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Location and Anisotropic Refinement of Deuterium Atoms in Deuterium Sodium Silicate–Deuterium Oxide (1/8) $Na_2D_2SiO_4.8D_2O$ by Neutron Diffraction; Hydrogen Bonding at 173 K

By Rudolf L. Schmid and J. Felsche

Fakultät für Chemie, Universität Konstanz, Postfach 5560, *D*-7750 *Konstanz, Federal Republic of Germany*

and G. J. McIntyre

Institut Laue – Langevin, BP 156 *X,* 38042 *Grenoble CEDEX, France*

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Abstract. $M_r = 302{\cdot}1$, orthorhombic, *Ibca*, $a = 11{\cdot}658\,(5)$, $b = 16{\cdot}927\,(4)$, $c = 11{\cdot}477\,(3)$ Å, $V = 2264{\cdot}79$ Å^3, $Z = 8$, $D_m = 1{\cdot}75$ (296 K), $D_x = 1{\cdot}77$ Mg m^{-3}, $\lambda = 1{\cdot}2640$ Å, $\mu(n) = 0{\cdot}001$ mm^{-1}, $F(000) = 160{\cdot}96$, $T = 173$ K, $R = 0{\cdot}037$ for 1015 independent reflections. All deuterium atoms have been located and the hydrogen-bond structure of $Na_2D_2SiO_4.8D_2O$ has been determined by single-crystal neutron diffraction. Coordinates and anisotropic temperature factors have been refined by full-matrix least squares for all atoms, deuterium atoms included. The crystal structure of $Na_2D_2SiO_4.8D_2O$ consists of isolated $[D_2SiO_4]^{2-}$ anions and linear chains of edge-linked $[Na(D_2O)_6]^+$ cations running parallel to the *a* axis which are connected by hydrogen bonds. Coordination numbers observed are CN = 6 for Na with almost octahedral geometry and CN = 4 and 5 for the D_2O-Na,D polyhedra.

Introduction. Two series of crystalline hydrate phases exist in the system Na_2O–SiO_2–H_2O: $Na_3HSiO_4.nH_2O$ ($n = 5,2,1,0$) with an Na_2O:SiO_2 ratio of 3:2; and $Na_2H_2SiO_4.nH_2O$ ($n = 8,7,5,4$) with an Na_2O:SiO_2 ratio of 1:1. Members of the first series are built up of isolated $[HSiO_4]^{3-}$ anions, as shown for $Na_3HSiO_4.5H_2O$ (Smolin, Shepelev & Butikova, 1973) and $Na_3HSiO_4.2H_2O$ (Schmid, Huttner & Felsche, 1979; Schmid, Szolnay, Felsche & Hutter, 1981), whereas the members of the second series are built up of isolated $[H_2SiO_4]^{2-}$ anions as shown for $Na_2H_2SiO_4.8H_2O$ (Jamieson & Dent-Glasser, 1966*a,b*), $Na_2H_2SiO_4.7H_2O$ (Dent-Glasser & Jamieson, 1976), $Na_2H_2SiO_4.5H_2O$ (Jamieson & Dent-Glasser, 1967; Williams & Dent-Glasser, 1971) and $Na_2H_2SiO_4.4H_2O$ (Jost & Hilmer, 1966).

The hydrogen-atom positions and the hydrogen-bonding schemes have been determined, in most cases by X-ray diffraction, for the above phases (see references above) except for $Na_2H_2SiO_4.8H_2O$ and $Na_2H_2SiO_4.4H_2O$. $Na_2H_2SiO_4.8H_2O$ is of particular interest as it shows unique thermal and physico-chemical properties as it is the only member of the 1:1 series which undergoes a solid–solid decomposition reaction forming a lower hydrate phase, namely $Na_2H_2SiO_4.4H_2O$. A knowledge of the complete structure, including the positions of the hydrogen atoms, should provide a sound basis upon which to explain these properties and which will be published elsewhere.

In this paper we present the results of a single-crystal neutron diffraction study on deuterated $Na_2H_2SiO_4.8H_2O$ (hereafter $Na_2D_2SiO_4.8D_2O$) at 173 K. The results of a 296 K measurement, including thermal-motion analysis and *X–N* analysis, will be published later.

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Table 1. *Final atomic parameters for* $Na_2D_2SiO_4.8D_2O$ *at* 173 K

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

	x	y	z	U_{eq}(Å^2)
Na	0·1231 (3)	0·1820 (2)	0·4103 (3)	0·0124 (8)
Si	0·3734 (3)	0·0	0·2500	0·0054 (8)
O(1)	0·2875 (2)	0·0563 (1)	0·1680 (2)	0·0092 (5)
O(2)	0·4443 (2)	0·0565 (1)	0·3343 (2)	0·0090 (5)
O(3)	0·1202 (2)	0·0359 (1)	0·4332 (2)	0·0130 (5)
O(4)	0·1079 (2)	0·1612 (1)	0·2024 (2)	0·0115 (5)
O(5)	0·4144 (2)	0·1780 (1)	0·0575 (2)	0·0142 (5)
O(6)	0·3262 (2)	0·1891 (1)	0·3847 (2)	0·0122 (5)
D(1)	0·2359 (2)	0·0246 (1)	0·1199 (2)	0·0195 (5)
D(31)	0·0998 (2)	0·0389 (1)	0·5161 (2)	0·0213 (5)
D(32)	0·0571 (2)	0·0066 (1)	0·3964 (2)	0·0218 (5)
D(41)	0·0452 (2)	0·1216 (1)	0·1948 (2)	0·0187 (5)
D(42)	0·1775 (2)	0·1293 (1)	0·2011 (2)	0·0211 (5)
D(51)	0·3712 (2)	0·1355 (1)	0·0936 (2)	0·0242 (5)
D(52)	0·4038 (2)	0·1709 (1)	−0·0248 (2)	0·0285 (5)
D(61)	0·3688 (2)	0·1425 (1)	0·3569 (2)	0·0197 (5)
D(62)	0·3572 (2)	0·2345 (1)	0·3449 (2)	0·0231 (5)

Table 2. *The hydrogen-bonding system in* $Na_2D_2SiO_4.8D_2O$ *at* 173 K

E.s.d.'s in parentheses correspond to the last significant digit.

Distances (Å)		Angles (°)	
		$[D_2SiO_4]^{2-}$ tetrahedron	
D(1)—O(1)	0·977 (3)		
D(1)···O(3)	1·799 (3)	O(1)—D(1)···O(3)	164·6 (2)
O(1)···O(3)	2·755 (3)		
Water molecules			
D(31)—O(3)	0·982 (3)	D(31)—O(3)—D(32)	105·1 (3)
D(32)—O(3)	0·983 (3)		
D(31)···O(2)	1·817 (3)	O(3)—D(31)···O(2)	173·0 (2)
O(3)···O(2)	2·794 (3)		
D(32)···O(2)	1·838 (3)	O(3)—D(32)···O(2)′	174·7 (2)
O(3)···O(2)′	2·818 (3)		
D(41)—O(4)	0·996 (3)	D(41)—O(4) D(42)	103·7 (2)
D(42)—O(4)	0·975 (3)		
D(41)···O(2)	1·646 (3)	O(4)—D(41)···O(2)	173·3 (2)
O(4)···O(2)	2·673 (3)		
D(42)···O(1)	1·821 (3)	O(4)—D(42)···O(1)	164·9 (2)
O(4)···O(1)	2·774 (3)		
D(51)- O(5)	0·970 (3)	D(51)—O(5) D(52)	105·1 (3)
D(52)—O(5)	0·960 (3)		
D(51)···O(1)	1·865 (3)	O(5)—D(51)···O(1)	177·8 (3)
O(5)···O(1)	2·836 (3)		
D(52)···O(4)	2·049 (3)	O(5)– D(52)···O(4)	175·6 (3)
O(5)···O(4)	3·008 (3)		
D(61) - O(6)	0·986 (3)	D(61)--O(6) D(62)	107·2 (3)
D(62)- O(6)	0·963 (3)		
D(61)···O(2)	1·721 (3)	O(6)—D(61)···O(2)	169·7 (3)
O(6)···O(2)	2·696 (3)		
D(62)···O(4)	1·891 (3)	O(6)—D(62)···O(4)	163·9 (3)
O(6)···O(4)	2·830 (3)		

Experimental. The single crystals of $Na_2D_2SiO_4.8D_2O$ were synthesized as follows at 293 K. (1) A solution of 6·5% (by weight) Na_2O, 6·2% SiO_2 and 87·3% D_2O was seeded with very small crystallites (< 0·1 mm in diameter) of the hydrogen compound. (2) When the seeded crystals had a diameter of about 5 mm, they were removed from the solution and then cleaved until about 0·1 mm in diameter. These crystallites were examined under a polarizing microscope and, if still single crystals, they were used as seed crystals for a new solution of the above concentration. (3) Step (2) was then repeated using seed crystals obtained from step (2). The deuteration grade obtained was ≥ 99% for the crystals yielded from step (3).

The crystal quality was checked by Laue back-scattering photography. D_m was obtained by the floating method.

Data collection on the D8 four-circle diffractometer at the ILL, Grenoble, crystal 3·0 × 1·7 × 2·1 mm; sample cleaved from a bigger crystal consisted of two crystallites misoriented by about 5°, one crystallite (that from which the data were collected) having 20 times the scattering power of the other; superpositions calculated from the orientation matrices; neutron wavelength 1·2640 Å, Cu(200) monochromator; constant temperature of 173 K using an Air Products Displex cryorefrigerator (Allibon, Filhol, Lehmann, Mason & Simms, 1981). 19 reflections used for calculating lattice parameters; 3 standard reflections, ±1% intensity variation; 1169 reflections measured up to $(\sin\theta)/\lambda = 0{\cdot}65$ Å^{-1}, 1062 unique reflections, $R_{int} = 0{\cdot}0074$, h 0–14, k 0–21, l 0–13; refinement and structure solution on the basis of 1015 reflections $[F_o \geq 3\sigma(F_o)]$, 47 reflections rejected; data reduction carried out with *COLL5N* (Lehmann & Wilson, 1982) based on the step-scan data – background algorithm of Lehmann & Larsen (1974); no correction for absorption, $\mu(n)_{calc} = 0{\cdot}001$ mm^{-1}; structure analysis and refinement on F with *SHELX* (Sheldrick, 1976), TR 440 computer, $w^{-1} = \sigma^2(F_o) = \sigma_c^2(F_o) + (kF_o)^2$, σ from Poisson counting statistics, $k = 0{\cdot}02$; scattering lengths for Si, Na, O and D from the compilation of Koester & Rauch (1981); deuterium-atom positions obtained by Fourier and Patterson methods using the heavy-atom coordinates given by Jamieson & Dent-Glasser (1966*b*); all parameters refined by full-matrix least squares with free site-occupation factors in the initial stage of the refinement but with fixed ones in the final iso- and anisotropic runs; isotropic refinement gave $R = 0{\cdot}055$; in final anisotropic refinement $R = 0{\cdot}037$ and $R_w = 0{\cdot}046$ with 151 parameters refined; $\Delta_{max}/\sigma = -0{\cdot}001$ in the last cycle.

Discussion. The atomic parameters are listed in Table 1, the bond lengths and angles of the hydrogen bonds are listed in Table 2.*

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* Lists of structure factors, anisotropic thermal parameters, angles and distances of the D_2O polyhedra and figures of the Na–D_2O polyhedra and the hydrogen bonding around the $[D_2SiO_4]^{2-}$ tetrahedron have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39084 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The crystal structure of $Na_2D_2SiO_4.8D_2O$ consists of isolated $[D_2SiO_4]^{2-}$ anions and chains of $[Na(D_2O)_6]^+$ cations which are edge-linked running parallel to the *a* axis (Jamieson & Dent-Glasser, 1966*b*).* These features are clearly visible in the diagram of the unit cell presented in Fig. 1. Fig. 2 shows the local geometry for the $[D_2SiO_4]^{2-}$ tetrahedron, including bond lengths and angles and its twofold symmetry.

Hydrogen bonding, which is mostly concentrated around the $[D_2SiO_4]^{2-}$ tetrahedron, plays an important role in this compound.* This shows up in Table 2 which gives the corresponding interatomic distances and angles. Table 2 and Fig. 1 indicate how the $[D_2SiO_4]^{2-}$ tetrahedra link the chains of the Na–D_2O octahedra to give a sheet-like character to the structure (Fig. 1) which shows up in a preferred cleavability perpendicular to the *b* axis of the crystal.

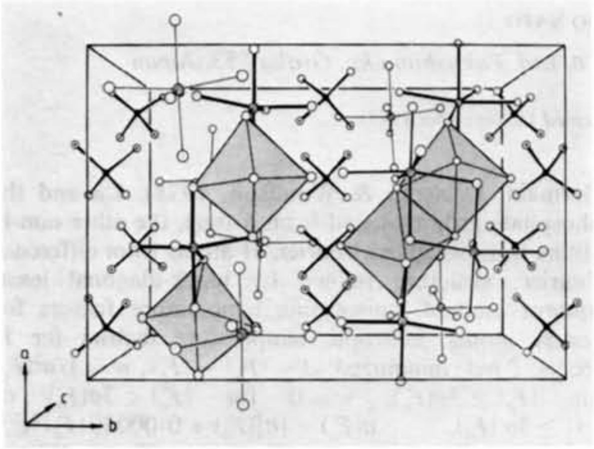

Fig. 1. The unit cell of $Na_2D_2SiO_4.8D_2O$ (*ORTEP*; Johnson, 1965). The figure shows the $[D_2SiO_4]^{2-}$ anions and the sheets of edge-linked and almost regular $[Na(D_2O)_6]^+$ cations. The deuterium atoms are omitted for clarity. ⊘ = Na ● = Si ○ = O ⊙ = OD group $[D_2SiO_4]^{2-}$ tetrahedron.

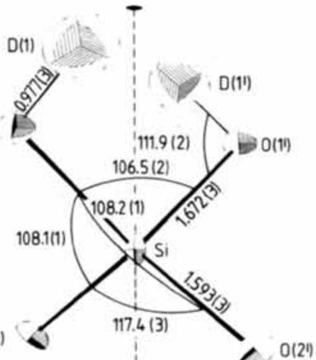

Fig. 2. The slightly distorted $[D_2SiO_4]^{2-}$ tetrahedron showing its twofold symmetry and the thermal ellipsoids of Si, O(1), O(2) and D(1). Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses.

All hydrogen bonds show normal behaviour, *i.e.* the longer and therefore the weaker the O···O contacts become, the shorter the O–D bonds become, a fact which can be observed in the O(5)···O(4) hydrogen bond of 3·008 (3) Å and an O(5)–D(52) bond of 0·960 (3) Å which is significantly shorter than the O(4)–D(41) bond of 0·996 (3) Å in the shorter O(4)···O(2) bond of 2·673 (3) Å. These data are listed in Table 2 and fit well to the bond length – bond strength correlation curves of Brown & Shannon (1973) and Donnay & Donnay (1973). This normal behaviour is also indicated by the corresponding angles, and especially the O–D···O angles which range between 150 and 180°, which is normal for O–H···O angles in most hydrogen-bonded crystal structures, *i.e.* when the hydrogen bond in question is not bifurcated (Baur, 1965). That the D_2O molecule itself is only slightly distorted, too, shows up in the D–O–D angles which range between 103 and 108°. The interatomic distances and angles in the hydrogen-bonding system of $Na_2D_2SiO_4.8D_2O$ are listed in Table 2.

The structure of $Na_2D_2SiO_4.8D_2O$ is very loosely packed. This not only shows up in the Na–O polyhedra, which have coordination number 6 and are similar to those observed in the alums, but also in the D_2O surroundings which have low coordination numbers of 4 with the exception of O(4) (CN = 5). In related structures the D_2O (H_2O) coordination numbers are often 5, especially in the hydrate series $Na_3HSiO_4.nH_2O$ (Smolin *et al.*, 1973; Schmid *et al.*, 1979, 1981). The coordination types are class 2 *G* [O(3)], class 3 *P* [O(4)] and class 2 *A* [O(5) and O(6)] according to Ferraris & Franchini-Angela (1972). O(5) and O(6) belong to the bridging D_2O molecules which link the Na–O octahedra at the edges. The above classification means that O(3), O(5) and O(6) are tetrahedrally coordinated with extra D and Na atoms along the oxygen lone pairs, whereas O(4) shows a trigonal bipyramidal coordination polyhedron with one extra D atom in the D–O–D plane and one D and one Na perpendicular to this plane.

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* See deposit footnote.

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Structure of Calcium Thymidine 5′-Phosphate Dihydrate, $Ca^{2+}.C_{10}H_{13}N_2O_8P^{2-}.2H_2O$

BY TOMOHIRO SATO

Shionogi Research Laboratories, Shionogi & Co. Ltd, Fukushima-ku, Osaka 553, *Japan*

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Abstract. $M_r = 396{\cdot}3$, monoclinic, $P2_1$, $a = 12{\cdot}821$ (5), $b = 11{\cdot}050$ (2), $c = 5{\cdot}543$ (1) Å, $\beta = 98{\cdot}95$ (3)°, $V = 775{\cdot}7$ (4) Å^3, $Z = 2$, $D_x = 1{\cdot}697$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}56$ mm^{-1}, $F(000) = 412$, $T = 298$ K, final $R = 0{\cdot}030$ for 2146 observed reflections. The molecule has a C(4′)-*exo* (E_4) sugar associated with an *anti* glycosidic bond rotation [torsion angle O(4′)—C(1′)—N(1)—C(6) = 65·7 (4)°]. The conformations about the C(4′)—C(5′) and C(5′)—O(5′) bonds are *trans–gauche* [torsion angle C(3′)—C(4′)—C(5′)—O(5′) = −60·4 (3)°] and *trans* [torsion angle C(4′)—C(5′)—O(5′)—P = −153·5 (2)°], respectively. All available H atoms participate in hydrogen bonding.

Introduction. The crystal structure of calcium thymidine 5′-phosphate hexahydrate has been reported (Trueblood, Horn & Luzzati, 1961). We have found another crystalline form of calcium thymidine 5′-phosphate and subjected it to X-ray analysis. This study is part of a series of crystallographic investigations of nucleic acid constituents.

Experimental. Crystals grown from water/2-methyl-2,4-pentanediol solution by vapor diffusion, colorless plates, crystal 0·04 × 0·20 × 0·40 mm used for data collection, Rigaku AFC-5 diffractometer, graphite-monochromator; lattice parameters refined by least-squares method (22 reflections, $29 < 2\theta < 40°$); intensities measured up to $2\theta = 60°$ ($\sin\theta/\lambda \leq 0{\cdot}704$ Å^{-1}), ω scan ($2\theta \leq 30°$), ω–2θ scan ($2\theta > 30°$), 3 standard reflections, no variation, 2363 independent reflections, h 0–15, k 0–12, $l = -6$–6, no absorption correction; structure solved by *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), Ca and the phosphate group located from E map, the other non-H atoms from weighted Fourier, H atoms from difference Fourier; structure refined by block-diagonal least-squares method, anisotropic temperature factors for non-H atoms, isotropic temperature factors for H atoms, $\sum w\Delta^2$ minimized, $\Delta = |F_o| - |F_c|$, $w = 1/\sigma^2(F_o)$ for $|F_c| \geq 3\sigma(F_o)$, $w = 0$ for $|F_c| < 3\sigma(F_o)$ or $|\Delta| \geq 3\sigma(F_o)$, $\sigma(F_o) = [\sigma_1^2(F_o) + 0{\cdot}00020|F_o|^2]^{1/2}$, $\sigma_1(F_o)$ is e.s.d. based on counting errors (Grant, Killean & Lawrence, 1969),* $R = 0{\cdot}030$ for 2146 reflections ($w \neq 0$), $R_w = 0{\cdot}033$, $S = 1{\cdot}05$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Refined atomic coordinates are given in Table 1. A perspective view of the molecule is shown in Fig. 1. Bond distances and angles are listed in Table 2.

The deoxyribose ring adopts a C(4′)-*exo* puckering. The pseudorotation coordinates of the five-membered ring (Sato, 1983) are $\Pi = 36{\cdot}8$ (3), $\Phi = 151{\cdot}5$ (5)°. A pucker quite similar to this has been observed in 5-acetyl-2′-deoxyuridine (Barr, Chananont, Hamor, Jones, O'Leary & Walker, 1980), but C(4′)-*exo* puckers are rather exceptional in the crystal structures of nucleosides and nucleotides so far observed. The sugar is associated with an *anti* base. The glycosidic torsion

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* Lists of structure factors, anisotropic temperature factors and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39024 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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