Crystal structures of rubidium scandium bis(hydrogenphosphate), $\text{RbSc}(\text{HPO}_4)_2$, and ammonium scandium bis(hydrogenphosphate), $\text{NH}_4\text{Sc}(\text{HPO}_4)_2$

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Abstract

$\text{H}_2\text{O}_8\text{P}_2\text{RbSc}$, monoclinic, $P12_1/c1$ (no. 14), $a = 5.3214(6)$ Å, $b = 8.9221(7)$ Å, $c = 14.758(1)$ Å, $\beta = 94.967(5)^\circ$, $V = 698.0$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.060$, $wR_{\text{ref}}(F^2) = 0.180$, $T = 295$ K.

$\text{H}_6\text{NO}_8\text{P}_2\text{Sc}$, monoclinic, $P12_1/c1$ (no. 14), $a = 5.3211(5)$ Å, $b = 8.8660(7)$ Å, $c = 14.791(1)$ Å, $\beta = 95.266(4)^\circ$, $V = 694.8$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.092$, $wR_{\text{ref}}(F^2) = 0.287$, $T = 295$ K.

Source of material

The isotypic compounds $M^I\text{Sc}(\text{HPO}_4)_2$ ($M^I = \text{Rb}, \text{NH}_4$) were prepared under mild hydrothermal conditions. For $\text{RbSc}(\text{HPO}_4)_2$, a mixture of 0.5000 g Sc_2O_3 (Abcr, 99.9 %), 0.3715 g RbOH (Alfa Aesar, 99 %), and 2.5079 g H_3PO_4 (Merck, 85 %) was heated at 363 K after addition of deionized water (10 ml) with continuous stirring until the components were completely dissolved (molar

ratio $\text{Sc} : \text{Rb} : \text{P} = 1 : 1 : 6$). The clear solution ($\text{pH} = 1$) was then transferred into a 20 ml Teflon-lined autoclave (filling degree 40 %) and heated at 443 K for seven days. $\text{NH}_4\text{Sc}(\text{HPO}_4)_2$ was synthesized from a mixture of 0.5000 g Sc_2O_3 (Abcr, 99.9 %), 0.2241 g H_3BO_3 (Alfa Aesar, 99.9 %) and 3.8302 g $(\text{NH}_4)_2\text{HPO}_4$ (Merck, 99 %) in the molar ratio $\text{NH}_4 : \text{Sc} : \text{P} = 1 : 1 : 8$. 10 ml of deionized water were added, and the system was stirred at 373 K. The pH value was adjusted to 1 by the addition of 3.0 ml HCl (37 %). The mixture was then filled into a 10 ml Teflon-lined autoclave (filling degree 30 %) and heated under autogenous pressure at 443 K for 24 days. The obtained reaction products were separated by filtration, washed with hot water/acetone and dried in air at 333 K. The products consisted of needle-shaped transparent crystals with dimensions ranging from 0.05 to 0.1 mm. The chemical composition $M^I\text{Sc}(\text{HPO}_4)_2$ ($M^I = \text{Rb}, \text{NH}_4$) was confirmed by EDXS and chemical analyses. IR spectra and the loss of water during TG analyses confirm the presence of P–OH groups.

Experimental details

The crystals of both compounds were affected by reticular merohedry twinning. The positions of Rb, Sc, P, O for $\text{RbSc}(\text{HPO}_4)_2$ and Sc, P, O, N for $\text{NH}_4\text{Sc}(\text{HPO}_4)_2$ were obtained from structural data of the isotypic compound $\text{CsSc}(\text{HPO}_4)_2$ [1]. Subsequent introduction of the twin matrix $[-1\ 0\ 0\ 0\ -1\ 0\ 0.5\ 0\ 1]$ and simultaneous refinement of the twin ratio together with the atomic coordinates and anisotropic thermal parameters led to reasonable structural models and residuals. The positions of the protons could not be determined from Fourier difference map analyses for both compounds $M^I\text{Sc}(\text{HPO}_4)_2$ ($M^I = \text{Rb}, \text{NH}_4$).

Discussion

The discovery of the microporous crystalline alumophosphates has stimulated many attempts to synthesize new open framework metal phosphates since these compounds have an enormous potential as catalysts, ion-exchangers, adsorbents and hosts for the preparation of host-guest materials [2–6]. Our investigation on the system $M^I_2\text{O} - \text{Sc}_2\text{O}_3 - \text{P}_2\text{O}_5 - \text{H}_2\text{O}$ ($M^I = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$) lead to the title compounds $M^I\text{Sc}(\text{HPO}_4)_2$ ($M^I = \text{Rb}, \text{NH}_4$) which are isotypes of $\beta\text{-RbV}(\text{HPO}_4)_2$ and $\text{NH}_4\text{V}(\text{HPO}_4)_2$ [7], $\text{CsSc}(\text{HPO}_4)_2$ [1].

In the crystal structure of $M^I\text{Sc}(\text{HPO}_4)_2$ ($M^I = \text{Rb}, \text{NH}_4$), the ScO_6 octahedra share their (six) corners with adjacent PO_4 tetrahedra. The PO_4 tetrahedra share three of their corners with neighbouring ScO_6 octahedra the fourth oxygen position is connected to the proton, which is consistent with the longer P–O distance [1,7]. The condensation of the hydrogenphosphate groups with the ScO_6 octahedra via common corners results in an overall three-dimensional framework containing channels running along

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[100]. The cross section of the channel is defined by twelve membered rings consisting of six scandium coordination octahedra and six hydrogenphosphate groups. M^I ($M^I = \text{Rb}, \text{NH}_4$) ions reside within the channels. Rb and N are surrounded by 11 oxygen atoms with the distances Rb—O ranging from 2.993(3) Å to 3.559 Å and the distance N—O ranges from 2.932(2) Å to 3.569(2) Å. The Sc—O distances in both structures range from 2.053(3) Å up to 2.144(3) Å and the P—O distances from 1.503(3) Å to 1.600(3) Å. The angles within the scandium octahedra and the hydrogenphosphate groups are in accordance with related phosphates [1,7,8] and borophosphates [9–12].

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.100 × 0.040 × 0.025 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	84.5 cm ⁻¹
Diffractometer, scan mode:	Rigaku AFC7, ϕ/ω
$2\theta_{\text{max}}$:	63.6°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	7960, 7962
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6533
$N(\text{param})_{\text{refined}}$:	111
Programs:	SHELXS-97 [13], SHELXL-97 [14], DIAMOND [15]

1. Rubidium scandium bis(hydrogenphosphate), RbSc(HPO₄)₂

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb(1)	4e	0.27415(9)	0.49937(5)	0.11343(3)	0.0285(3)	0.0314(3)	0.0386(3)	0.0047(2)	-0.0033(2)	-0.0049(2)
Sc(1)	4e	0.2578(1)	0.03765(8)	0.15001(4)	0.0143(3)	0.0133(3)	0.0112(3)	-0.0003(3)	0.0017(3)	-0.0007(2)
P(1)	4e	0.7241(2)	0.8406(1)	0.06132(6)	0.0136(5)	0.0133(4)	0.0118(4)	-0.0006(3)	0.0017(4)	-0.0010(3)
P(2)	4e	0.2198(2)	0.7613(1)	0.31075(6)	0.0111(4)	0.0134(4)	0.0132(4)	-0.0009(3)	0.0013(4)	0.0009(3)
O(1)	4e	0.9143(5)	0.9522(3)	0.1010(2)	0.016(1)	0.022(2)	0.023(1)	-0.002(1)	0.004(1)	-0.001(1)
O(2)	4e	0.7420(5)	0.8169(3)	-0.0396(2)	0.020(1)	0.016(1)	0.015(1)	-0.004(1)	0.006(1)	-0.000(1)
O(3)	4e	0.4553(5)	0.8786(3)	0.0822(2)	0.016(1)	0.017(1)	0.026(1)	-0.000(1)	0.008(1)	-0.005(1)
O(4)	4e	0.2106(5)	0.1801(3)	0.3962(2)	0.031(2)	0.013(1)	0.023(1)	-0.004(1)	0.005(1)	-0.004(1)
O(5)	4e	0.2625(5)	0.9121(3)	0.2684(2)	0.021(1)	0.016(1)	0.018(1)	-0.005(1)	0.001(1)	0.004(1)
O(6)	4e	0.4180(5)	0.6485(3)	0.2922(2)	0.016(1)	0.016(1)	0.018(1)	0.005(1)	-0.004(1)	0.001(1)
O(7)	4e	-0.0459(5)	0.7025(3)	0.2840(2)	0.014(1)	0.017(1)	0.019(1)	0.000(1)	-0.002(1)	0.006(1)
O(8)	4e	0.2389(5)	0.8006(3)	0.4169(2)	0.022(1)	0.021(1)	0.014(1)	-0.002(1)	0.004(1)	-0.004(1)

2. Ammonium scandium bis(hydrogenphosphate), NH₄Sc(HPO₄)₂

Table 3. Data collection and handling.

Crystal:	colorless prism, size 0.075 × 0.065 × 0.025 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	15.31 cm ⁻¹
Diffractometer, scan mode:	Rigaku AFC7, ϕ/ω
$2\theta_{\text{max}}$:	63.26°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	7912, 7912
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5752
$N(\text{param})_{\text{refined}}$:	111
Programs:	SHELXS-97 [13], SHELXL-97 [14], DIAMOND [15]

Table 4. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	4e	0.2744(7)	0.4974(5)	0.1118(3)	0.039(2)	0.051(2)	0.045(2)	0.005(2)	-0.000(2)	-0.002(2)
Sc(1)	4e	0.2595(1)	0.03701(8)	0.14962(5)	0.0231(4)	0.0257(4)	0.0241(4)	-0.0003(3)	0.0020(3)	0.0001(3)
P(1)	4e	0.7249(2)	0.8387(1)	0.06007(6)	0.0226(5)	0.0253(5)	0.0232(5)	0.0002(4)	0.0017(4)	-0.0015(3)
P(2)	4e	0.2184(2)	0.7594(1)	0.30972(6)	0.0225(5)	0.0247(5)	0.0250(5)	-0.0014(4)	0.0031(4)	0.0015(4)
O(1)	4e	0.9152(5)	0.9524(3)	0.0988(2)	0.027(1)	0.037(2)	0.030(1)	-0.004(1)	-0.000(1)	-0.010(1)
O(2)	4e	0.7398(5)	0.8116(3)	-0.0408(2)	0.031(1)	0.030(1)	0.023(1)	0.001(1)	0.001(1)	0.002(1)
O(3)	4e	0.4574(4)	0.8770(3)	0.0795(2)	0.020(1)	0.028(1)	0.034(2)	0.002(1)	0.004(1)	-0.005(1)
O(4)	4e	0.2104(5)	0.1787(3)	0.3939(2)	0.039(2)	0.029(1)	0.034(2)	-0.004(1)	0.005(1)	-0.001(1)
O(5)	4e	0.2668(5)	0.9088(3)	0.2657(2)	0.029(2)	0.030(1)	0.030(2)	-0.003(1)	0.006(1)	0.005(1)
O(6)	4e	0.4143(5)	0.6426(3)	0.2923(2)	0.026(1)	0.028(1)	0.028(1)	0.002(1)	0.003(1)	-0.000(1)
O(7)	4e	-0.0496(5)	0.7024(3)	0.2831(2)	0.026(1)	0.026(1)	0.029(1)	-0.003(1)	0.000(1)	0.004(1)
O(8)	4e	0.2382(5)	0.7997(3)	0.4151(2)	0.029(1)	0.037(2)	0.028(1)	0.001(1)	0.001(1)	0.000(1)

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