Hydrogen Bonds in $Na_2S{\cdot}5H_2O$: *X*-Ray Diffraction † and Vibrational Spectroscopic Study

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The crystal structure (at 295 K) and Raman spectra (at 295 and 75 K) of $Na_2S{\cdot}5H_2O$ have been studied paying attention to the hydrogen bonds. Crystals are orthorhombic, space group *Cmcm*, with $a = 6.476(1)$, $b = 12.536(2)$, $c = 8.686(1)$ Å, and $Z = 4$; $R = 0.024$ for 474 independent reflections collected using Mo-K_α radiation. The structure contains three different kinds of O–H ··· S bonds with O ··· S = 3.30, 3.32, and 3.45 Å, and with H ··· S = 2.35, 2.36, and 2.53 Å. At 75 K the uncoupled O–D frequencies of the isotopically dilute HOD molecules are 2 379, 2 398, and 2 473 cm^{-1}.

In the course of systematic studies on O–H ··· S type hydrogen bonds in salt hydrates, the title compound, $Na_2S{\cdot}5H_2O$, became of particular interest for mainly two reasons. (*i*) This compound was reported [1] to contain only two independent water molecules within a relatively simple crystal structure with exclusively O–H ··· S type hydrogen bonds but without O–H ··· O type bonds as observed by us for compounds investigated so far ($Na_2S{\cdot}9H_2O$,[2] $Na_3PS_4{\cdot}8H_2O$,[3] $Na_3AsS_4{\cdot}8H_2O$,[4,5] and $Na_3SbS_4{\cdot}9H_2O$ [5,6]). Assignments of O–H(D) vibrational frequencies should therefore be straightforward. (*ii*) It has recently been shown that at comparable bond distances of O–H(D) ··· S groups the O–H(D) stretching frequencies are significantly smaller in $Na_2S{\cdot}9H_2O$ than in thiosalt (salts containing S^{2-} as part of complex anions, *e.g.* PS_4^{3-}) hydrates,[2–7] which indicated hydrogen-bond effects in the sulphide to be stronger than in the latter compounds. The title compound therefore provided the opportunity to check and, perhaps, to expand this interesting result. In order to obtain the necessary spectroscopic and structural data, Raman spectra have been measured and the structure was refined to locate also the H atoms, which has not been achieved previously.[1] Since neutron diffraction facilities were not available *X*-ray single-crystal diffraction was used, which, as recently demonstrated,[2,4] by special constraining techniques provides the positions of H atoms with sufficient accuracy for correlations with spectroscopic data.

Experimental

Crystal Growth.—Crystals of $Na_2S{\cdot}5(H,D)_2O$ were grown by slowly cooling hot solutions of $Na_2S{\cdot}9H_2O$ (30 g) and NaOH (10 g) in H_2O (20 cm^3) or H_2O–D_2O (18 : 2 cm^3). Seed crystals in well thermostatted closed vessels, with stirring, and temperatures in the range 335—320 K and cooling rates of *ca.* 0.2 K per day were used. Prismatic crystals with volumes up to 2 cm^3 were obtained and cut to the desired shape.

X-*Ray Diffraction Measurements and Refinement.*—A crystal (0.3 × 0.15 × 0.10 mm) was enclosed in a thin-walled glass capillary and then mounted on a computer-controlled Philips PW 1100 four-circle diffractometer. Data were collected with graphite-monochromatized Mo-K_α radiation within one half of the reflection sphere ($\theta \leqslant 30°$) using the θ—2θ scan mode with a scan range $\Delta\omega = (1 + 0.6 \tan \theta)°$. Three periodically monitored reference reflections displayed no significant deviations from their initial intensities. 2 070 Reflections were measured and corrected for Lorentz and polarization effects but not for absorption ($\mu = 0.54$ mm^{-1}). They were then averaged to 593 symmetry independent non-extinguished reflections, 474 of which with $F_o > 6\sigma(F_o)$ were used in subsequent calculations.

Crystal data.—Good agreement was shown with previous data: [1] $Na_2S{\cdot}5H_2O$, $M = 168.04$, orthorhombic, space group *Cmcm* (no. 63), $a = 6.476(1)$, $b = 12.536(2)$, $c = 8.686(1)$ Å, $Z = 4$, $D_c = 1.58$, $F(000) = 352$, $T = 295$ K.

Full-matrix least-squares refinement started with the known atomic positions of Na, S, and O.[1] It converged with anisotropic thermal parameters to $R = 0.04$. At this stage approximate positions of the H atoms could be taken from a difference map. In the subsequent calculations the H atoms were refined as parts of rigid H_2O molecules adopting H–O–H ≈ 108° and O–H = 0.96 Å for the nuclear H positions and O–H = 0.8 Å for the centre of the spherical scattering function of H.[8] The final refinement included a correction for extinction, adjusted 33 parameters, and converged with 474 observed reflections and weights $w = 1/[\sigma^2(F_o) + 0.000\,13F_o^2]$ to $R = 0.024$ ($R' = 0.026$). Atomic co-ordinates are given in Table 1. Calculations were carried out using SHELX.[9]

Raman Spectra.—Raman spectra of $Na_2S{\cdot}5H_2O$ and isotopically dilute HOD samples (H_2O–D_2O, 95 : 5) were measured with a Jarrel-Ash 25-300 Raman spectrometer (slit width < 4 cm^{-1}) at $T = 295$ and 75 K. The low-temperature measurements were performed with an Oxford Instruments CF100 cryogenic unit equipped with a vacuum-tight sample holder. For excitation, the 647.1 nm line of a Coherent Radiation CR 500K Kr-ion laser was used operating with *ca.* 30 mW at the sample. Room and low-temperature spectra showed only the usual differences (small frequency shifts and decreasing linewidths at decreasing temperatures) which provides strong evidence that there are no significant structural changes within the temperature range under consideration. This is of importance with respect to the subsequently given assignments, since the O–H(D) stretching frequencies which are of major interest are clearly distinguished only in the low-temperature spectra.

Results and Discussion

The *X*-ray study confirms the earlier work [1] with respect to heavy-atom positions, but provides improved precision for

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† *Supplementary data available* (No. SUP 23864, 6 pp.): thermal parameters, observed and calculated structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Fractional atomic co-ordinates ($\times 10^5$) with estimated standard deviations in parentheses

Atom	Wyckoff position	Site symmetry	x	y	z
Na(1)	4 a	$2/m$	0	0	0
Na(2)	4 c	mm	50 000	4 314(8)	75 000
S	4 c	mm	0	31 286(5)	75 000
O(1)	4 c	mm	0	9 273(18)	25 000
O(2)	16 h	1	25 979(15)	12 191(7)	57 356(11)
H(1) *	8 g	m	12 106	13 693	25 000
H(2) *	16 h	1	19 377	18 271	61 929
H(3) *	16 h	1	33 247	14 755	48 463

* Co-ordinates of the H atoms were obtained by refining rigid H_2O molecules with fixed internuclear O–H = 0.96 Å, H(1)–O(1)–H(1) = 109.5, and H(2)–O(2)–H(3) = 106.6°. The e.s.d.s of the H(2)–O(3)–H(3) rotation angles average 1.3°.

Table 2. Interatomic distances (Å), angles (°), and assignments of uncoupled O–D frequencies (cm^{-1}) (structural data at T = 295 K, frequencies at T = 75 K) [a]

(*a*) Distances

Na(1)–O(1)	2.463(2)	×2 [b]	S–Na(2)	2.887(1)	×1
Na(1)–O(2)	2.361(2)	×4	S–H(1)	2.533(1)	×2
			S–H(2)	2.351(4)	×4
			S–H(3)	2.362(4)	×4
Na(2)–S	2.887(1)	×1			
Na(2)–O(2)	2.397(2)	×4			

(*b*) Angles

O(1)–Na(1)–O(1)	180	×1
O(1)–Na(1)–O(2)	86.2(1)	×4
O(1)–Na(1)–O(2)	93.8(1)	×4
O(2)–Na(1)–O(2)	180	×2
O(2)–Na(1)–O(2)	89.1(1)	×2
O(2)–Na(1)–O(2)	90.9(1)	×2
S–Na(2)–O(2)	114.3(1)	×4
O(2)–Na(2)–O(2)	79.5(1)	×2
O(2)–Na(2)–O(2)	80.9(1)	×2
O(2)–Na(2)–O(2)	131.3(1)	×2

(*c*) Hydrogen bonds and ligands to the water molecules

A B C	B–C	A–C	$\widehat{BAC}$	$\widehat{ABC}$	$\widehat{BAB'}$	$\widehat{CAC'}$	A–L	$\widehat{LAL'}$	$\tilde{\nu}$(O–D) cm^{-1}
O(1)–H(1) ··· S O(1)–H(1) ··· S	2.533(1)	3.448(2)	15.2	159.1	109.5	139.8(1)	Na(1) 2.463(2)	123.7(1)	2 473
O(2)–H(2) ··· S	2.351(4)	3.303(2)	6.1	171.4	106.6	117.0(1)	Na(1) 2.361(2)	111.6(1)	2 379
O(2)–H(3) ··· S	2.362(4)	3.315(2)	5.8	171.9			Na(2) 2.397(2)		2 398

[a] O–H = 0.96 Å and H–O–H = 91.5 + 0.129 × $\widehat{CAC'}$, where $\widehat{CAC'}$ is the acceptor–oxygen–acceptor angle,[4] were fixed during the refinement of the H_2O molecules. [b] Indicates the multiplicity of bonds within the co-ordination polyhedron.

them and, moreover, location of the hydrogen atoms. Bond lengths and angles are given in Table 2; views of the structure are shown in Figures 1 and 2. The structure consists of $Na(1)(H_2O)_6$ octahedra and $Na(2)S(H_2O)_4$ tetragonal pyramids which, *via* corner-sharing links, are interconnected to form $Na_2S(H_2O)_5$ layers parallel to (010). The two independent water molecules of the structure exhibit tetrahedral co-ordinations, both being bonded to two Na and donating hydrogen bonds to two S atoms. Different from our previously studied hydrates, $Na_2S{\cdot}9H_2O$,[2] $Na_3PS_4{\cdot}8H_2O$,[3] $Na_3AsS_4{\cdot}8H_2O$,[4] $Na_3SbS_4{\cdot}9H_2O$,[6] and $Na_2S_2O_3{\cdot}5H_2O$,[7,10] the structure of $Na_2S{\cdot}5H_2O$ contains exclusively straight O–H ··· S type hydrogen bonds but no O–H ··· O bonds. Two of the different kinds of O–H ··· S bonds (six bonds per formula unit) reinforce the $Na_2S(H_2O)_5$ layers, while one of them (four bonds per formula unit) establishes connections between adjacent layers. As an outstanding feature common to $Na_2S{\cdot}5H_2O$ and $Na_2S{\cdot}9H_2O$, both salts contain a monoatomic divalent anion in a highly hydrated environment. In the title compound the sulphide ion is co-ordinated by one Na and ten H which form the co-ordination polyhedron shown in Figure 3, while in $Na_2S{\cdot}9H_2O$ the sulphide ion is completely hydrated and co-ordinated by twelve H atoms which define the corners of a distorted icosahedron. The mean value of H ··· S distances (2.392 Å) within the $SH_{10}Na$ polyhedron of $Na_2S{\cdot}5H_2O$ compares well with the figure for the SH_{12} polyhedron of $Na_2S{\cdot}9H_2O$, 2.386 Å.

The Raman spectra (Figure 4) are in full agreement with the structural data. Apart from the lattice modes ($\tilde{\nu} < 250$ cm^{-1}), which will not be considered in greater detail, the spectral features essentially correspond to what is expected for two distinct kinds of water molecules, one with site symmetry *mm* and one with site symmetry 1: six librational frequencies ($450 < \tilde{\nu} < 850$ cm^{-1}), two bending frequencies ($1\,650 < \tilde{\nu} < 1\,700$ cm^{-1}), and four stretching frequencies ($3\,100 < \tilde{\nu} < 3\,300$ cm^{-1}) of the H_2O molecules [Figure 4(*a*)]; three uncoupled O–D frequencies ($2\,350 < \tilde{\nu} < 2\,500$ cm^{-1}) of the isotopically dilute HOD molecules [Figure 4(*b*)]. Assuming a monotonic relationship between uncoupled O–D frequencies and bond distances, the assignments given in Table 2 (*c*) are obtained. Because of the above mentioned very simple structure of the title compound, these assignments are straightforward and even more reliable than in previous studies on O–H(D) ··· S bonds.[2,3,5,7]

The H-bond distances and the corresponding O–D frequencies fit perfectly into the previously available picture of O–H(D) ··· S bonds. At comparable bond distances the uncoupled O–D frequencies are very similar to those of $Na_2S{\cdot}9H_2O$ [2] and, therefore, simultaneously again significantly below those of other thiosalt hydrates (by *ca.* 100 cm^{-1}).[3,5,7]

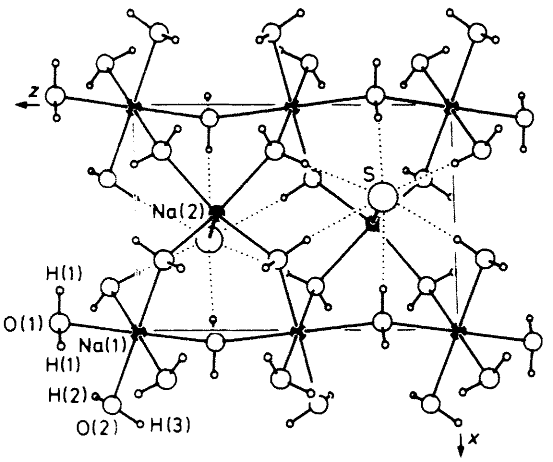

Figure 1. View of a $Na_2S(H_2O)_5$ layer at $y \sim 0$. Dotted lines represent hydrogen bonds

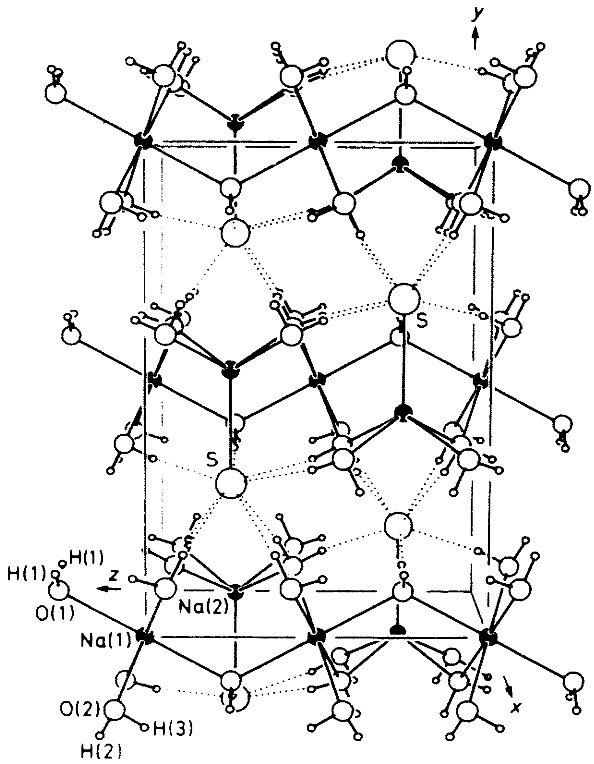

Figure 2. Perspective view of the structure of $Na_2S{\cdot}5H_2O$

The present study thus confirms the recent findings about a systematic relationship between the O–H(D) stretching frequency shift upon H-bond formation, which can be taken as a measure for the H-bond strength, and the net charges of the different types of sulphur atoms acting as proton acceptors.

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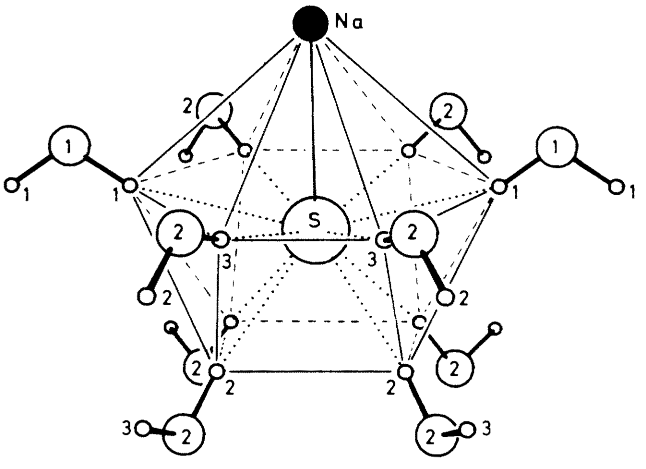

Figure 3. The $S(H_2O)_{10}Na$ co-ordination polyhedron

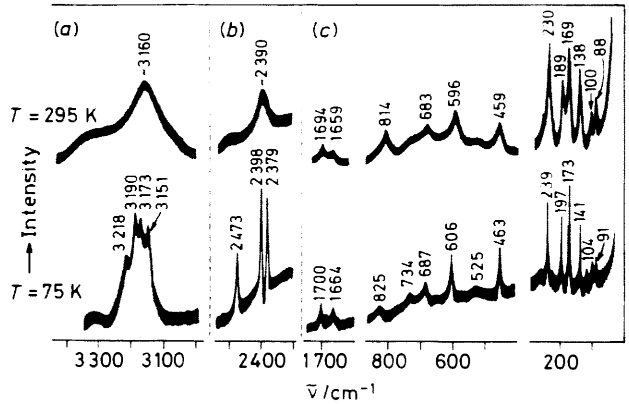

Figure 4. Raman spectra of $Na_2S{\cdot}5(H,D)_2O$: (*a*) and (*c*) 100% H_2O, (*b*) H_2O–D_2O (95 : 5)

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