Fig. 1. [GeCl(H₂PO₂)]: a-axis projection.

$(M-O-P-O-)_\infty$ (M = Ge or Sn) extending parallel to c. Long bridges of the type $M-O-P-O-M$ are present in other phosphinates (Weakley, 1978a,b, 1979). The nearest neighbours of each M atom (two O atoms and one Cl) define the base of a trigonal pyramid. The bond angles (Table 2) are close to 90° at Ge and 86° at Sn. The bond lengths and angles at Sn are within the ranges found for other compounds with pyramidal $Sn^{II}Cl_3$ or $Sn^{II}O_3$ groups (Zubieta & Zuckerman, 1978). The bond-length differences $(Sn-O) - (Ge-O)$ and $(Sn-Cl) - (Ge-Cl)$ are both ca 0·21 Å, and imply a covalent radius for Ge^{II} of about 1·32 Å, compared with 1·22 Å for Ge^{IV} (Alcock, 1972). The Ge—Cl length of 2·35 Å is to be compared with 2·25, 2·54 Å in pyramidal [GeCl₂(Ph₃P)] (Bokii, Struchkov, Kolesnikov, Rogazhin & Nefedov, 1975) and with 2·32 Å for pyramidal $GeCl_3^-$ in the rhombohedral form of Cs[GeCl₃] (Christensen & Rasmussen, 1965). In [Ge(C₄H₈O₂)Cl₂] (Kulishov, Bokii, Struchkov, Nefedov, Kolesnikov & Perl'mutter, 1970) the Ge—Cl bonds are shorter (2·25, 2·28 Å) but in

compensation the Ge—O bonds are rather long (2·41, 2·48 Å).

Each M atom in [MCl(H₂PO₂)] makes several contacts with atoms in neighbouring chains, on the side remote from the ligand atoms, at distances less than the van der Waals radii sum though much greater than normal covalent bond lengths. Alcock (1972), reviewing secondary bonding, gives van der Waals radii as: O, 1·52; Cl, 1·75; Ge, 1·95; Sn, 2·10 Å. On the basis of these values, the Ge···Cl, Sn···Cl, and Sn···O contacts listed in Table 2 (but not the Ge···O contact) indicate weak bonds which serve to cross-link the chains. For comparison, the Ge···Cl weak contacts in Cs[GeCl₃] and [Ge(C₄H₈O₂)Cl₂] are 3·13 and 3·51 Å respectively. As in Cs[GeCl₃], the overall coordination (3 + 3) in [GeCl(H₂PO₂)] is distorted octahedral.

References

ALCOCK, N. W. (1972). Adv. Inorg. Chem. Radiochem. 15, 1–58.

BOKII, N. G., STRUCHKOV, YU. T., KOLESNIKOV, S. P. ROGAZHIN, I. S. & NEFEDOV, O. M. (1975). Izv. Akad. Nauk SSSR Ser. Khim. pp. 812–815.

CHRISTENSEN, A. N. & RASMUSSEN, S. E. (1965). Acta Chem. Scand. 19, 421–428.

EVEREST, D. A. (1951). J. Chem. Soc. pp. 2903–2905.

EVEREST, D. A. (1952). J. Chem. Soc. pp. 1670–1672.

KULISHOV, V. I., BOKII, N. G., STRUCHKOV, YU. T., NEFEDOV, O. M., KOLESNIKOV, S. P. & PERL'MUTTER, B. L. (1970). Zh. Strukt. Khim. 11, 71–74.

SHELDRICK, G. M. (1976). SHELX 76. Program for crystal structure determination. Univ. of Cambridge, England.

WEAKLEY, T. J. R. (1978a). Acta Cryst. B34, 281–282.

WEAKLEY, T. J. R. (1978b). Acta Cryst. B34, 3756–3758.

WEAKLEY, T. J. R. (1979). Acta Cryst. B35, 42–45.

ZUBIETA, J. A. & ZUCKERMAN, J. J. (1978). Prog. Inorg. Chem. 24, 251–475.

The Structure of Trisodium Hydrogensilicate Dihydrate

By R. Schmid, G. Huttner and J. Felsche

Fakultät für Chemie, Universität Konstanz, Federal Republic of Germany

Abstract. Na₃HSiO₄.2H₂O, orthorhombic, Pbca, a = 10·470 (4), b = 18·704 (12), c = 6·059 (3) Å, Z = 8, D_c = 2·218 Mg m⁻³, V = 1186·5 Å³, λ(Mo Kα) = 0·7107 Å. The structure consists of [HSiO₄]³⁻ tetrahedra, linearly arranged along the a axis and connected by Si—O···H—O—Si hydrogen bonds. These chains are linked to each other by the Na atoms, and by hydrogen bonds from the water molecules. The Na atoms show irregular coordination with five or six oxygens within the first coordination sphere. The two crystallographically independent water molecules are chemically different. One H₂O forms two hydrogen

bonds to link two chains, whereas the second forms only one hydrogen bond to an $[HSiO_4]^{3-}$ tetrahedron and has an additional short O–H bond.

Introduction. The present work was carried out to correlate data obtained from thermal analysis with the actual structure of $Na_3HSiO_4.2H_2O$. By means of chemical and thermal analysis (TG, DTG, DTA) we found that the composition of the compound is $3Na_2O.2SiO_2.5H_2O$ and is therefore very similar to $3Na_2O.2SiO_2.11H_2O$ which Smolin, Shepelev & Butikova (1973) showed to be $Na_3HSiO_4.5H_2O$. By means of X-ray analysis carried out on $3Na_2O.2SiO_2.5H_2O$ we were able to show that $3Na_2O.2SiO_2.5H_2O$ is actually $Na_3HSiO_4.2H_2O$. Crystals of $Na_3HSiO_4.2H_2O$ were obtained at 299 K

Table 1. *Final atomic parameters for* $Na_3HSiO_4.2H_2O$

Numbers in parentheses give the e.s.d.'s corresponding to the last significant digit.

	x	y	z	B (Å^2)
Si	0.06928 (6)	0.12864 (3)	0.2285 (1)	0.67 (2)
Na(1)	0.0052 (1)	0.18222 (5)	−0.2820 (2)	1.32 (2)
Na(2)	0.28389 (9)	0.10802 (5)	0.5269 (2)	1.10 (2)
Na(3)	−0.04991 (8)	−0.01521 (4)	0.2387 (2)	1.03 (2)
O(1)	−0.0039 (1)	0.09777 (7)	0.0166 (3)	0.88 (3)
O(2)	0.2114 (2)	0.16015 (8)	0.1798 (3)	1.01 (3)
O(3)	0.0766 (2)	0.07116 (8)	0.4291 (3)	0.98 (3)
O(4)	−0.0185 (2)	0.19823 (8)	0.3279 (3)	1.08 (3)
O(5)	0.2693 (2)	0.03459 (9)	0.8523 (3)	1.45 (4)
O(6)	0.2435 (2)	0.19889 (8)	−0.2318 (3)	1.33 (3)
H(41)	−0.110 (3)	0.190 (1)	0.314 (5)	1.50 (0)
H(51)	0.170 (3)	0.007 (2)	0.410 (5)	1.50 (0)
H(52)	0.270 (2)	0.062 (2)	−0.050 (5)	1.50 (0)
H(61)	0.230 (3)	0.190 (2)	−0.070 (5)	1.50 (0)
H(62)	0.240 (2)	0.241 (2)	0.263 (5)	1.50 (0)

Table 2. *Bond lengths* (Å) *and angles* (°), *with e.s.d.'s in parentheses corresponding to the last significant digit*

Hydrogen bonds

H(41)–O(4)	0.97 (3)		H(61)–O(6)	1.03 (3)
H(41)···O(2)	1.95 (3)		H(61)···O(2)	1.60 (3)
O(4)···O(2)	2.917 (2)		O(6)···O(2)	2.619 (2)
H(51)–O(5)	1.07 (3)		H(62)–O(6)	1.12 (3)
H(51)···O(3)	1.54 (3)		H(62)···O(2)	1.63 (3)
O(5)···O(3)	2.594 (2)		O(6)···O(2)	2.710 (2)

O(4)–H(41)···O(2)	171 (3)		O(6)–H(61)···O(2)	170 (3)
O(5)–H(51)···O(3)	167 (3)		O(6)–H(62)···O(2)	161 (2)

Water molecules

$H_2O(1)$			$H_2O(2)$	
H(51)–O(5)–H(52)	104 (3)		H(61)–O(6)–H(62)	102 (2)
Na(3)–O(5)–Na(2)	87.63 (6)		Na(2)–O(6)–Na(1)	90.82 (7)
H(51)–O(5)–Na(2)	129 (2)		Na(2)–O(6)–Na(1')	75.59 (6)
H(51)–O(5)–Na(3)	123 (2)		Na(1)–O(6)–Na(1')	165.49 (8)
H(52)–O(5)–Na(2)	105 (2)		H(61)–O(6)–Na(2)	120 (2)
H(52)–O(5)–Na(3)	105 (2)		H(61)–O(6)–Na(1)	91 (2)
			H(61)–O(6)–Na(1')	92 (1)
			H(62)–O(6)–Na(2)	137 (1)
			H(62)–O(6)–Na(1)	95 (1)
			H(62)–O(6)–Na(1')	98 (1)

under closed-system conditions from solutions containing 82.9% H_2O, 14.8% Na_2O and 2.3% SiO_2 (wt %) and were in the form of rectangular prismatic needles. The percentages refer to the original composition of the solution.

The compound is extremely hygroscopic, hence the crystals had to be sealed in glass tubes for the data collection. The dimensions of the crystal were 0.1 × 0.15 × 0.3 mm. The intensity data were not corrected for absorption. 1163 intensities were collected on a Syntex R3 four-circle diffractometer at 173 K (Mo $K\alpha$, $\lambda = 0.71069$ Å). 72 intensities with values $<3\sigma$ were rejected.

The structure was solved by direct methods (Germain, Main & Woolfson, 1971) and subsequently refined by full-matrix least squares using the Syntex *EXTL* structure-solving system. The final R values were 0.031 for 1091 reflections and 0.041 for all observed reflections. The atomic fractional coordinates are reported in Table 1.*

As low-temperature X-ray studies at 173 K showed identical symmetry and nearly identical lattice constants compared with those obtained for the compound at room temperature, the structure was solved at 173 K. All H atoms were unambiguously located by the difference Fourier method and their positions refined by least squares.

Structure factors were calculated with scattering factors taken from *International Tables for X-ray Crystallography* (1965, 1974).

Discussion. The structure of $Na_3HSiO_4.2H_2O$ consists of $[HSiO_4]^{3-}$ tetrahedra linearly arranged along the a axis and joined by Si–O···H–O–Si hydrogen bonds of 2.917 Å between O(4) of the hydroxyl group and O(2) of the next $[HSiO_4]^{3-}$ tetrahedron. These chains are linked by the Na atoms and by two hydrogen bonds from $H_2O(2)$ to H(61) and H(62) with hydrogen-bond distances between O(6) and O(2) of 2.619 and 2.711 Å. However, $H_2O(1)$ forms only one hydrogen bond with H(51) connecting O(5) and O(3) at a distance of 2.594 Å and an O–H···O angle of 167°. $H_2O(1)$ also forms a short O–H bond of 0.80 Å to H(52), see Table 2. This is a remarkable feature, although one must take into consideration that a certain amount of shortening of Y–H bonds is inherent in the X-ray method. Fig. 1 shows the structure.

O–H distances in water molecules in crystalline structures range from 0.86 to 1.04 Å (Baur, 1965, 1972; Ferraris & Franchini-Angela, 1972). However, in $Na_3HSiO_4.2H_2O$ all water O–H bonds involved in hydrogen bonds tend to be longer than is normal for

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such systems, despite the shortening of the O—H bonds inherent in the X-ray method.

Thus the relative shortness of O(5)—H(52) and the relative length of O(5)—H(51) could be explained by the shortness and strength of the one almost linear hydrogen bond formed by $H_2O(1)$.

The strengths of the hydrogen bonds involving the water molecules can be verified by thermal decomposition of the compound. Here the beginning of the
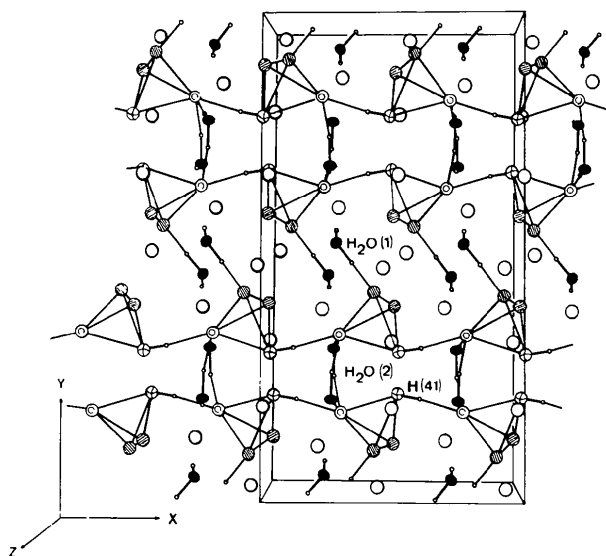

Fig. 1. General view of the structure of $Na_3HSiO_4.2H_2O$ along z. The figure shows the Si—O···H—O—Si-bonded chains of $[HSiO_4]^{3-}$ tetrahedra, the water molecules $H_2O(1)$ and $H_2O(2)$ and the Na atoms. It can be seen that $H_2O(2)$ forms two hydrogen bonds linking two chains at about $0.25z$ and $0.75z$, whereas $H_2O(1)$ forms only one hydrogen bond to a neighbouring $[HSiO_4]^{3-}$ tetrahedron. These two H_2O species are therefore not only crystallographically but also chemically different. As $H_2O(2)$ forms two hydrogen bonds it is released significantly later than $H_2O(1)$ if the compound is studied by thermal analytical methods. ⊕ O(1), ◎ O(2), ◍ O(3), ⬮ O(4), ● O(5,6), ○ Na(1,2,3).

removal of $H_2O(2)$, which forms two hydrogen bonds, is at 425 K, a high temperature for water in crystalline hydrates.

The three crystallographically different Na atoms, Na(1), Na(2) and Na(3), have very distorted coordination polyhedra, Fig. 2. Only Na(1) is roughly octahedrally coordinated with coordination number six. The surroundings of Na(2) and Na(3) are more complicated. These Na atoms effectively have two spheres of coordination. In the first sphere each Na atom has five close O neighbours with Na—O distances ranging from ca $2.3-2.5$ Å. As these polyhedra are very distorted, two second-sphere O atoms fit very well in the gaps created by the distortion. The Na—O distances of the second sphere of coordination are in the range ca $2.9-3.4$ Å. A significant gap from 2.5 to 2.9 Å exists between the radii of the inner and outer spheres. Such a gap does not exist in the Na—O coordination polyhedra of $Na_3HSiO_4.5H_2O$, which have only first-sphere coordination (Smolin et al., 1973).

Neither does this gap exist for Na(1), which is octahedrally coordinated, but long Na—O distances involving Na(1) also occur. Na—O distances of 2.759 and 2.817 Å are long for contacts from first-sphere oxygens to octahedrally coordinated Na atoms, but similar values have been reported in $Na_2H_2SiO_4.5H_2O$, $Na_2H_2SiO_4.7H_2O$ and $Na_3HSiO_4.5H_2O$ (Williams & Dent Glasser, 1971; Dent Glasser & Jamieson, 1976; Jamieson & Dent Glasser, 1966a,b; Smolin et al., 1973), with Na—O distances of 2.759, 2.80 and 2.86 Å.

The water O(5) and O(6) atoms from $H_2O(1)$ and $H_2O(2)$ have very specific surroundings. $H_2O(1)$ almost forms a tetrahedron with H(51) and H(52), and Na(2) and Na(3) which are bonded along the oxygen lone pairs. This is an $A2$ coordination type (Ferraris & Franchini-Angela, 1972). There are additional Na atoms around O(5), Na(2'), Na(3') and Na(3''), but these atoms are at distances of about 3 Å and are therefore more weakly bonded, see Fig. 3(a).
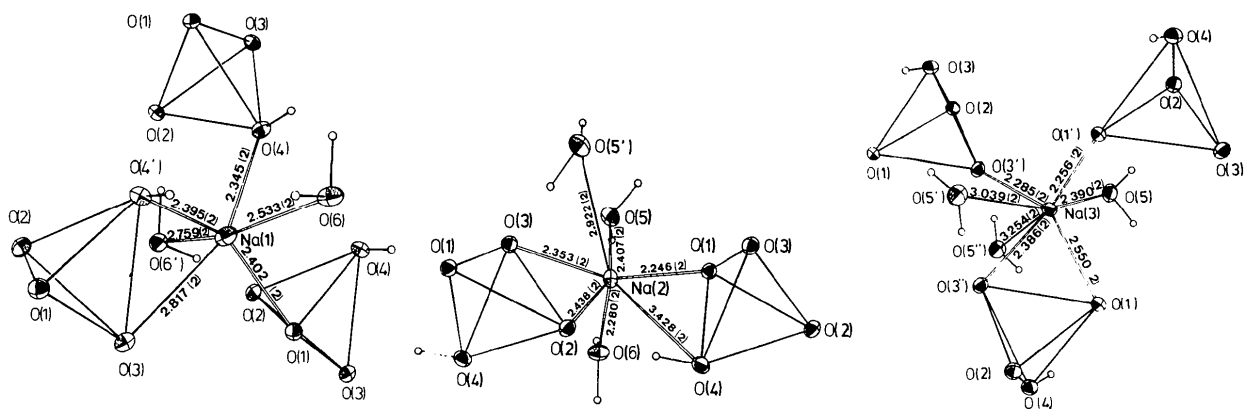

Fig. 2. Oxygen coordination around the three different Na atoms, showing some interatomic distances (Å). Numbers in parentheses are the e.s.d.'s corresponding to the last significant digit.
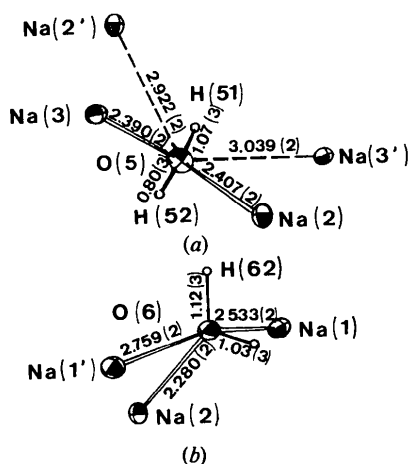
Fig. 3. The water molecules showing interatomic distances (Å) with e.s.d.'s in parentheses. (a) The coordination of $H_2O(1)$. Na(3″) is hidden by O(5) and therefore is omitted. (b) The coordination of $H_2O(2)$.
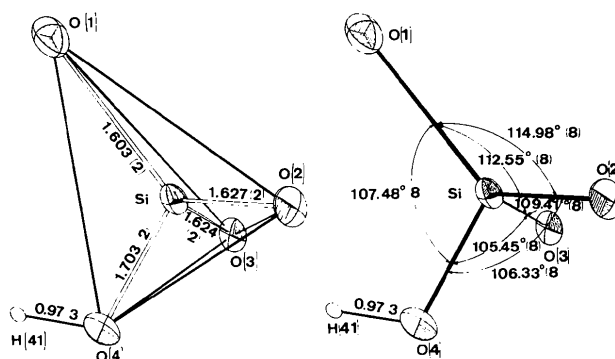

Fig. 4. The $[HSiO_4]^{3-}$ tetrahedron, showing interatomic distances (Å) and angles (°). Numbers in parentheses are the e.s.d.'s corresponding to the last significant digit.

$H_2O(2)$ has only three neighbouring Na atoms in O3-type coordination (Ferraris & Franchini-Angela, 1972), see Fig. 3(b).

In the $[HSiO_4]^{3-}$ tetrahedron, bond lengths and angles are also in agreement with values in the $[HSiO_4]^{3-}$ tetrahedron of $Na_3HSiO_4.5H_2O$ and the $[H_2SiO_4]^{2-}$ tetrahedra of the $Na_2H_2SiO_4.nH_2O$ silicate hydrates with $n = 4, 5, 7, 8$. Normal Si—O and Si—OH distances are about 1·6 and 1·7 Å, respectively, and O—Si—O and O—Si—OH angles about 115 and 109°, respectively (Jost & Hilmer, 1966; Smolin et al., 1973; Dent Glasser & Jamieson, 1976). Angles and distances in the $[HSiO_4]^{3-}$ tetrahedron are reported in Fig. 4.

Nevertheless it is the $[HSiO_4]^{3-}$ tetrahedron which makes the fundamental difference between the structures of $Na_3HSiO_4.2H_2O$ and $Na_3HSiO_4.5H_2O$. Pairs of $[HSiO_4]^{3-}$ tetrahedra are centrosymmetrically arranged in $Na_3HSiO_4.5H_2O$, which are linked by two parallel hydrogen bonds formed by the two H atoms from the hydroxyl groups (Smolin et al., 1973).

References

BAUR, W. H. (1965). Acta Cryst. 19, 909–916.

BAUR, W. H. (1972). Acta Cryst. B28, 1456–1465.

DENT GLASSER, L. S. & JAMIESON, P. B. (1976). Acta Cryst. B32, 705–710.

FERRARIS, G. & FRANCHINI-ANGELA, M. (1972). Acta Cryst. B28, 3572–3583.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). Acta Cryst. A27, 368–376.

International Tables for X-ray Crystallography (1965). Vol. I, 2nd ed. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JAMIESON, P. B. & DENT GLASSER, L. S. (1966a). Acta Cryst. 20, 373–376.

JAMIESON, P. B. & DENT GLASSER, L. S. (1966b). Acta Cryst. 20, 688–693.

JOST, K.-H. & HILMER, W. (1966). Acta Cryst. 21, 583–589.

SMOLIN, YU. I., SHEPELEV, YU. F. & BUTIKOVA, I. K. (1973). Sov. Phys. Crystallogr. 18, 173–176.

WILLIAMS, P. P. & DENT GLASSER, L. S. (1971). Acta Cryst. B27, 2269–2275.