Acta Cryst. (1987). C**43**, 1015–1019

Location and Anisotropic Refinement of Deuterium Atoms in Disodium Dideuteriumsilicate Heptahydrate (D_2O) by Neutron Diffraction; Hydrogen Bonding at 296 K and Thermal Properties

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(*Received* 15 *April* 1986; *accepted* 5 *January* 1987)

Abstract. $Na_2[SiO_2(OD)_2].7D_2O$, $M_r = 282\cdot1$, monoclinic, $P2_1/c$, $a = 8\cdot959$ (2), $b = 13\cdot501$ (4), $c = 10\cdot021$ (3) Å, $\beta = 119\cdot65$ (2)°, $V = 1053\cdot4$ Å^3, $Z = 4$, $D_m = 1\cdot79$, $D_x = 1\cdot78$ Mg m^{-3}, $\lambda = 1\cdot1874$ Å, $\mu(n) = 0\cdot001$ mm^{-1}, $F(000) = 72\cdot82$, $T = 296$ K, $R = 0\cdot0472$ for 1677 independent reflections. The crystal structure of $Na_2[SiO_2(OD)_2].7D_2O$ consists of dimeric units of hydrogen-bonded $[SiO_2(OD)_2]^{2-}$ tetrahedra approximately directed along [100] and layers of edge-linked Na—O octahedra also directed roughly along [100]. CN = 6 for both Na atoms with short Na—O distances [mean Na—O = 2·432 (4) Å]. CN = 4 and 5 for the D_2O molecules. One D_2O molecule [W(11)] shows only O—D coordination [O—D = 0·963 (4) and 0·991 (3), O···D = 1·939 (4), 1·996 (3) and 2·062 (4) Å] without any O—Na contacts. Because of this isolated D_2O molecule which shows three additional weak hydrogen bonds (O···O $\simeq$ 3·0 Å), the thermal stability of this phase is rather low within the given hydrate series and equals that of $Na_2[SiO_2(OH)_2].8H_2O$ [m.p. = 326 K (2) for both phases within experimental error].

Introduction. Two series of crystalline hydrate phases exist in the alkali-rich section of the system Na_2O—SiO_2—H_2O: $Na_3[SiO_3(OH)].nH_2O$ (n = 5,2,1,0) with an Na_2O:SiO_2 ratio of 3:2 and $Na_2[SiO_2(OH)_2].nH_2O$ (n = 8,7,5,4) with an Na_2O:SiO_2 ratio of 1:1. The members of the first series are built up of isolated $[SiO_3(OH)]^{3-}$ anions as shown by X-ray single-crystal structure analysis for $Na_3[SiO_3(OH)].5H_2O$ (Smolin, Shepelev & Butikova, 1973) and $Na_3[SiO_3(OH)].2H_2O$ (Schmid, Huttner & Felsche, 1979; Schmid, Szolnai, Felsche & Huttner, 1981). The members of the second series are built up of isolated $[SiO_2(OH)_2]^{2-}$ anions as has been shown by X-ray and neutron single-crystal structure analysis: $Na_2[SiO_2(OH)_2].8H_2O$ [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)], $Na_2[SiO_2(OH)_2].5H_2O$ [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)].

Both series of hydrate phases show quite different thermal properties. The phases of the 3:2 series undergo thermal decomposition in a peritectical scheme of reaction with a subsequent series of sub-hydrates (Schmid & Felsche, 1983, 1984), whereas the four hydrate phases of the 1:1 series show congruent melting. The phase transition is irreversible. The supercooled melts show glass points at temperatures between 223 and 273 K reproducibly (Felsche, Ketterer & Schmid, 1984, 1985). It is this supercooled melt property which emphasizes the parent character of these hydrates for the polymeric sodium silicate water-glass materials. Especially with respect to its melting behaviour, $Na_2[SiO_2(OH)_2].7H_2O$ is a significant exception within this series. $Na_2[SiO_2(OH)_2].4H_2O$ (m.p. = 365 K) and $Na_2[SiO_2(OH)_2].5H_2O$ (m.p. = 365 K) and $Na_2[SiO_2(OH)_2].5H_2O$ (m.p. = 346 K) show a normal correlation of increasing melting points with decreasing nH_2O whereas the melting point of the heptahydrate is equal to that of the octahydrate (m.p. = 326 K) (Felsche, Ketterer & Schmid, 1985). In order to provide a better understanding of this unique behaviour in silicate hydrate chemistry, we will elaborate correlations of hydrogen bonding with the thermal behaviour of the hydrate series $Na_2[SiO_2(OH)_2].nH_2O$.

In this paper we will report on a single-crystal neutron diffraction study on $Na_2[SiO_2(OD)_2].7D_2O$ at 296 K.

Experimental. Single crystals of $Na_2[SiO_2(OD)_2].7D_2O$ were synthesized from solutions containing 11·19% Na_2O, 11·53% SiO_2 and 76·92% D_2O (by weight) at 298 K by isothermal crystal growth. The single-crystal quality was checked by polarizing microscopy and by the Laue back-scattering method. D_m was measured by the flotation method. Crystal dimensions were 1·5 × 2 × 4 mm.

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Neutron integrated intensities were measured on the *P*32 four-circle diffractometer at CEN, Grenoble, at room temperature (296 K). Data reduction was carried out using the program *COLL5N* (Lehmann & Wilson, 1982) which uses the step-scan profile-analysis algorithm of Lehmann & Larsen (1974). Program for structure analysis and refinement *SHELX*76 (Sheldrick, 1976); TR 440 computer. Unit weights. Standard reflection (192) measured every 50 observations, intensity variation max. 1%. Lattice parameters refined on the basis of 17 reflections. Neutron wavelength 1·1874 Å; Cu(200) monochromator. Total of 2305 intensities measured in the range $2\theta = 0$–65°; $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}6290$ Å^{-1}; min. *h*, *k* and *l* −9, 0 and 0; max. *h*, *k* and *l* 9, 16 and 10. Total number of unique reflections observed 1802; total number of observations used in refinement 1677, with 125 unobserved $[I < 3\sigma(I)]$; $R_{\text{int}} = 0{\cdot}0148$. Least-squares refinement based on *F* magnitudes. Total number of parameters refined 272 (2 × 136) in the final blocked-diagonal full-matrix least-squares refinement. Final $R = 0{\cdot}0472$ and $wR = 0{\cdot}0487$. Max. Δ/σ in the last cycle of refinement 0·009.

The D, Si and O(1) positional parameters were obtained by Fourier methods starting from phases calculated with the atomic parameters given by Dent-Glasser & Jamieson (1976) [parameters of Si and O(1) were questionable with respect to the sign of *y*].

Scattering lengths for Si, Na, O and D were taken from the compilation by Koester & Rauch (1981).

Discussion. The final atomic parameters are listed in Table 1;* the bond lengths and angles observed in the hydrogen-bonding system, in the Na—O and in the *W*(O)—D/Na polyhedra are listed in Table 2. For the sake of clarity and a better understanding of the structure, the oxygen atoms of the D_2O molecules are named *W* instead of O in this work.

The crystal structure consists of dimeric structural units of hydrogen-bonded $[SiO_2(OD)_2]^{2-}$ tetrahedra which are centrosymmetrically arranged sharing edges (see Fig. 1). These units are directed approximately along [100]. It is of importance that these dimeric groupings are centrosymmetrically linked by two hydrogen bonds formed between O(1) and O(4) of 2·618 (4) Å. The second O—D group, O(3)—D(31), of the tetrahedron forms a hydrogen bond to a D_2O molecule [*W*(10)]. It is of interest that in the 1:1 silicate hydrate series the linkage of the $[SiO_2(OH)_2]^{2-}$ tetrahedra, forming either chains or dimers, is *via* the edges by parallel hydrogen bonds {Jost & Hilmer (1966) and Schmid, Felsche & McIntyre (1985) for $Na_2[SiO_2(OH)_2].4H_2O$; Jamieson & Dent-Glasser (1967) and Williams & Dent-Glasser (1971) for $Na_2[SiO_2(OH)_2].5H_2O$}. The only exception is $Na_2[SiO_2(OH)_2].8H_2O$ which shows isolated $[SiO_2(OH)_2]^{2-}$ tetrahedra (Jamieson & Dent-Glasser, 1966*a*,*b*; Schmid, Felsche & McIntyre, 1984).

Table 1. *Final atomic parameters for* $Na_2[SiO_2(OD)_2].7D_2O$ *at* 296 K

The numbers in parentheses give the e.s.d.'s corresponding to the last significant digit. The equivalent *U* values are given as follows: $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}]$ after diagonalization of the **U** tensor. The oxygen atoms of the D_2O molecules are given as *W*'s.

	x	*y*	*z*	U_{eq}(Å^2)
Na(1)	0·3452 (5)	0·2379 (3)	0·2611 (4)	0·026 (2)
Na(2)	0·3444 (4)	0·0738 (2)	0·9891 (4)	0·020 (2)
Si	0·7085 (3)	0·0781 (2)	0·5017 (3)	0·008 (1)
O(1)	0·6504 (3)	−0·0320 (1)	0·4394 (2)	0·016 (1)
O(2)	0·7912 (3)	0·1397 (1)	0·4172 (2)	0·015 (1)
O(3)	0·8494 (3)	0·0739 (1)	0·6903 (2)	0·017 (1)
O(4)	0·5446 (3)	0·1404 (1)	0·4920 (2)	0·015 (1)
W(5)	0·1627 (3)	0·2084 (2)	0·8483 (3)	0·024 (1)
W(6)	0·5018 (3)	0·0787 (2)	0·8553 (3)	0·024 (1)
W(7)	0·1928 (3)	0·0876 (2)	0·1325 (3)	0·027 (1)
W(8)	0·1368 (3)	0·1700 (1)	0·5280 (3)	0·018 (1)
W(9)	0·5193 (3)	0·2013 (2)	0·1534 (2)	0·018 (1)
W(10)	0·8525 (3)	0·0424 (2)	0·2044 (3)	0·022 (1)
W(11)	0·8371 (3)	0·1618 (1)	0·9489 (3)	0·021 (1)
D(31)	0·9522 (3)	0·0350 (2)	0·7177 (2)	0·027 (1)
D(41)	0·4668 (3)	0·0975 (1)	0·5141 (2)	0·023 (1)
D(51)	0·1405 (3)	0·2526 (2)	0·9133 (2)	0·031 (1)
D(52)	0·0539 (4)	0·1861 (2)	0·7689 (3)	0·046 (2)
D(61)	0·4481 (3)	0·0581 (2)	0·7452 (2)	0·026 (1)
D(62)	0·6083 (3)	0·1104 (2)	0·8803 (3)	0·030 (1)
D(71)	0·1947 (4)	0·0374 (2)	0·2008 (3)	0·045 (2)
D(72)	0·0763 (3)	0·1113 (2)	0·0769 (3)	0·040 (1)
D(81)	0·2035 (3)	0·1111 (1)	0·5422 (2)	0·025 (1)
D(82)	0·0167 (3)	0·1506 (2)	0·5042 (3)	0·028 (1)
D(91)	0·6264 (3)	0·1809 (2)	0·2463 (2)	0·026 (1)
D(92)	0·5470 (3)	0·2553 (2)	0·1053 (2)	0·028 (1)
D(101)	0·8293 (3)	0·0736 (2)	0·2815 (3)	0·032 (1)
D(102)	0·8534 (4)	0·0944 (2)	0·1403 (3)	0·041 (1)
D(111)	0·8237 (3)	0·2347 (2)	0·9401 (3)	0·028 (1)
D(112)	0·8374 (3)	0·1396 (2)	0·8577 (3)	0·033 (1)

Thus it is evident that the higher the H_2O content in a given 1:1 sodium silicate hydrate, the lower the degree of polymerization (*via* hydrogen bonding) of the tetrahedra. The correlation observed is: chain–dimer–monomer. However, since no hydrate phase with less than four moles of H_2O per formula unit has so far been found which might be built of isolated $[SiO_2(OH)_2]^{2-}$ tetrahedra, one cannot say definitely if this correlation holds in general for this hydrate series.

Distances and angles in the $[SiO_2(OD)_2]^{2-}$ tetrahedron are slightly different from those obtained by Dent-Glasser & Jamieson (1976). Whereas the Si—O(1) and Si—O(2) bonds are equal within experimental limits [1·596 (3) and 1·606 (4) (n) and 1·595 (8) and 1·607 (7) Å (X-ray) respectively: O(1) and O(2) are the non-hydroxyl oxygen atoms], the corresponding distances in the OD and OH oxygen–Si bonds are different. The corresponding data obtained in this work are Si—O(3) = 1·676 (3) and Si—O(4) = 1·654 (4), 1·686 (6) and 1·643 (8) Å for the X-ray data obtained by Dent-Glasser & Jamieson (1976). Similar deviations can be observed for the angular dimensions.

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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 43700 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Nevertheless, the O—Si—O, O—Si—OD and DO—Si—OD angles show regular behaviour, as is to be expected for $[SiO_2(OH)_2]^{2-}$ tetrahedra. The values correlate well with those compiled by Dent-Glasser & Jamieson (1976) for the whole 1:1 series of sodium silicate hydrates. The data observed are also in agreement with those observed in pectolite, $Ca_2Na[Si_3O_8(OH)]$ (Takeuchi, Kudoh & Yamanaka, 1976; Takeuchi & Kudoh, 1977) and rosenhahnite, $Ca_3[Si_3O_8(OH)_2]$ (Wan & Ghose, 1977). The data for the Si—O and Si—OH bonds as well as the corresponding O—Si—O angles also agree with values obtained by *ab initio* calculations for the hypothetical $Si(OH)_4$ molecule and a corresponding $[SiO_4]^{4-}$ species (Newton & Gibbs, 1980). Minimum potential distances for an Si—OH bond are 1·653 Å and 1·605 Å for an Si—O bond. In these calculations, the angles around the Si atom show the same well known variation in the Si—O bond length (short bonds ⇒ wide angle and *vice versa*) as is observed in the real structures.

Table 2. *Bond lengths* (Å) *and angles* (°) *in* $Na_2[SiO_2(OD)_2].7D_2O$ *at* 296 K *with e.s.d.'s in parentheses corresponding to the last significant digit* (*the oxygen atoms of the* D_2O *molecules are denoted by W*)

(*a*) Hydrogen-bonding system

The $[D_2SiO_4]^{2-}$ tetrahedron			
D(31)–O(3)	0·975 (4)		
D(31)···*W*(10)	1·847 (4)		
O(3)···*W*(10)	2·816 (4)	O(3)–D(31)···*W*(10)	171·8 (4)
D(41)–O(4)	1·011 (4)		
D(41)···O(1)	1·608 (4)		
O(4)···O(1)	2·618 (4)	O(4)–D(41)···O(1)	176·2 (4)
The D_2O molecules			
D(52)–*W*(5)	0·952 (3)	D(51)–*W*(5)–D(52)	106·8 (4)
D(51)–*W*(5)	0·974 (4)		
D(51)···*W*(8)	1·679 (4)		
W(5)···*W*(8)	2·645 (4)	*W*(5)–D(51)···*W*(8)	170·8 (3)
D(62)–*W*(6)	0·959 (4)	D(61)–*W*(6)–D(62)	106·6 (4)
D(62)···*W*(11)	1·939 (4)		
W(6)···*W*(11)	2·894 (4)	*W*(6)–D(62)···*W*(11)	173·1 (4)
D(61)–*W*(6)	1·000 (3)		
D(61)···O(1)	1·646 (4)		
W(6)···O(1)	2·645 (4)	*W*(6)–D(61)···O(1)	175·4 (4)
D(71)–*W*(7)	0·958 (4)	D(71)–*W*(7)–D(72)	106·2 (4)
D(72)–*W*(7)	0·963 (4)		
D(72)···*W*(11)	1·996 (3)		
W(7)···*W*(11)	2·957 (4)	*W*(7)–D(72)···*W*(11)	175·9 (4)
D(82)–*W*(8)	0·982 (3)	D(81)–*W*(8)–D(82)	109·2 (3)
D(82)···O(2)	1·767 (3)		
W(8)···O(2)	2·735 (3)	*W*(8)–D(82)···O(2)	168·3 (2)
D(81)–*W*(8)	0·996 (3)		
D(81)···O(1)	1·628 (3)		
W(8)···O(1)	2·608 (3)	*W*(8)–D(81)···O(1)	166·9 (2)
D(92)–*W*(9)	0·971 (4)	D(91)–*W*(9)–D(92)	108·0 (3)
D(92)···O(4)	1·802 (4)		
W(9)···O(4)	2·756 (4)	*W*(9)–D(92)···O(4)	166·5 (3)
D(91)–*W*(9)	0·989 (3)		
D(91)···O(2)	1·709 (3)		
W(9)···O(2)	2·691 (3)	*W*(9)–D(91)···O(2)	171·3 (3)
D(102)–*W*(10)	0·954 (4)	D(101)–*W*(10)–D(102)	106 7 (3)
D(101)–*W*(10)	0·988 (4)		
D(101)···O(2)	1·795 (4)		
W(10)···O(2)	2·781 (4)	*W*(10)–D(101)···O(2)	175·4 (3)
D(112)–*W*(11)	0·963 (4)	D(111)–*W*(11)–D(112)	106·3 (3)
D(112)···O(3)	1·946 (4)		
W(11)···O(3)	2·902 (4)	*W*(11)–D(112)···O(3)	170·6 (2)
D(111)–*W*(11)	0·991 (3)		
D(111)···O(2)	1·717 (3)		
W(11)···O(2)	2·706 (3)	*W*(11)–D(111)···O(2)	177·3 (2)
The 'weak' hydrogen bonds			
D(52)–*W*(5)	0·952 (3)		
D(52)···O(3)	2·201 (4)		
W(5)···O(3)	3·047 (4)	*W*(5)–C(52)···O(3)	147·5 (3)
D(71)–*W*(7)	0·958 (4)		
D(71)···O(3)	2·008 (4)		
W(7)···O(3)	2·952 (4)	*W*(7)–D(71)···O(3)	168·4 (4)
D(102)–*W*(10)	0·954 (4)		
D(102)···*W*(11)	2·062 (4)		
W(10)···*W*(11)	2·970 (4)	*W*(10)–D(102)···*W*(11)	158·5 (4)

(*b*) Bond lengths in the Na–O polyhedra (CN = 6)

Na(1)–*W*(5)	2·319 (4)	Na(2)–*W*(9)	2·362 (4)
Na(1)–*W*(9)	2·346 (6)	Na(2)–*W*(6)	2·379 (6)
Na(1)–*W*(8)	2·404 (4)	Na(2)–*W*(5)	2·382 (4)
Na(1)–*W*(7)	2·430 (4)	Na(2)–*W*(7)	2·423 (6)
Na(1)–O(4)	2·488 (4)	Na(2)–*W*(10)	2·439 (4)
Na(1)–*W*(6)	2·771 (4)	Na(2)–*W*(6)	2·538 (6)

Table 2 (*cont.*)

(*c*) Angles in the D_2O–Na/D polyhedra (CN = 4 and 5)

Na(1)–*W*(5)–Na(2)	93·4 (2)	Na(1)–*W*(6)–Na(2)	82·8 (1)
Na(1)–*W*(5)–D(51)	118·4 (3)	Na(1)–*W*(6)–D(61)	89·2 (2)
N(1)–*W*(5)–D(52)	113·9 (3)	Na(1)–*W*(6)–D(62)	87·8 (2)
Na(2)–*W*(5)–D(51)	112·2 (2)	Na(1)–*W*(6)–Na(2)	164·5 (2)
Na(2)–*W*(5)–D(52)	111·8 (3)	Na(2)–*W*(6)–D(61)	121·2 (3)
D(51)–*W*(5)–D(52)	106·8 (4)	Na(2)–*W*(6)–D(62)	131·0 (3)
		Na(2)–*W*(6)–Na(2)	85·7 (2)
		D(61)–*W*(6)–D(62)	106·6 (4)
		D(61)–*W*(6)–Na(2)	105·7 (2)
		D(62)–*W*(6)–Na(2)	91·9 (2)
Na(1)–*W*(7)–D(71)	113·9 (3)	Na(1)–*W*(8)–D(81)	102·7 (2)
Na(1)–*W*(7)–D(72)	101·1 (3)	Na(1)–*W*(8)–D(82)	134·7 (3)
Na(1)–*W*(7)–Na(2)	92·6 (2)	Na(1)–*W*(8)–D(51)	94·5 (1)
D(71)–*W*(7)–D(72)	106·2 (4)	D(81)–*W*(8)–D(81)	109·2 (2)
D(71)–*W*(7)–Na(2)	123·5 (3)	D(81)–*W*(8)–D(51)	104·5 (3)
D(72)–*W*(7)–Na(2)	116·6 (3)	D(82)–*W*(8)–D(51)	107·4 (2)
Na(1)–*W*(9)–D(91)	100·5 (3)	Na(2)–*W*(10)–D(31)	97·7 (2)
Na(1)–*W*(9)–D(92)	117·5 (3)	Na(2)–*W*(10)–D(101)	123·1 (3)
Na(1)–*W*(9)–Na(2)	96·4 (2)	Na(2)–*W*(10)–D(102)	100·5 (2)
D(91)–*W*(9)–D(92)	108·0 (3)	D(31)–*W*(10)–D(101)	115·6 (2)
D(91)–*W*(9)–Na(2)	116·9 (3)	D(31)–*W*(10)–D(102)	112·3 (3)
D(92)–*W*(9)–Na(2)	116·4 (2)	D(101)–*W*(10)–D(102)	106·7 (3)
D(62)–*W*(11)–D(111)	105·3 (2)		
D(62)–*W*(11)–D(112)	92·9 (2)		
D(62)–*W*(11)–D(102)	75·4 (2)		
D(62)–*W*(11)–D(72)	135·7 (1)		
D(111)–*W*(11)–D(112)	106·3 (3)		
D(111)–*W*(11)–D(102)	118·1 (3)		
D(111)–*W*(11)–D(72)	116·2 (2)		
D(112)–*W*(11)–D(102)	135·5 (2)		
D(112)–*W*(11)–D(71)	89·9 (2)		
D(102)–*W*(11)–D(72)	72·1 (2)		

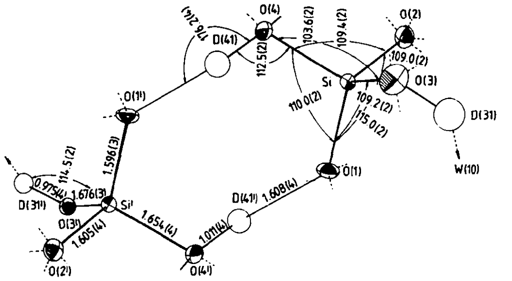

Fig. 1. Graphic representation of the centrosymmetric and dimeric structural unit of two hydrogen-bonded $[SiO_2(OD)_2]^{2-}$ tetrahedra in $Na_2[SiO_2(OD)_2].7D_2O$, (*ORTEP*; Johnson, 1965). The second OD group of the tetrahedron is hydrogen-bonded to a D_2O molecule [*W*(10)]. Bond lengths (Å) and angles (°) are given with e.s.d.'s in parentheses. View down *z*. Full lines represent Na—O bonds, dashed lines represent O···D contacts.

All oxygen atoms in the structure of $Na_2[SiO_2(OD)_2].7D_2O$ are involved in hydrogen bonding (see Table 2). The corresponding hydrogen-bonding data show the usual behaviour and fit well into the bond length–bond strength correlation schemes of Brown & Shannon (1973) or Donnay & Donnay (1973), which means that the longer a given O···O contact is found to be, the shorter will be the corresponding donor O—H/D bond. This clearly shows up in the weak hydrogen bonds (see Table 2). The observed values for the O—D bonds are O(5)—D(52) = 0·952 (3), O(7)—D(72) = 0·958 (4) and O(10)—D(102) = 0·954 (4) Å. The corresponding D···O acceptor contacts range between 2·0 and 2·2 Å for O···O contacts close to 3·0 Å (see Table 2). Although these O—D distances are similar to those found for non-hydrogen-bonded OH groups, these groups must be considered as weak hydrogen bonds, but as hydrogen bonds nevertheless, since all of the D atoms in question are undoubtedly situated between oxygen atoms. However, one of the O—D···O angles of the weak hydrogen bonds is more acute than the others, with *W*(5)—D(52)···O(3) = 147·5 (3)°. Furthermore, it is interesting that the O atom of *W*(11) shows no neighbouring Na atoms and is only bonded and coordinated by D atoms (see Fig. 2). Both structural facts, the weak hydrogen bonds as well as the unusual coordination of *W*(11), may explain the low thermal stability of $Na_2[SiO_2(OH)_2].7H_2O/Na_2[SiO_2(OD)_2].7D_2O$, *i.e.* its melting point of 326 K which is equal to that of $Na_2[SiO_2(OH)_2].8H_2O$ (Felsche, Ketterer & Schmid, 1984). For the bonding angles O—D···O, ranging between 166 and 178°, all hydrogen-bonding data correlate well with those compiled by Baur (1965), Ferraris & Franchini-Angela (1972), Ferraris & Ivaldi (1984) and Chiari & Ferraris (1982).

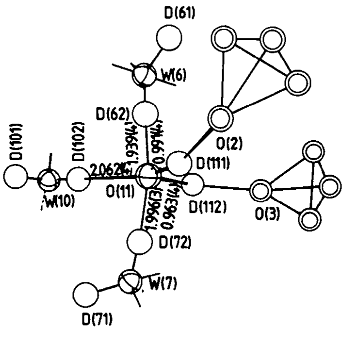

Fig. 2. The hydrogen-bonding scheme around *W*(11). This water molecule represents the only known one in sodium silicate hydrate chemistry which is not bonded to any sodium atom. It only shows O—D contacts *via* hydrogen bonding. CN = 5 for *W*(11) in a class 3 *T* type of coordination (Ferraris & Franchini-Angela, 1972). The distances of the O—D contacts and bonds are given with e.s.d.'s in parentheses. Full lines represent Na—O bonds, dashed lines represent O···D contacts.

The water oxygen coordination is not uniform in $Na_2[SiO_2(OD)_2].7D_2O$ as observed in $Na_2[SiO_2(OH)_2].4H_2O$ [CN = 4 for *W*—Na/H polyhedra: Jost & Hilmer (1966), Schmid, Felsche & McIntyre (1985)]. Nevertheless, CN = 4 is also observed in the water polyhedra of $Na_2[SiO_2(OD)_2].7D_2O$, *i.e.* *W*(5), *W*(7), *W*(8), *W*(9) and *W*(10). The coordination types are 2 *A* [two Na along lone sp^3 orbitals of *W*(5), *W*(9), *W*(10)] and 2 *G* [one Na and one hydrogen-bonded D along the lone-pair orbitals of *W*(8) and *W*(10)]. CN = 5 trigonal bipyramid, sp^2) is observed for O(6) and O(11). The corresponding coordination types are 3 *O* (three Na) and 3 *T* (three D) respectively. The coordination classes are given after Ferraris & Franchini-Angela (1972). The angular dimensions in the O(*W*)—Na/D polyhedra are listed in Table 2. D—O—D angles in $Na_2[SiO_2(OD)_2].7D_2O$ range between 106 and 109° and are therefore more consistent compared with the corresponding data given for $Na_2[SiO_2(OH)_2].5H_2O$ by Williams & Dent Glasser (1971) which range between 100 and 113° (see Table 2). The Na—O polyhedra in $Na_2[SiO_2(OD)_2].7D_2O$ are almost regular octahedral (CN = 6) with Na—O bonds which are significantly shorter than in $Na_2[SiO_2(OH)_2].8H_2O$ (Jamieson & Dent-Glasser, 1966*a*,*b*; Schmid, Felsche & McIntyre, 1984) and are similar to those observed in $Na_2[SiO_2(OH)_2].5H_2O$ (Williams & Dent-Glasser, 1971). Whereas in the octahydrate no Na—O bonds shorter than 2·4 Å are observed, about half of these bonds in the heptahydrate are shorter than 2·4 Å. Furthermore, it is evident by comparison that some of the Na—O bonds obtained by this neutron diffraction study are significantly different from those given by Dent-Glasser & Jamieson (1976) which might be due to differences between the centres of gravity of the electron shells of the atoms in question and the actual positions of the nuclei obtained by neutron diffraction. On the other hand, this might also be an effect of deuteration. But whatever the reason for this – such significant differences are also observed in the $[SiO_2(OD)_2]^{2-}$ anion – it might be worth studying more intensively.

The authors are indebted to Professor H. Fuess, University of Frankfurt, and the CENG for generous allocation of measuring time at the *P*32 instrument and admission to the SILOE reactor. Thanks are due to the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, for financial support.

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Redetermination of the Structures of $CuTaS_3$ and Nb_2Se_9

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(*Received* 12 *September* 1986; *accepted* 16 *December* 1986)

Abstract. Copper tantalum trisulfide, $CuTaS_3$: $M_r =$ 340·69, orthorhombic, *Pnma*, $a = 9{\cdot}488\,(5)$, $b =$ 3·486 (2), $c = 11{\cdot}754\,(5)$ Å, $V = 388{\cdot}7$ Å^3, $Z = 4$, $D_x = 5{\cdot}83$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}7093$ Å, $\mu =$ 346·4 cm^{-1}, $F(000) = 598$ (with anomalous dispersion), $T = 120$ K, R(on F_o^2) $= 0{\cdot}091$ for 984 averaged reflections (including those having $F_o^2 < 0$). The general features of the structure are as reported by Crevecoeur & Romers [*Proc. K. Ned. Akad. Wet. Ser. B* (1964), **67**, 289–291]. The structure resembles a honeycomb with large empty channels along [010]. The honeycomb network is established *via* the interconnection of slabs with the four-atom repeat Cu—Ta—Ta—Cu. The Cu—Ta distance is short [2·781 (2) Å], suggesting a Cu—Ta interaction. Diniobium nonaselenide, Nb_2Se_9: $M_r =$ 896·45, triclinic, $P\bar{1}$, $a = 8{\cdot}160(2)$, $b = 8{\cdot}284(2)$, $c = 13{\cdot}060(3)$ Å, $\alpha = 121{\cdot}22(2)$, $\beta = 124{\cdot}00(2)$, $\gamma =$ 91·74 (2)°, $V = 558{\cdot}3$ Å^3, $Z = 2$, $D_x = 5{\cdot}33$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}7093$ Å, $\mu = 309{\cdot}5$ cm^{-1}, $F(000) = 765$ (with anomalous dispersion), $T = 120$ K, R(on F_o^2) $= 0{\cdot}093$ for 3250 reflections (including those having $F_o^2 < 0$). The structure is comprised of one-dimensional chains that run along the c axis, as reported by Meerschaut, Guemas, Berger & Rouxel [*Acta Cryst.* (1979), B**35**, 1747–1750]. The chains contain Nb atoms in bicapped trigonal prisms of Se atoms. The chains contain Nb—Nb bonds [$d = 2{\cdot}895$ (2) Å] as well as Se—Se bonds. In addition to Se pairs, the structure also contains an Se_5 unit.

Introduction. During the search for new ternary chalcogenides we have synthesized many known binary and ternary compounds. The structures and physical properties of most of these compounds were well known. But among these compounds were $CuTaS_3$ and Nb_2Se_9 whose structures were known with limited accuracy owing either to poor crystal quality or to the method of analysis. For $CuTaS_3$ the data were obtained from visually estimated intensities from Weissenberg photographs (Crevecoeur & Romers, 1964). The intensity data for Nb_2Se_9 were obtained from a twinned crystal with Weissenberg multiple-film techniques