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Structure of Trisodium Hydrogenorthosilicate Monohydrate

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Abstract. $Na_3HSiO_4.H_2O$, $M_r = 180{\cdot}08$, monoclinic, $P2_1/c$, $a = 7{\cdot}898\,(1)$, $b = 5{\cdot}960\,(1)$, $c = 11{\cdot}142\,(1)$ Å, $\beta = 105{\cdot}57\,(1)^\circ$, $V = 505{\cdot}3$ Å^3, $Z = 4$, $D_m = 2{\cdot}25$ (flotation), $D_x = 2{\cdot}36$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0{\cdot}7107$ Å, $\mu(x) = 0{\cdot}63$ mm^{-1}, $F(000) = 360$, $T = 296$ K, $R = 0{\cdot}019$ for 758 independent reflections. The crystal structure of $Na_3[SiO_3(OH)].H_2O$ consists of chains of hydrogen-bonded $[SiO_3(OH)]^{3-}$ tetrahedra which are arranged along the twofold screw axis. The hydrogen bonds of the chain $O_3SiOH\cdots O_3SiOH$ are short and strong [O(1)—H···O(4) = 2·597 (3) Å, 172 (4)°]. The chains are interconnected by the Na atoms and hydrogen bonds from the H_2O molecule. CN = 6 and 5 are observed for the Na atoms and CN = 5 for O(5) of the H_2O molecule.

Introduction. Two series of crystalline hydrate phases exist in the alkali-rich section of the system Na_2O–SiO_2–H_2O: $Na_2[SiO_2(OH)_2].nH_2O$ (n = 8,7,5,4) series with a Na_2O:SiO_2 ratio of 1:1 and $Na_3[SiO_3(OH)].nH_2O$ (n = 5,2,1,0) series with a Na_2O:SiO_2 ratio of 3:2.

Both series are of considerable interest in our fundamental study on the melting mechanisms of hydrate phases because of their different thermal properties. The four members of the 1:1 series show congruent but irreversible melting. Extensive thermoanalytical experiments suggest a close relationship between the supercooled melts of the 1:1 series hydrates which show glass points between 227 and 273 K and the well known waterglass materials in the more SiO_2-rich section of the sodium–silicate–water system (Felsche, Ketterer & Schmid, 1984, 1985). This is in contrast to the 3:2 series. These hydrates undergo thermal decomposition in a peritectic scheme of reaction,

$$Na_3[SiO_3OH].5H_2O \xrightarrow[N_2]{314\ K} \alpha\text{-}Na_3[SiO_3OH].2H_2O + 3H_2O\uparrow$$

$$\alpha\text{-}Na_3[SiO_3OH].2H_2O \xrightarrow[N_2]{358\ K} Na_3[SiO_3OH].1H_2O + 1H_2O\uparrow$$

$$Na_3(SiO_3OH].1H_2O \xrightarrow[N_2]{413\ K} Na_3[SiO_3OH] + 1H_2O\uparrow$$

as recently shown by thermogravimetry, differential thermal analysis and X-ray powder diffraction heating experiments (Schmid & Felsche, 1983, 1984).

The members of the 1:1 series show monomeric dihydroxo anions $[SiO_2(OH)_2]^{2-}$. Special features of the hydrogen-bonding system around the silicate tetrahedra and in the packing of sodium–oxygen polyhedra have been revealed by X-ray and neutron single-crystal structure analyses: $Na_2[SiO_2(OH)_2].8H_2O$ [Jamieson & Dent-Glasser, 1966*a*, *b* (X-ray); Schmid, Felsche & McIntyre, 1984 (neutron)], $Na_2[SiO_2(OH)_2].7H_2O$ [Dent-Glasser & Jamieson, 1976 (X-ray); Felsche, Ketterer, Schmid & Gregson, 1987 (neutron)], $Na_2[SiO_2(OH)_2].5H_2O$ [Jamieson & Dent-Glasser, 1967 (X-ray); Williams & Dent-Glasser, 1971 (neutron)] and $Na_2[SiO_2(OH)_2].4H_2O$ [Jost & Hilmer, 1966 (X-ray); Schmid, Felsche & McIntyre, 1985 (neutron)].

In the 3:2 series the most characteristic building units are tetrahedral hydrogenorthosilicate anions $[SiO_3(OH)]^{3-}$ which are linked to each other by hydrogen bonds from their OH groups. Dimeric units of edge-sharing tetrahedra show up in the pentahydrate $Na_3[SiO_3(OH)].5H_2O$ (Smolin, Shepelev & Butikova, 1973). Endless chains $\cdots HOSiO_2O\cdots HOSiO_2O\cdots$ have been revealed in α- and β-$Na_3[SiO_3(OH)].2H_2O$ (Schmid, Huttner & Felsche, 1979; Schmid, Zsolnay, Felsche & Huttner, 1981). We report here on the crystal structure of the monohydrate $Na_3[SiO_3(OH)].H_2O$.

Experimental. Single crystals of $Na_3[SiO_3(OH)].H_2O$ were synthesized from aqueous solutions containing 16·93% Na_2O, 2·42% SiO_2 and 80·65% H_2O (by weight; starting concentrations) at 338 K. The solutions were kept in a closed volume which contained NaOH pellets as a drying agent using small glass containers for the solutions. The crystals are extremely hygroscopic and sensitive against attack by CO_2. Thus all experimental work in the course of preparation and polarizing microscopy had to be done under thorough exclusion of CO_2 and H_2O in a specially prepared glove box (Braun MB 200). For all the analytical procedures of Buerger–precession and Weissenberg experiments as well as in the intensity collection on the diffractometer, the crystal had to be sealed in a quartz capillary. Quartz tubes turned out to be more suitable than the regular type of lithium borate glass tubes. D_m was measured by the flotation method using CCl_4 and CH_3I as flo-

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tation liquids. The crystal examined showed a flat prismatic shape of dimensions 3·0 × 0·2 × 0·07 mm.

A total of 1864 reflections were measured on a CAD-4 diffractometer (Enraf–Nonius, Delft) up to $(\sin\theta/\lambda)_{\max} = 0{\cdot}595$ Å^{-1} with $h_{\min} = -9$, $h_{\max} = 9$; $k_{\min} = -4$, $k_{\max} = 4$; $l_{\min} = 0$, $l_{\max} = 13$. Refined lattice parameters from 25 reflections with $6 < \theta < 16°$. Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å. $\omega/2\theta$ scans. Three standard reflections were measured every 4000 s during the experiment; reflections $\bar{2}11$, $\bar{1}35$ and $\bar{1}31$ showed max. intensity variation of 1%. After data reduction, the raw intensities were corrected for absorption employing the empirical absorption correction method using ψ-scan data $0 < \psi < 360°$ of eight reflections with $80 < \chi < 90°$. Max. correction was 0·9434, min. correction was 0·9992. A total of 853 unique reflections remained after merging equivalent reflections, yielding $R_{\rm int} = 0{\cdot}011$. The structure was solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). Difference Fourier map revealed the H-atom positions. 95 parameters were refined by full-matrix least squares based on 758 F magnitudes; unit weights. 95 reflections with $I < \sigma(I)$ were rejected as unobserved. Final $R = 0{\cdot}019$, $wR = 0{\cdot}023$ $S = 0{\cdot}625$. Secondary-extinction correction was applied with $|F_c^*| = |F_c|/(1 + gI_c)$, refined $g = 4{\cdot}30 \times 10^{-6}$. Largest final least-squares (Δ/σ) ratio = 0·03. Maximal $\Delta\rho = +0{\cdot}23$ e Å^{-3}, minimal $\Delta\rho = -0{\cdot}22$ e Å^{-3} in final difference Fourier synthesis. Scattering factors for neutral atoms taken from *International Tables for X-ray Crystallography* (1974). All computer programs used from the Enraf–Nonius *Structure Determination Package* (Enraf–Nonius, 1986).

Table 1. *Final atomic parameters for* $Na_3[SiO_3(OH)].H_2O$ *at* 296 K *with e.s.d.'s in parentheses*

$$B_{\rm eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	$B_{\rm eq}$(Å^2)
Si	0·6907 (1)	0·2087 (1)	0·3647 (1)	0·61 (1)
Na(1)	0·2500 (1)	0·0102 (2)	0·3342 (1)	1·24 (2)
Na(2)	0·3990 (1)	0·3071 (2)	0·5667 (1)	1·30 (2)
Na(3)	0·9772 (1)	−0·2439 (2)	0·4391 (1)	1·21 (2)
O(1)	0·4902 (2)	0·2715 (3)	0·3826 (1)	1·10 (3)
O(2)	0·7694 (2)	0·0138 (3)	0·4636 (1)	0·89 (3)
O(3)	0·8098 (2)	0·4343 (3)	0·3914 (1)	0·90 (3)
O(4)	0·6631 (2)	0·1359 (3)	0·2198 (1)	0·97 (3)
O(5)	0·0739 (2)	0·3471 (3)	0·2789 (2)	1·48 (3)
H(11)	0·553 (4)	0·887 (6)	0·156 (3)	1·3 (7)*
H(51)	−0·001 (4)	0·398 (5)	0·316 (3)	1·0†
H(52)	0·143 (4)	0·466 (6)	0·285 (3)	0·8 (7)*

* Refined isotropically.

† Refined with isothermal temperature factor fixed at 1·0 Å^2.

Table 2. *Bond lengths* (Å) *and angles* (°) *in* $Na_3[SiO_3(OH)].H_2O$ *at* 296 K *with e.s.d.'s in parentheses*

The hydrogen-bonding system

The $[SiO_3(OH)]^{3-}$ tetrahedron			
H(11)—O(1)	0·83 (5)		
H(11)···O(4)	1·78 (5)	O(1)—H(11)···O(4)	172 (4)
O(1)···O(4)	2·597 (3)	Si—O(1)—H(11)	113 (3)
The H_2O molecule			
H(51)—O(5)	0·87 (4)		
H(51)···O(3)	1·92 (4)	O(5)—H(51)···O(3)	166 (4)
O(5)···O(3)	2·756 (3)		
H(52)—O(5)	0·88 (4)		
H(52)···O(4)	1·85 (4)	O(5)—H(52)···O(4)	159 (4)
O(5)···O(4)	2·695 (3)	H(51)—O(5)—H(52)	100 (4)

Bond lengths in the Na–O polyhedra

Na(1)—O(1)	2·402 (2)	Na(2)—O(2)	2·302 (2)
Na(1)—O(2)	2·304 (2)	Na(2)—O(3)	2·394 (2)
Na(1)—O(3)	2·470 (2)	Na(2)—O(4)	2·338 (2)
Na(1)—O(4)	2·456 (2)	Na(3)—O(2)	2·317 (2)
Na(1)—O(5)	2·427 (2)	Na(3)—O(2′)	2·428 (2)
Na(1)—O(5′)	2·710 (2)	Na(3)—O(3)	2·310 (2)
Na(2)—O(1)	2·359 (2)	Na(3)—O(3′)	2·446 (2)
Na(2)—O(1′)	2·670 (2)	Na(3)—O(5)	2·414 (2)

Discussion. The final atomic parameters for $Na_3[SiO_3(OH)].H_2O$ are listed in Table 1.† The bond lengths and angles of interest in the hydrogen-bonding system and the Na–O polyhedra are listed in Table 2.

The crystal structure of $Na_3[SiO_3(OH)].H_2O$ is built up of hydrogen-bonded $[SiO_3(OH)]^{3-}$ tetrahedra forming endless chains along the [010] direction (Fig. 1). Bond lengths and angles in the tetrahedron are given in Fig. 2. The hydrogen bond between O(1) and O(4′) of adjacent tetrahedra has a length of 2·597 (3) Å. The angle O(1)—H(1)···O(4′) [172 (4)°] suggests a nearly linear geometry of the hydrogen bond. This hydrogen bond is stronger than the corresponding bonds in both forms of the dihydrate $Na_3[SiO_3(OH)].2H_2O$ which show bond lengths of 2·639 (4) Å in the high-temperature form (Schmid, Zsolnay, Felsche & Huttner, 1981) and of 2·917 (2) Å in the low-temperature form (Schmid, Huttner & Felsche, 1979).

It is worthwhile mentioning that the pentahydrate of the given 3:2 series does not show the chain geometry of hydrogen-bonded $[SiO_3(OH)]^{3-}$ tetrahedra but rather dimeric groupings. The hydrogen bonds of the edge-sharing bitetrahedra in $Na_3[SiO_3(OH)].5H_2O$ show even shorter lengths of 2·560 (3) Å, however (Smolin, Shepelev & Butikova, 1973). The hydrogen bonds correlate well with the Si—OH distances in the given series of hydrates $Na_3[SiO_3(OH)].nH_2O$. The values observed are 1·690 (2) Å for the monohydrate, 1·685 (3) for the high- and 1·703 (2) Å for the low-temperature form

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† Lists of structure factors, anisotropic thermal parameters and a table containing all bond lengths and angles in the structure have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52728 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of the dihydrate and 1·677 (3) Å for the pentahydrate. Comparison of the angles O—Si—O with the angles O—Si—OH in $Na_3[SiO_3(OH)].H_2O$ (Fig. 2) and with the corresponding data observed in the tetrahedra of the other 3:2 hydrates also agrees well with the observation that O—Si—OH < O—Si—O in silicate tetrahedra.

Coordination numbers for the Na–O polyhedra in $Na_3[SiO_3(OH)].H_2O$ are 6 for Na(1) and 5 for Na(2) and Na(3). This is in contrast to the higher hydrates of this series where CN = 6 and 7 are commonly observed. Mean Na—O bond lengths are 2·422 Å for $Na_3[SiO_3(OH)].H_2O$, 2·568 and 2·574 Å for both forms of $Na_3[SiO_3(OH)].2H_2O$ and 2·527 Å for the pentahydrate [Schmid, Huttner & Felsche (1979); Schmid, Zsolnay, Felsche & Huttner (1981); Smolin, Shepelev & Butikova (1973)].

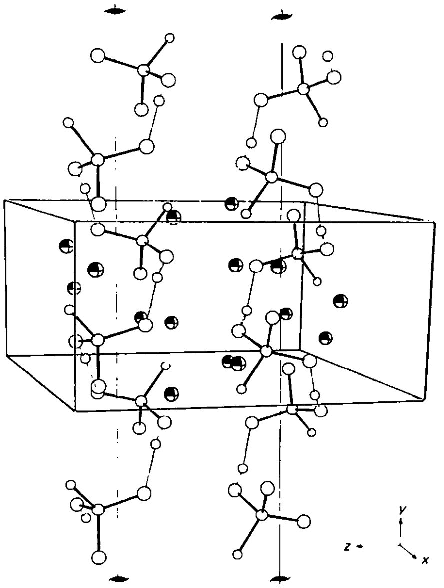

Fig. 1. Endless chains of hydrogen-bonded $[SiO_3(OH)]^{3-}$ tetrahedra following the 2_1 screw axis along [010]. Shaded spheres show sodium ions. Hydrate water molecules are not shown for clarity.

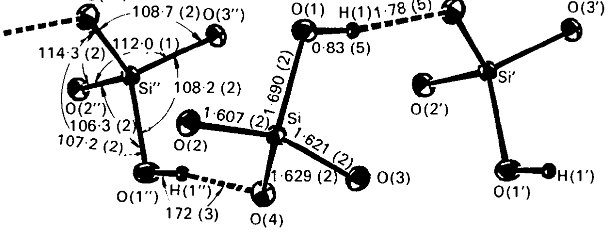

Fig. 2. Bond lengths (Å) and angles (°) shown for the hydrogen-bonded $[SiO_3(OH)]^{3-}$ tetrahedra.

The coordination number of the O atom O(5) of the H_2O molecule of $Na_3[SiO_3(OH)].H_2O$ is 5. The coordination is of class 3 type *O* geometry with one Na in the H—O—H plane and two further Na atoms perpendicular, one Na above and one Na below that plane following the proposal given by Ferraris & Franchini-Angela (1972). No hydrogen bonding is observed between adjacent O atoms O(5) of the water molecule. All hydrogen bonding observed is between the oxygens of the silicate tetrahedra and O(5) of the water molecules and also between the oxygens of adjacent tetrahedra. The corresponding hydrogen-bonding data are listed in Table 2. O—H distances in the monohydrate show systematic shortening due to the features of X-ray scattering. O—H···O angles range between 159 and 171°, values which are regular and are also commonly observed in neutron diffraction data. The hydrogen atom H(51) of the water molecule did not refine positive definitely with *B* set free and had to be refined with *B* fixed at 1·0 Å^2. Fixing the temperature factor of H(51) at 1·0 Å^2, which was approximately the mean of the *B* values of the other H atoms did not influence its positional parameters. Neutron diffraction experiments have been started to improve the given data.

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$K_2Mo_3AlP_8O_{28}$: a Tunnel Structure Isotypic with $Na_{0\cdot5}MoP_2O_7$

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Abstract. $K_2Mo_3AlP_8O_{28}$, $M_r = 544\cdot39$, triclinic, $P\bar{1}$, $a = 4\cdot8171\ (8)$, $b = 7\cdot133\ (2)$, $c = 7\cdot998\ (2)$ Å, $\alpha = 90\cdot53\ (2)$, $\beta = 92\cdot95\ (2)$, $\gamma = 105\cdot18\ (2)°$, $V = 264\cdot8\ (2)$ Å^3, $Z = 0\cdot5$, $D_x = 3\cdot41$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0\cdot71073$ Å, $\mu = 2\cdot568$ mm^{-1}, $T = 294$ K, $F(000) = 260\cdot50$, $R = 0\cdot061$, $wR = 0\cdot068$ for 856 observed reflections. The host lattice of this phase is built up from MoO_6 and AlO_6 octahedra sharing corners with PO_4 tetrahedra and belongs to the $Na_{0\cdot5}MoP_2O_7$-type structure. The tunnels are fully occupied by K^+ ions and one kind of octahedral site is only occupied by molybdenum, whereas molybdenum and aluminium are distributed at random over the second kind of site.

Introduction. The structural study of the mixed-valence molybdenum phosphate $Na_{0\cdot30}MoP_2O_7$, (Leclaire, Grandin & Raveau, 1988), has shown the possibility of formation of non-stoichiometric oxides, with large tunnels partly occupied by sodium. In spite of the great size of such octagonal tunnels, no isostructural potassium compound was obtained in the system K–Mo–P–O. In this latter system, another phase, $K_{0\cdot17}MoP_2O_7$, with a different structure was indeed isolated (Leclaire, Borel, Grandin & Raveau, 1989). Considering the mixed valence of molybdenum Mo^{III}/Mo^{IV}, the substitution of aluminium for Mo^{III} was investigated. The present study reports on the structure of a new diphosphate $K_2Mo_3AlP_8O_{28}$, isotypic with $Na_{0\cdot5}MoP_2O_7$.

Experimental. The crystals of this phase were isolated from a nominal composition $K_2Mo_2P_8O_{25}$. This synthesis was performed in two steps. Firstly, an appropriate mixture of K_2CO_3, $H(NH_4)_2PO_4$ and MoO_3 was heated to 673 K in air to eliminate CO_2, H_2O and NH_3. Secondly, the resulting finely ground product, mixed with an appropriate amount of molybdenum, was placed in an alumina crucible and sealed in an evacuated silica ampoule. This sample was then heated to 1073 K for 48 h and quenched at room temperature.

Purple crystals $0\cdot148 \times 0\cdot024 \times 0\cdot024$ mm. Enraf–Nonius CAD-4 diffractometer. Mo $K\alpha$ radiation. Unit cell: least squares on 25 reflections $\pm 2\theta$: $36 \le 2\theta \le 44°$. Intensity: measurement by ω–θ scan of $(1\cdot25 + 0\cdot35\tan\theta)°$ and with a $(1 + \tan\theta)$ mm counter slit; determined by a study of some reflections in the $\omega\theta$ plane. Scan speed adjusted so as to obtain $\sigma(I)/I \le 0\cdot018$ or to approach it in a time limited to 60 s. Three standard reflections (332, 323, 046) monitored for count, every 2000 s, and for orientation every 600 reflections; no appreciable trends. 4552 reflections measured, 4552 unique. 856 reflections ($h_{\max} = 9$, $k_{\max} = 14$, $l_{\max} = 15$), $2 \le \theta \le 45°$ with $I/\sigma(I) \ge 3$ used to solve and refine the structure. No correction made for extinction or absorption. Structure solved by heavy-atom method. Refinement by full-matrix least squares using F's. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations performed on a MicroVAX II with the *SDP* system (B.A. Frenz & Associates Inc., 1982). 65 parameters refined. $w = 1/\sigma(I)$. $(\Delta/\sigma)_{\max} = 0\cdot004$, $\Delta\rho \le 1\cdot8$ e Å^{-3}, $R = 0\cdot061$, $wR = 0\cdot068$, $S = 0\cdot98$. Atomic parameters are given in Table 1.* The refinement of the occupancy factor of the 0·5, 0·5, 0·5 position using molybdenum diffusion tables leads to a number of electrons corresponding to $\frac{1}{2}$ Mo and $\frac{1}{2}$ Al distributed at random over this position in agreement with microprobe analysis.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52811 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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