Crystal structure of sodium scandium bis(monohydrogenphosphate), $NaSc(HPO_4)_2$

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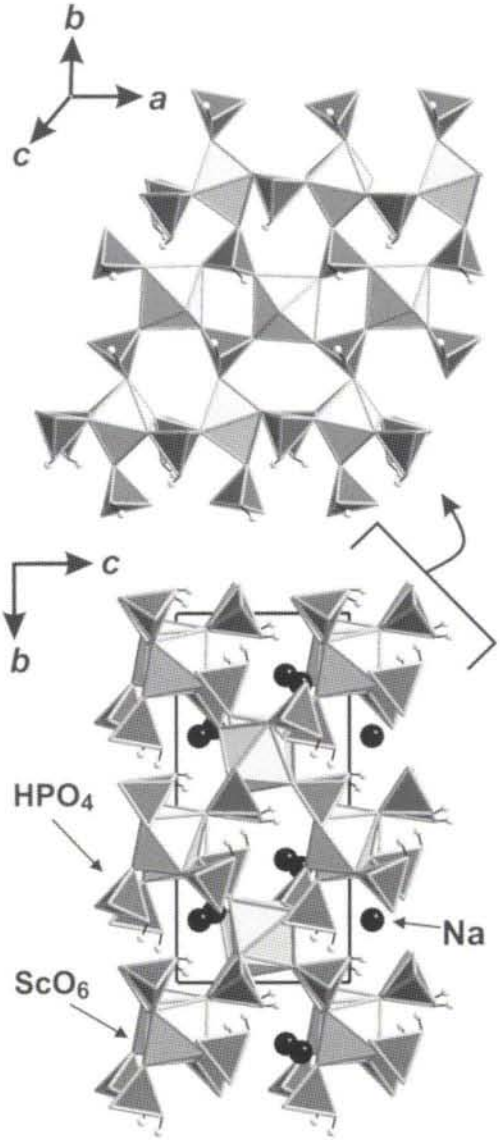

Abstract

$H_2NaO_8P_2Sc$, monoclinic, $C1c1$ (no. 9),
$a = 10.4446(9)$ Å, $b = 16.371(2)$ Å, $c = 9.0553(7)$ Å,
$\beta = 122.420(3)°$, $V = 1307.1$ Å^3, $Z = 8$,
$R_{gt}(F) = 0.023$, $wR_{ref}(F^2) = 0.054$, $T = 293$ K.

Source of material

Single crystals of $NaSc(HPO_4)_2$ were obtained as minority phase during hydrothermal investigations in the system Na_2O–Sc_2O_3–B_2O_3–P_2O_5(–H_2O). Specimens could be isolated from suspensions with a typical composition of 0.500 g (3.626 mmol) Sc_2O_3 (ABCR, 99.9 %), 1.383 g (3.626 mmol) $Na_4B_4O_7 \cdot 10H_2O$ (Aldrich, A.C.S.) and 6.688 g (58.008 mmol) phosphoric acid (85 %, Merck, p.a.) in 5 ml of water. Filled in 20 ml Teflon autoclaves (degree of filling: 30-40 %), the reaction mixture was kept at 443 K for six days. The raw product was filtrated and washed with water and acetone and finally dried in air at 333 K.

Discussion

The number of scandium phosphates is comparatively small, although they attracted attention as ionic conductors [1-4]. Also complex scandium phosphate frameworks have been reported recently [5,6]. Acid quasi-ternary scandium phosphates have never been investigated systematically and $NaSc(HPO_4)_2$ represents the first acid alkali metal scandium phosphate. Monohydrogenphosphates with the general composition $M^IM^{III}(HPO_4)_2$ known up to date are: $(NH_4)Fe(HPO_4)_2$ [7], $RbFe(HPO_4)_2$ [8], $(NH_4)In(HPO_4)_2$ [9], $LiIn(HPO_4)_2$ [10] and $M^IV(HPO_4)_2$ (M^I = NH_4, Rb [11], $M^I = NH_4$ [12]). All these structures comprise complex partial structures of alternating $M^{III}O_6$ octahedra and HPO_4 tetrahedra that, connected via common corners, build four-membered rings of polyhedra. Only the crystal structure of $LiIn(HPO_4)_2$ [10] contains an anionic arrangement which is identical to that of the title compound (in terms of topology), but not isotypic.

The crystal structure of $NaSc(HPO_4)_2$ was solved in the acentric space group $C1c1$ [Flack parameter $x = 0.02(2)$]. It comprises scandium in sixfold coordination by oxygen with Sc—O distances ranging from 1.996(2) Å to 2.146(2) Å. Each corner of these distorted octahedra (∠O–Sc–O = 82.80(6)° – 96.30(6)° for adjacent oxygen atoms) is shared by a HPO_4 group. The hydrogenphosphate tetrahedra (d(P—O = 1.506(2) Å – 1.594(2) Å, ∠O–P–O = 103.15(9)° – 113.49(9)°) themselves share the three unprotonated oxygen atoms with adjacent ScO_6 polyhedra. In this manner six- and four-membered rings of alternating octahedra and tetrahedra are formed. As a linear arrangement of the four-membered rings is found (equatorial positions of the ScO_6 octahedra), it is possible to describe the structure by a ladder motif (figure, top) which is a common structural feature in many phosphates. These polyhedral ladders can either be isolated or connected to sheets or 3D networks [13,14]. The title compound comprises waved ladders running along [100] that are connected to adjacent ladders (perpendicular in latitudinal direction) via the apical oxygen atoms of the ScO_6 octahedra forming a 3D network. Sodium is located in the cavities of the network (figure, bottom) and is six- to sevenfold coordinated by oxygen in the Na—O distance range between 2.3 Å and 3.0 Å.

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Table 1. Data collection and handling.

Crystal:	colorless fragment, size 0.04 × 0.1 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	16.88 cm^{-1}
Diffractometer, scan mode:	Rigaku R-axis RAPID, ω
$2\theta_{max}$:	70.8°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9861, 4494
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4459
$N(param)_{refined}$:	225
Programs:	SHELXL-97 [15], DIAMOND [16]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(101)	4a	0.9653	−0.0297	1.0151	0.25(5)
H(121)	4a	0.9377	0.1197	1.2609	0.15(3)
H(131)	4a	0.5299	0.0919	1.3586	0.04(1)
H(151)	4a	0.3945	−0.0627	1.0431	0.11(2)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sc(1)	4a	0.00000(4)	0.13331(2)	0.00001(4)	0.0069(2)	0.0081(1)	0.0090(1)	0.0001(1)	0.0038(1)	−0.0002(1)
Sc(2)	4a	0.47028(4)	0.11256(2)	0.96206(4)	0.0079(2)	0.0082(1)	0.0086(1)	0.0001(1)	0.0047(1)	−0.0002(1)
P(1)	4a	0.37304(6)	0.19231(3)	0.24762(6)	0.0085(2)	0.0095(2)	0.0107(2)	−0.0017(2)	0.0057(2)	−0.0029(1)
P(2)	4a	0.80470(5)	0.22482(3)	0.17431(6)	0.0079(2)	0.0093(2)	0.0104(2)	−0.0017(2)	0.0047(2)	−0.0018(1)
P(3)	4a	0.67509(6)	0.01552(3)	0.82124(6)	0.0097(2)	0.0091(2)	0.0094(2)	−0.0011(2)	0.0055(2)	−0.0023(1)
P(4)	4a	0.15861(6)	−0.00204(3)	0.85168(6)	0.0082(2)	0.0087(2)	0.0096(2)	−0.0003(2)	0.0044(2)	−0.0014(1)
Na(1)	4a	0.5374(1)	0.33222(8)	0.1314(1)	0.0326(6)	0.0444(7)	0.0247(5)	−0.0055(5)	0.0140(5)	−0.0118(5)
Na(2)	4a	0.6039(1)	0.19032(6)	0.7168(1)	0.0240(5)	0.0166(4)	0.0374(5)	0.0042(4)	0.0165(4)	0.0105(4)
O(1)	4a	0.6367(2)	−0.04113(9)	0.6694(2)	0.0176(8)	0.0182(6)	0.0133(6)	−0.0023(5)	0.0079(5)	−0.0084(5)
O(2)	4a	0.4082(2)	0.1603(1)	0.1174(2)	0.0220(9)	0.0274(8)	0.0207(7)	−0.0021(6)	0.0148(6)	−0.0113(6)
O(3)	4a	0.0872(2)	0.07532(9)	0.8674(2)	0.0178(8)	0.0120(6)	0.0169(6)	0.0026(5)	0.0113(6)	−0.0023(5)
O(4)	4a	0.0532(2)	−0.04301(9)	0.6786(2)	0.0169(8)	0.0184(7)	0.0147(6)	−0.0032(6)	0.0064(5)	−0.0072(5)
O(5)	4a	0.5368(2)	0.05690(9)	0.8032(2)	0.0139(7)	0.0178(7)	0.0144(6)	0.0022(5)	0.0099(5)	−0.0015(5)
O(6)	4a	0.4424(2)	0.27618(8)	0.3112(2)	0.0157(8)	0.0124(6)	0.0168(6)	−0.0057(5)	0.0096(5)	−0.0057(5)
O(7)	4a	0.7863(2)	0.08076(8)	0.8380(2)	0.0114(7)	0.0141(6)	0.0156(6)	−0.0041(5)	0.0038(5)	−0.0005(5)
O(8)	4a	0.6390(2)	0.20562(9)	0.0367(2)	0.0115(7)	0.0136(6)	0.0169(6)	−0.0046(5)	0.0048(5)	−0.0016(5)
O(9)	4a	0.2034(2)	0.19279(9)	0.1732(2)	0.0088(7)	0.0177(6)	0.0160(6)	−0.0029(5)	0.0054(5)	−0.0055(5)
O(10)	4a	0.7545(2)	−0.0435(1)	−0.0148(2)	0.0227(9)	0.0187(7)	0.0175(7)	0.0057(6)	0.0116(6)	0.0063(5)
O(11)	4a	0.9071(2)	0.21212(9)	0.1058(2)	0.0176(8)	0.0169(7)	0.0233(7)	−0.0004(6)	0.0144(6)	−0.0049(5)
O(12)	4a	0.8561(2)	0.1643(1)	0.3340(2)	0.0209(8)	0.0205(7)	0.0188(7)	−0.0056(6)	0.0054(6)	0.0080(6)
O(13)	4a	0.4532(2)	0.13553(9)	0.4170(2)	0.0190(8)	0.0157(7)	0.0185(7)	0.0011(5)	0.0062(6)	0.0049(5)
O(14)	4a	0.3133(2)	0.01640(9)	0.8775(2)	0.0126(8)	0.0148(6)	0.0292(8)	−0.0038(5)	0.0119(6)	−0.0081(6)
O(15)	4a	0.1835(2)	−0.0643(1)	−0.0026(2)	0.031(1)	0.0232(8)	0.0200(7)	0.0058(7)	0.0133(7)	0.0099(6)
O(16)	4a	0.8229(2)	0.31013(8)	0.2501(2)	0.0144(7)	0.0109(6)	0.0161(6)	−0.0021(5)	0.0052(5)	−0.0067(5)

References

1. Suzuki, T.; Yoshida, K.; Uematsu, K.; Kodama, T.; Toda, K.; Ye, Z.-G.; Ohashi, M.; Sato, M.: Structure refinement of lithium ion conductors $Li_3Sc_2(PO_4)_3$ and $Li_{3-2x}(Sc_{1-x}M_x)_2(PO_4)_3$ (M = Ti, Zr) with $x = 0.10$ by neutron diffraction. Solid State Ionics **113** (1998) 89-96.
2. Suzuki, T.; Yoshida, K.; Uematsu, K.; Kodamo, T.; Toda; K.; Ye, Z. G.; Sato, M.: Stabilization of superionic conduction phase in $Li_3Sc_2(PO_4)_3$. Solid State Ionics **104** (1997) 27-33.
3. Susman, S.; Delbecq, C. J.; Brun, T. O.; Prince, E.: Fast ion transport in the NASICON analog $Na_3Sc_2(PO_4)_3$: Structure and conductivity. Solid State Ionics **9** (1983) 839-844.
4. Tamura, S.; Imanaka, N.; Adachi, G.: A new trivalent cationic conducting solid electrolyte with NASICON-type structure. Solid State Ionics **136/137** (2000) 423-426.
5. Riou, D.; Fayon, F.; Massiot, D.: Hydrothermal Synthesis, Structure Determination, and Solid-State NMR Study of the First Organically Templated Scandium Phosphate. Chem. Mater. **14** (2002) 2416-2420.
6. Bull, I.; Young, V.; Teat, S. J.; Peng, L.; Grey, C. P.; Parise, J. P.: Hydrothermal Synthesis and Structural Characterization of Four Scandium Phosphate Frameworks. Chem. Mater. **15** (2003) 3818-3825.
7. Yakubovich, O. V.: $(NH_4)Fe[HPO_4]_2$ Crystalline-Structure. Kristallografiya **38** (1993) 43-48.
8. Lii, K.-H.; Wu, L.-S.: $RbFe(HPO_4)_2$: an iron(III) phosphate with an intersecting tunnel structure. J. Chem. Soc., Dalton Trans. (1994) 1577-1580.
9. Mao, S.-Y.; Li, M.-R.; Mi, J.-X.; Chen, H.-H.; Deng, J.-F.; Zhao, J.-T.: Crystal structure of ammonium indium di(hydrogenmonophosphate), $(NH_4)In(PO_3(OH))_2$. Z. Kristallogr. NCS **217** (2002) 311-312.
10. Gurbanova, O. A.; Belokoneva, E. L.; Dimitrova, O. V.; Al'-Ama, A. G.: The new phosphate $LiIn[PO_3(OH)]_2$: Synthesis and crystal structure. Russ. J. Inorg. Chem. **46** (2001) 1302-1307.
11. Haushalter, R. C.; Wang, Z.-W.; Thompson, M. E.; Zubieta, J.: Hydrothermal synthesis and structural characterization of reduced vanadium phosphate: α-$Rb(V(III)(HPO_4)_2)$, β-$Rb(V(III)(HPO_4)_2)$ and $NH_4(V(III)(HPO_4)_2)$, octahedral-tetrahedral framework solids. Inorg. Chim. Acta **232** (1995) 83-89.
12. Bircsak, Z.; Harrison, W. T. A.: α-ammonium vanadium hydrogen phosphate, α-$(NH_4)V(HPO_4)_2$. Acta Crystallogr. C**54** (1994) 1195-1197.
13. Hawthorne, F. C.: Structural Aspects of Oxide and Oxysalt Crystals. Acta Crystallogr. B**50** (1994) 481-510.
14. Hawthorne, F. C.: Structure and chemistry of phosphate minerals. Mineral. Magaz. **63** (1998) 141-164.
15. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
16. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 2.0f. Crystal Impact GbR, Bonn, Germany 1998.