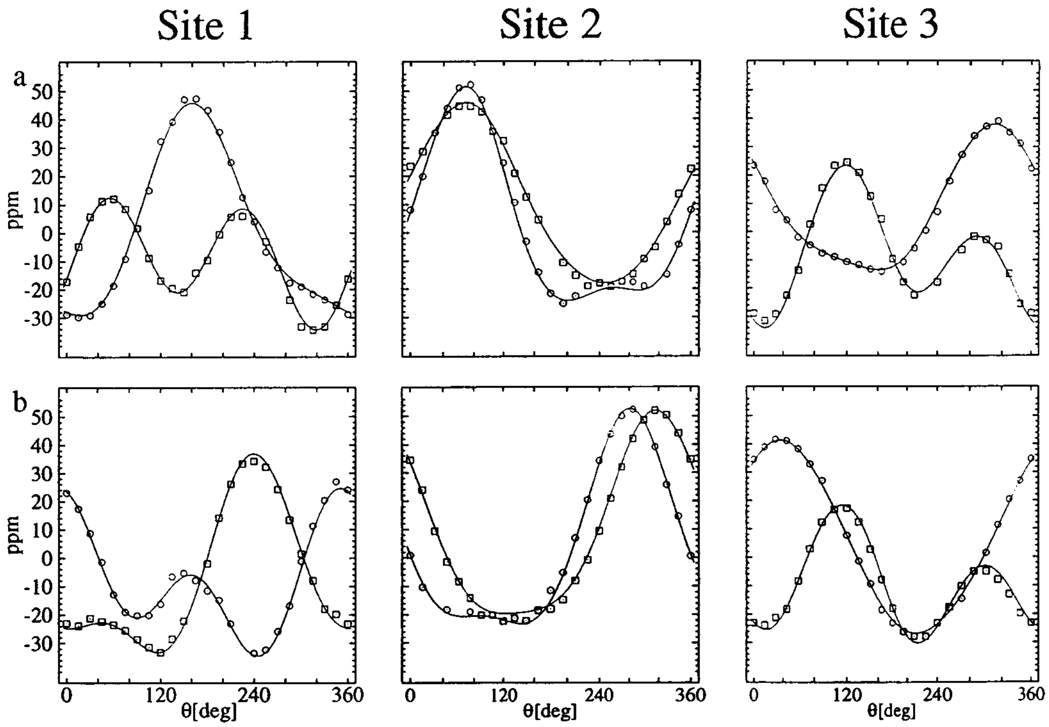

Figure 5. Rotation plots for the three crystallographically distinct ^{31}P sites. The NMR probe rotation axes are not parallel to the crystallographic axes giving rotation plots for each site, which are not exact mirrors of each other.

Table 6. ^{31}P Chemical Shielding Anisotropy Parameters (δ_σ, η_σ, δ_{iso}) for $Rb_2Zn_2(HPO_4)_3$

site	δ_σ (ppm)[a]	η_σ	δ_{iso} (ppm)[a]
1	−47.4(7)	0.28(2)	−3.3(3)
2	−48.9(6)	0.09(3)	2.0(3)
3	−48.9(7)	0.25(2)	−2.6(3)

[a] All principal elements and isotropic chemical shifts are in ppm relative to 85% H_3PO_4.

Single-Crystal ^{31}P NMR. A typical single-crystal ^{31}P NMR spectrum of $Rb_2Zn_2(HPO_4)_3$, which displays six resonances of equal intensity, is shown in Figure 4. Preliminary analyses of the rotation plots shown in Figure 5 indicate the presence of only three crystallographically distinct P sites because the magnitudes of the six shielding tensors are pairwise equal. The three phosphorus positions split up in 2 × 3 magnetically inequivalent positions because of the mirror symmetry (the NMR tensors are insensitive to translation and inversion). This observation is in agreement with the space group $P2_1/c$ and three phosphorus atoms in the asymmetric unit. Magnetically inequivalent but crystallographically equivalent nuclei have the same magnitude but different orientations of their NMR tensors.

The rotation plots for the three phosphorus sites are shown in Figure 5 where circles and squares indicate the two magnetically nonequivalent P atoms for each site and the solid lines correspond to the optimized parameters listed in Table 6. The observed isotropic chemical shift values are in the range of values found for other hydrogen phosphates.[34] Site 2 has almost axial symmetry ($\eta_\sigma = 0.09(3)$) and is therefore tentatively assigned to P(2) because this phosphorus atom is coordinated to three framework oxygens and one oxygen acting as a hydrogen bond donor. The two other P sites, 1 and 3, have similar NMR parameters corresponding to an asymmetric chemical shift tensor, which possibly is P(1) and P(3) each having one oxygen acting as hydrogen bond donor and another as acceptor. The two rotation plots for each site are not exact mirrors of each other because the NMR probe rotation axes are not parallel to the crystallographic axes.

Comparison with Related Materials. The crystal structures of rubidium zinc (hydrogen) orthophosphates are usually built from alternating phosphorus (the units H_2PO_4/HPO_4/PO_4) and zinc tetrahedra connected by rubidium ions and hydrogen bonds. Rubidium shows large coordination flexibility with coordination numbers (CN) in the range 8−11 in these materials.[19,20] An exceptionally low CN of 5 and calculated oxidation state of 0.54 are found for one Rb ion in $Rb_2Zn_2(HPO_4)_3$ presented here. The crystal structures of $RbZn(H_2PO_4)(HPO_4)\cdot H_2O$ and $RbZn_2(HPO_4)(PO_4)$ can be described as one- and two-dimensional chains and layers of alternating ZnO_4 and PO_4 tetrahedra connected by rubidium ions and hydrogen bonds.[19,20] The compound $RbZnPO_4$ has a three-dimensional framework structure built from ZnO_4 and PO_4 tetrahedra with rubidium placed in the eight ring channels of the zeolite ABW type structure.[35]

Apparently, only three alkali metal zinc monohydrogen phosphates are known: $Na_2Zn(HPO_4)_2\cdot 4H_2O$, $Rb_2Zn_2(HPO_4)_3$, and $CsZn_{2.5}(HPO_4)_3\cdot 2H_2O$.[10,36] The sodium- and cesium-containing phases are built from ZnO_4 and HPO_4 layers intersected by open 12- and 8-rings where the alkali ions and water molecules are placed. Hydrogen phosphates often form complex crystal structures because of hydrogen bonds, e.g., the trigonal structure of $RbFe(HPO_4)_2$, which has a very long *c* axis of 52.75 Å.[37] The structure of $Rb_2Zn_2(HPO_4)_3$ is no exception because this new material has a complex three-dimensional crystal structure built from spiral chains of phosphorus and zinc tetrahedra.

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Conclusion

A new rubidium zinc orthophosphate, $Rb_2Zn_2(HPO_4)_3$, has been crystallized after a nucleation period of 4.5 months, implying an unusual method of synthesis. This technique may provide other new materials with a range of different compositions. $Rb_2Zn_2(HPO_4)_3$ has a complex crystal structure built from spiral chains of alternating ZnO_4 and PO_4 tetrahedra with connecting rubidium ions. X-ray diffraction and ^{31}P NMR on single-crystal samples have proven to be exceptionally useful in providing complementary structural information about long-range crystalline order and the magnitude and orientation of the ^{31}P NMR tensors, i.e., the first and second coordination sphere of the nuclei. It has been observed that phosphorus and zinc coordinated to oxygen form an almost ideal net work, which is in contrast to the coordination of the rubidium ions. This study reveals the extraordinarily large coordination flexibility of rubidium, which shows exceptionally low coordination numbers and calculated oxidation states.

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Supporting Information Available: One X-ray crystallographic data file in CIF format is available. This material is available free of charge via the Internet at http://pubs.acs.org.

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