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Hydrogen Bonds in $Na_2S{\cdot}9D_2O$: Neutron Diffraction, X-ray Diffraction and Vibrational Spectroscopic Studies

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The structure of $Na_2S{\cdot}9D_2O$, space group $P4_122/P4_322$, $a = 9.337(1)$, $c = 12.783(2)$ Å, $Z = 4$, has been refined by neutron and X-ray diffraction in order to get accurate data on the hydrogen bonds. The structure is dominated by discrete $[Na(D_2O)_5]$ and $[Na(D_2O)_4]$ spiral chains which are built up from $Na(D_2O)_6$ octahedra. The five different water molecules of the structure (O–D = 0.949–0.983 Å, D–O–D = 104.6–107.5°) have approximately tetrahedral coordination figures. They form six different O–D···S bonds to the S^{2-} ions which are located between the Na–D_2O chains on twofold axes. As an outstanding feature of the structure the S^{2-} ions are completely hydrated and have a slightly distorted icosahedral coordination by twelve D atoms. The O–D···S bonds are characterized by O···S distances of 3.274–3.506 Å (mean value 3.353 Å), D···S distances of 2.294–2.550 Å (mean value 2.386 Å) and O–D···S angles of 172.1–179.6°. Three different O–D···O bonds which establish links within and between the Na–D_2O chains, measure O···O = 2.730–2.768 Å, D···O = 1.793–1.838 Å, and with O–D···O angles of 165.3–172.4° tend to be more bent than the O–D···S bonds. Single crystal Raman spectra were measured at 295 and 75 K on the D_2O, H_2O and isotopically dilute HOD compounds. The uncoupled O–D(H) stretching frequencies which were found in the range $\tilde{\nu}(OD) = 2344–2532$ [$\tilde{\nu}(OH) = 3143–3424$] cm^{-1} can be reasonably well assigned to the nine different O–D(H) groups of the structure. The frequencies indicate considerable hydrogen bonding effects for both O···O type and O···S type hydrogen bonds.

Introduction

The crystal structures of $Na_2S{\cdot}9H_2O$ and of the isotypic $Na_2Se{\cdot}9H_2O$ have been determined by [1] from X-ray film data. Now, in the course of continuing studies on salts with hydrogen bonds between water molecules and sulfur [2–6], a re-examination of the title compound by neutron and X-ray diffraction was necessary to obtain accurate structural data including the location of the hydrogen atoms. $Na_2S{\cdot}9D_2O$ instead of the hydrate was used for the diffraction studies to avoid the strong incoherent scattering behaviour of H with neutron radiation. In order to characterize the hydrogen bonds in this salt not only by their geometry but also by their bond strength, vibrational spectroscopic studies have been performed. The results of both diffraction and spectroscopic studies are presented in this paper.

Crystal Growth and Preparation

Large single crystals of $Na_2S{\cdot}9(H,D)_2O$, required for neutron diffraction and vibrational spectroscopy, were grown by slow cooling of saturated solutions of Na_2S in either H_2O, D_2O, 95% H_2O + 5% D_2O or 5% H_2O + 95% D_2O. Well thermostated closed vessels of 300 ml capacity, seed crystals, vigorous stirring and temperatures in the range of 315–311 K at a cooling rate of 0.3 K per day were used in typical runs. Tetragonal prisms of optical quality with weights of up to 20 g were obtained. They were stored in mineral oil in order to prevent dehydration and D–H isotope exchange. The crystals were cut to the desired shape with a diamond saw under petrol ether.

Neutron Diffraction Measurements and Refinement

A crystal of $Na_2S{\cdot}9D_2O$ was cut to a cube with an edge length of 4 mm, coated with epoxy resin and quenched with liquid nitrogen in order to reduce extinction effects. It was then mounted on the four circle neutron diffractometer P110 at the research reactor FR2, Kernforschungszentrum Karlsruhe.

TABLE I. Crystal Data.

Tetragonal, space group $P4_122\text{-}D_4^3$ or $P4_322\text{-}D_4^7$ (No. 91/95)			
	$Na_2S\cdot9H_2O$	$Na_2S\cdot9D_2O$	
	at room temperature (295 K)		at 130 K
a [A]	9.335(1)	9.337(1)	9.228(3)
c [A]	12.775(2)	12.783(2)	12.693(5)
V [A^3]	1113.2	1114.4	1080.9
Mr	240.18	258.29	258.29
Z	4	4	4
Dc	1.433	1.539	1.587

TABLE II. $Na_2S\cdot9D_2O$. Fractional Atomic Coordinates $\times10^5$ with e.s.d.'s in Parentheses. Neutron Values are listed above the X-ray Values.[a]

Atom	x/a	y/b	z/c
Na(1)	50000	30552(112)	00000
	50000	30661(9)	00000
Na(2)	14729(106)	00000	75000
	14697(10)	00000	75000
S	50000	18950(124)	50000
	50000	18840(6)	50000
O(1)	49998(55)	49998(55)	12500
	49867(14)	49867(14)	12500
O(2)	18870(55)	98988(59)	55002(40)
	18758(13)	99048(14)	55039(14)
O(3)	46618(50)	11743(52)	12438(37)
	46573(12)	11773(13)	12400(11)
O(4)	33043(47)	18065(46)	72933(35)
	33020(13)	18168(13)	72942(10)
O(5)	29963(50)	23731(52)	28066(37)
	29947(13)	23784(14)	28184(11)
D(1)	49754(67)	58976(49)	08828(37)
	49734	58547	08476
D(21)	20455(54)	88942(49)	53683(38)
	19990	89161	53186
D(22)	27652(62)	03762(56)	53188(45)
	27261	04122	53016
D(31)	47171(52)	02281(50)	09199(38)
	47127	02478	09216
D(32)	54586(52)	12647(56)	17047(34)
	54547	12754	17086
D(41)	29237(48)	27800(51)	73845(36)
	30339	27957	74141
D(42)	38002(52)	18342(57)	66239(34)
	37882	17680	66334
D(51)	34426(51)	18597(56)	22552(37)
	34377	18565	22581
D(52)	35349(52)	21364(53)	34292(39)
	35803	22697	34505

[a] The X-ray parameters of the D atoms were obtained by refining rigid D_2O molecules with the corresponding O's as reference points and with fixed O–D = 0.96 Å and D–O–D = 108°. The standard deviations for the rotation of the D atoms around the O's are on average 2°.

A mean neutron wavelength $\lambda_N = 0.9203$ Å and the ω-scan technique were used to measure at room temperature the intensities of 1291 symmetry independent reflections with $(\sin\theta)/\lambda < 0.768$ $Å^{-1}$. 535 of these reflections had $I > 3\sigma(I)$. The data were corrected for the Lorentz effect, but not for absorption, which was negligibly small due to the use of the deuterium compound ($\mu R \sim 0.02$).

The atomic coordinates of Na, S and O, as given by [1], were used to phase a Fourier synthesis from which all D atoms could be located. Atomic coordinates, anisotropic temperature factors for all atoms and an isotropic extinction parameter [7] were refined simultaneously by full matrix least-squares. Since the ratio between the number of reflections with $I > 3\sigma(I)$ and the number of variables was low (535/139), additional 395 reflections with $I < 3\sigma(I)$ and with $F_c > F_o$ were included in the calculation of the least-squares matrix. $1/\sigma^2$ (F_o) weights were used. The final refinement converged to $R = \Sigma(F_o - F_c)/\Sigma F_o = 0.053$ and $Rw = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2} = 0.041$ for the 535 reflections with $I > 3\sigma(I)$. The largest correction for extinction was a factor 0.65 to F_c of the (302) reflection. The coherent nuclear scattering lengths from [8] were used: $b_{Na} = 3.62$, $b_S = 2.847$, $b_O = 5.80$ and $b_D = 6.67$ fm. Final atomic parameters are given in Tables II and III.

X-ray Diffraction Measurements and Refinement

Small cubes of $Na_2S\cdot9H_2O$ and $Na_2S\cdot9D_2O$ with edgelengths of about 0.3 mm were sealed in Lindemann capillaries to prevent dehydration and were then transferred to a PHILIPS PW 1100 four circle diffractometer which was operated with graphite monochromatized Mo Kα radiation. Cell dimensions for both H and D compounds at room temperature and for the D compound at 130 K were determined by least-squares refinement from the θ values of about fifty reflections in each case (Table I). Reflection intensities were measured only for $Na_2S\cdot9D_2O$ at room temperature. The $\omega/2\theta$ scan mode with a scan width of 1°, a scan speed of 2° min^{-1} and a detector aperture of 1 × 1° was used to measure one octant of the reciprocal space in the range $(\sin\theta)/\lambda = 0.05\text{–}0.70$ $Å^{-1}$ (more than 2000 reflections). The data were averaged and yielded 1007 symmetry independent reflections, 866 of which with $I > 3\sigma(I)$ were used for further calculations. A correction for absorption was not necessary ($\mu R \sim 0.05$).

Full matrix least-squares refinement started with the atomic positions given by [1] and converged with anisotropic temperature factors and a correction for isotropic extinction [7] to R = 0.04. At this stage D

TABLE III. $Na_2S \cdot 9D_2O$. Thermal Parameters $\times 10^4$ ($Å^2$).[a] Neutron Values are listed above the X-ray Values.

	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na(1)	294(46)	207(40)	275(39)	0	50(41)	0
	346(5)	245(4)	304(6)	0	−15(5)	0
Na(2)	280(48)	238(42)	332(43)	0	0	−41(41)
	288(6)	271(5)	436(7)	0	0	51(6)
S	158(45)	152(42)	265(46)	0	−17(42)	0
	239(3)	208(3)	243(4)	0	22(3)	0
O(1)	233(13)	U_{11}	238(25)	15(25)	4(18)	$-U_{13}$
	294(5)	U_{11}	282(7)	12(12)	−4(6)	$-U_{13}$
O(2)	284(22)	244(23)	503(27)	65(22)	−16(26)	−34(22)
	382(7)	282(7)	575(9)	58(8)	−23(8)	−60(8)
O(3)	272(23)	268(23)	241(16)	12(16)	−51(19)	−17(19)
	366(8)	316(7)	302(9)	16(6)	−30(7)	−26(7)
O(4)	282(22)	181(19)	265(20)	1(18)	−10(18)	17(17)
	334(7)	273(7)	316(8)	7(6)	−12(7)	39(7)
O(5)	202(19)	376(27)	275(19)	4(18)	29(20)	−2(20)
	279(7)	398(8)	401(10)	35(6)	0(7)	−32(7)
D(1)	437(25)	360(24)	389(22)	−25(23)	−23(21)	55(21)
	550					
D(21)	434(26)	295(22)	545(28)	71(19)	−34(26)	−43(22)
	550					
D(22)	473(31)	403(27)	695(36)	31(22)	42(31)	28(26)
	550					
D(31)	450(30)	337(27)	406(23)	−2(18)	−32(23)	−60(21)
	550					
D(32)	344(23)	415(27)	399(23)	−13(20)	−10(21)	−11(21)
	550					
D(41)	362(22)	363(24)	376(20)	4(17)	−9(22)	6(20)
	550					
D(42)	399(24)	358(23)	371(20)	12(20)	22(21)	21(20)
	550					
D(51)	384(25)	437(26)	442(24)	30(23)	60(22)	−77(24)
	550					
D(52)	346(22)	388(26)	425(23)	68(20)	44(20)	10(21)
	550					

[a] The anisotropic temperature factors are in the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{23}b^*c^*kl)]$. The isotropic ones are in the form: $\exp[-8\pi^2 U_{iso}(\sin\theta/\lambda)^2]$.

atoms could be clearly recognized in a difference map. Conventional refinement including the D atoms converged to R = 0.024 and gave O–D bond distances of 0.80–0.96 Å, D–O–D bond angles of 102–113° and isotropic temperature factors of U = 0.033–0.074 $Å^2$. To obtain more realistic nuclear D positions from the X-ray data the D atoms were then refined as parts of rigid D_2O molecules adopting D–O–D = 108° and an internuclear distance O–D = 0.96 Å. Since the usual spherical scattering function was used for the D atoms, the nonspherical scattering behaviour of bonded hydrogen [9] was taken into account by placing the scattering centers not at the nuclear D positions but on the O–D lines, 0.86 Å apart from the O atoms (see also [2]). The isotropic temperature factors of the D atoms were arbitrarily fixed at U = 0.055 $Å^2$. The final refinement converged to R = 0.025, $Rw = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2} = 0.030$ and $S = [\Sigma w(F_o - F_c)^2/(866 - 85)]^{1/2} = 1.12$, where $w = 1/(\sigma^2(F_o) + 0.0004 \times F_o^2)$. The largest correction for extinction was a factor 0.63 to F_c of the (004) reflection. Scattering factors for neutral atoms without correction for anomalous dispersion were used [10]. Final atomic parameters are given in Tables II and III.

Comparison of Neutron and X-ray Results

The present work confirms the earlier study [1] on the heavy atoms but provides improved precision for them and moreover accurate location of the deuterium atoms. The atomic coordinates, which in the earlier study were determined from X-ray film data on the hydrate, differ from those obtained here by 0.00–0.12 Å, on average by 0.05 Å.

TABLE IV. $Na_2S\cdot 9D_2O$. Interatomic Distances (Å) and Angles (°) calculated from the X-ray Coordinates of Na and S, and from the Neutron Coordinates of O and D. E.s.d. s in Parentheses.

(a) NaO_6 octahedra						∢O–Na–O
Na(1)–O(1)	×2	2.411(4)	O(1)–O(1)		3.196(1)	83.0(2)
–O(3)	×2	2.397(5)	–O(3)	×2	3.586(7)	96.4(2)
–O(5)	×2	2.485(5)	–O(3)	×2		172.4(2)
Mean value		2.431	–O(5)		3.312(7)	85.1(2)
			–O(5)	×2	3.671(6)	97.1(2)
			O(3)–O(3)		3.242(7)	85.1(2)
			–O(5)	×2	3.463(7)	90.3(2)
			–O(5)	×2	3.375(7)	87.4(2)
			O(5)–O(5)			177.0(2)
Na(2)–O(2)	×2	2.380(5)	O(2)–O(2)		3.749(7)	103.9(2)
–O(2)	×2	2.588(5)	–O(2)	×2	4.055(7)	109.3(2)
–O(4)	×2	2.418(5)	–O(2)	×2	3.251(7)	81.6(2)
Mean value		2.462	–O(4)	×2		169.2(2)
			–O(4)	×2	3.203(7)	83.7(2)
			O(2)–O(2)			162.7(2)
			–O(4)	×2	3.190(7)	79.1(2)
			–O(4)	×2	3.499(7)	88.6(2)
			O(4)–O(4)		3.415(6)	89.8(2)

(b) Coordination around S

S–D(1)	×2	2.359(5)
–D(22)	×2	2.550(6)
–D(31)	×2	2.311(5)
–D(41)	×2	2.294(5)
–D(42)	×2	2.359(5)
–D(52)	×2	2.441(5)

(c) Hydrogen bonds and ligands to the water molecules

A B C	A–B	B–C	A–C	∢BAC	∢ABC	∢BAB′	∢CAC′	L	A–L	∢LAL′
O(1)–D(1)····S	0.961(7)	2.359(5)	3.319(5)	1.4(4)	178.0(6)	106.3(7)	103.4(2)	Na(1)	2.411(4)	116.1(2)
D(1′)···S	0.961(7)	2.359(5)	3.319(5)	1.4(4)	178.0(6)			Na(1′)	2.411(4)	
O(2)–D(21)···O(5)	0.964(7)	1.793(7)	2.752(7)	4.9(4)	172.4(6)	106.1(7)	111.5(2)	Na(2)	2.588(5)	97.6(2)
–D(22)···S	0.962(7)	2.550(6)	3.506(5)	5.2(4)	172.8(6)			Na(2′)	2.380(5)	
O(3) D(31)···S	0.977(7)	2.311(5)	3.284(5)	4.7(4)	173.3(5)	107.5(7)	116.9(2)	Na(1)	2.397(5)	104.8(2)
–D(32)···O(4)	0.953(7)	1.797(7)	2.730(7)	9.6(4)	165.3(6)			O(5)	2.768(7)	
O(4)–D(41)···S	0.983(7)	2.294(5)	3.274(4)	3.4(4)	175.1(5)	104.6(6)	104.1(2)	Na(2)	2.418(5)	105.5(2)
D(42)···S′	0.973(7)	2.359(5)	3.333(5)	0.3(4)	179.6(5)			O(3)	2.730(7)	
O(5)–D(51)···O(3)	0.949(7)	1.838(7)	2.768(7)	9.2(4)	166.1(6)	105.5(6)	103.4(2)	Na(1)	2.485(5)	101.7(2)
D(52)···S	0.967(7)	2.441(5)	3.401(5)	5.7(4)	172.1(5)			O(2)	2.752(7)	
mean values	0.965					106.0	107.9	⟨Na–O⟩	2.447	
mean values O–D···O	0.955	1.809	2.750		167.9					
mean values O–D···S	0.970	2.386	3.353		175.2					

A comparison of our present neutron and X-ray investigation results shows acceptable agreement for the atomic coordinates (Table II), systematic differences for the anisotropic temperature factors (Table III) and considerably varying standard deviations for both sorts of figures, depending on the atomic species and the type of radiation. The corresponding neutron and X-ray positions of Na, S and O deviate by 0.003–0.017 Å, on average 0.011 Å. A half normal probability plot [11] of $(\chi_N - \chi_X)/(\sigma_N^2 + \sigma_X^2)^{1/2}$, where χ are the individual coordinates and σ their associated e.s.d.s, shows a slope of 1.4 ($\delta_p$max = 3.03), which indicates either the presence of small non-random differences between the neutron

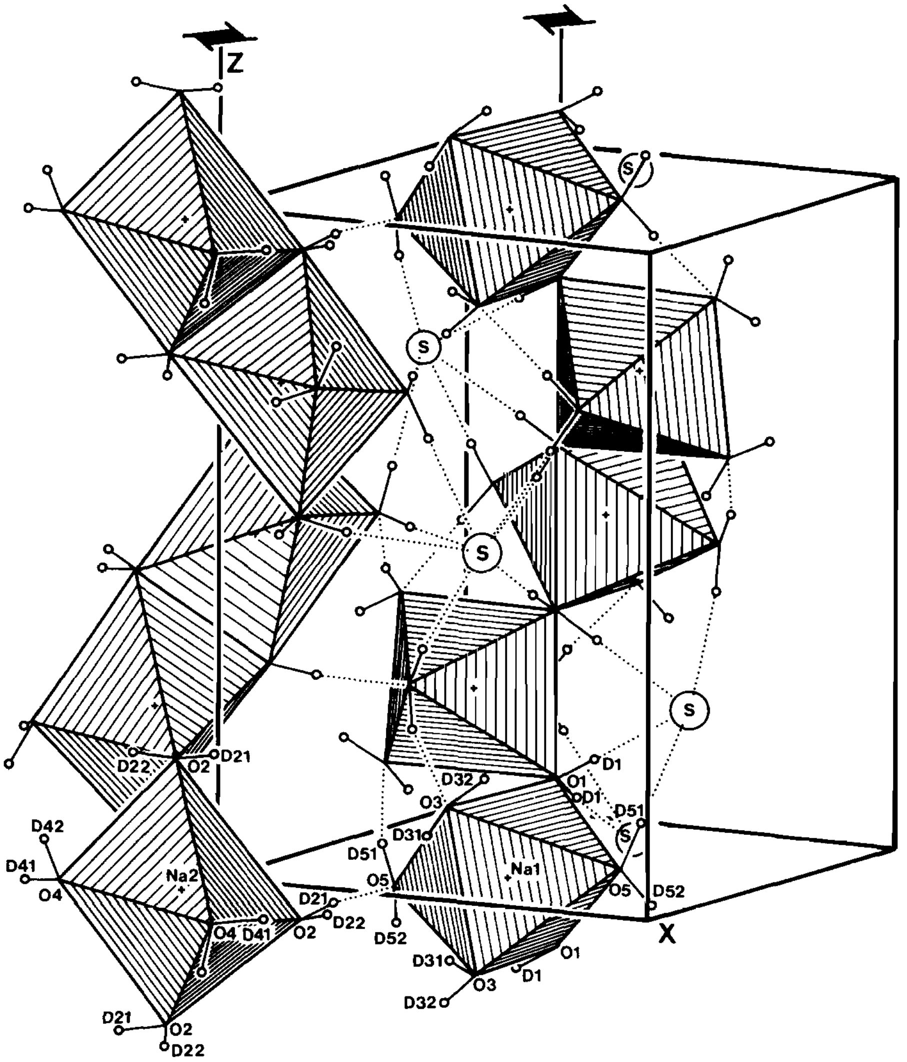

Fig. 1. $Na_2S \cdot 9D_2O$. A partial view of the structure.

and X-ray parameters or an underestimation of the standard deviations. A careful inspection showed that the X-ray oxygen positions are with respect to the corresponding neutron positions, slightly shifted off the pair of D atoms bonded to each oxygen, on average by 0.006 Å. Since we observed a comparable situation in an other combined neutron and X-ray diffraction study with higher precision for the neutron parameters of O than in the present case [12], we are quite sure that this systematic effect arises from the asphericity of the electron distribution around O, due to chemical bonding and its influence on the X-ray oxygen positions [13, 14]. Interatomic distances and angles (Table IV) have, therefore, been calculated from the X-ray parameters of Na and S, and from the neutron parameters of O and D.

For the temperature factors of Na, S and O the neutron values are systematically smaller than the X-ray values, a feature which has also been observed in other combined neutron and X-ray investigations [12], and may have its origin in different influences of thermodiffuse scattering effects on the experimental net intensities of neutron and X-ray reflections.

The method to refine the D atoms from the X-ray data as part of rigid D_2O molecules with a preassumed geometry produced similarly satisfying results as obtained in a previous investigation [2]. In the present case the X-ray determined nuclear D-positions deviate from the much more precisely determined neutron positions by only 0.06 Å on average and at most 0.13 Å.

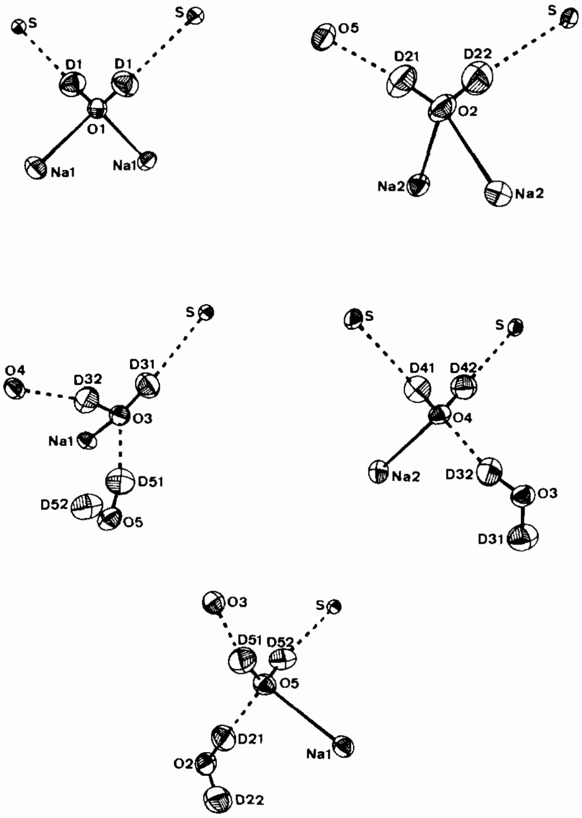

Fig. 2. Coordination figures of the D_2O molecules in $Na_2S \cdot 9D_2O$.

The Structure

The structure of $Na_2S \cdot 9D_2O$ consists of discrete $[Na(D_2O)_5]$ and $[Na(D_2O)_4]$ spiral chains, built up from $Na(D_2O)_6$ octahedra, and of sulfide ions, located between these chains (Fig. 1). The spiral chains are directly linked via O–D···O bonds and indirectly via O–D···S bonds to the sulfide ions. Interatomic distances and angles are given in Table IV.

There are two types of $Na(D_2O)_6$ octahedra in the unit cell. The $Na(1)O_6$ octahedra are linked by sharing pairs of neighboring vertices to form infinite spiral chains with the composition $Na(D_2O)_5$. The $Na(2)O_6$ octahedra are linked by sharing pairs of non-parallel edges to form infinite spiral chains as well, though with the composition $Na(D_2O)_4$. Both types of spiral chains extend along c and have the same chirality, which determines the chiral space group of the salt to be either $P4_122$ or $P4_322$. The $Na(1)O_6$ octahedron is quite regular with Na–O bonds of 2.397–2.485 Å and O–Na–O angles which deviate at most 7.6° from the ideal values 90 and 180°. The $Na(2)O_6$ octahedron is appreciably more distorted, having Na–O bonds of 2.380–2.588 Å and O–Na–O angles which deviate up to 19.3° from 90 and 180°. The strong distortion of this octahedron is apparently caused by a considerable stretching of the $Na(D_2O)_4$ chain parallel c rather than by the presence of edge-sharing octahedral links. This stretching, however, is necessary because the repeat period of the chain would otherwise be much shorter than that of the $Na(D_2O)_5$ chain, which is already slightly compressed parallel to c.

Although Na ions are frequently found to have partially hydrated octahedral coordinations [15], chains built up exclusively from $Na(H_2O, D_2O)_6$ octahedra were encountered only in a few structures. A $Na(H_2O)_4$ spiral chain of the same type as in $Na_2S \cdot 9D_2O$ has already been observed in $Na_2SiO_2(OH)_2 \cdot 8H_2O$ [16]. Other types of $Na(H_2O)_4$ octahedral chains are known from $Na_6Cu(P_2O_7)_2 \cdot 16H_2O$ (a straight chain, [17]), $Na_2Co(NCS)_4 \cdot 8H_2O$ (the simplest possible zig-zag chain, [18]), $Na_2SO_4 \cdot 10H_2O$ and $Na_2B_4O_5(OH)_4 \cdot 8H_2O$ (zig-zag chains with one additional NaO_6 octahedron inserted between each zig and zag, [19]). A $Na(H_2O)_5$ octahedral chain like that of the title compound has until now not been observed in any other hydrate, although this type of chain is well known from several pentafluoride structures, like CrF_5 [20].

Bond distances and angles for the five different water molecules are listed in Table IVc. The O–D bonds, 0.949–0.983 Å, and the D–O–D angles, 104.6–107.5°, are in the usual range [21]. Figure 2 shows that all water molecules have approximately tetrahedral coordinations. Two of the molecules bridge a pair of Na ions and donate two hydrogen bonds: $D_2O(1)$ – located on a twofold axis – to two sulfur atoms, and $D_2O(2)$ to one oxygen and one sulfur atom. Neutron diffraction determined examples for these coordinations are known from $Na_3SbS_4 \cdot 9D_2O$ [2]. The remaining three D_2O molecules of $Na_2S \cdot 9D_2O$ are linked to one Na only and accept one hydrogen bond. Of these molecules, $D_2O(4)$ donates two hydrogen bonds to two sulfur atoms, a situation also observed in $Na_2S_2O_3 \cdot 5H_2O$ [22], while $D_2O(3)$ and $D_2O(5)$ donate hydrogen bonds to one oxygen and one sulfur.

Three of the nine different hydrogen bonds in $Na_2S \cdot 9D_2O$ (Table IVc) are of the O–D···O type, six of the O–D···S type. The O–D···O bonds are quite uniform (O···O = 2.730–2.768 Å, D···O = 1.793–1.838 Å and O–D···O = 165.3–172.4°) and in a range which is frequently observed for hydrated Na salts. One of the bonds, O(5)–D(51)···O(3), is an intrachain hydrogen bond and reinforces the $Na(1)(D_2O)_5$ spiral chain. The remaining two O–D···O type bonds establish direct links between both sorts of NaO spiral chains. The six O–D···S bonds are characterized by O···S distances of 3.274–3.506 Å and D···S distances of 2.294–2.550 Å, the corresponding mean values being 3.353 and 2.386 Å, respectively. With O–D···S angles of

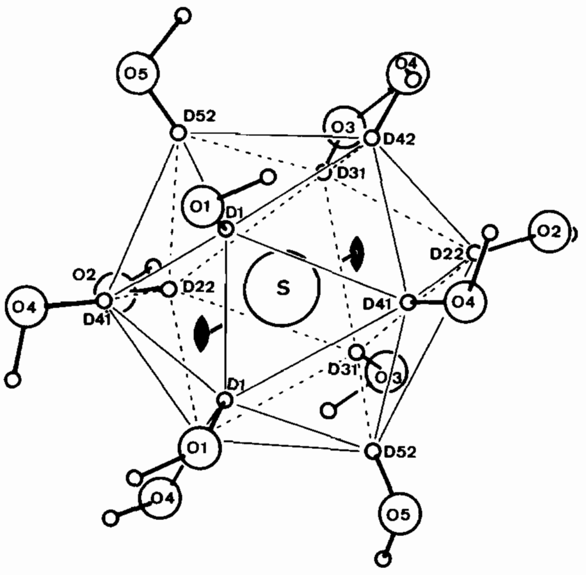

Fig. 3. $Na_2S{\cdot}9D_2O$. A view of the icosahedral coordination figure of S.

172.1–179.6° these bonds tend to be more linear than the O–D···O bonds. According to a previous paper [2] the O···S distances of 66 different O–H, D···S bonds, mostly derived from X-ray data, were found to vary from 3.21 to 3.52 Å, with a mean value of 3.324 Å, excluding a neutron diffraction determined bifurcated bond. While five of the O–D···S bonds in the title compound are quite close to the above given mean value (3.324 Å), there is one bond, O(2)–D(22)···S, with a distinctly larger O···S distance of 3.506 Å.

The correlation between the H–O–H (D–O–D) angles of the water molecules and the acceptor–O–acceptor angles, as found by [21] for a larger number of hydrates, but for none with S as acceptor, is qualitatively observed in the title compound, too.

The sulfide ion is located between the chains of Na octahedra on a twofold axis. It is surrounded by twelve water molecules, each one pointing almost exactly to the anion with one of its D atoms. This gives the sulfide ion a slightly distorted icosahedral coordination by twelve D atoms at D···S distances of 2.294–2.550 Å (Fig. 3). The presence of a monoatomic divalent anion in a completely hydrated icosahedral coordination is an outstanding feature of the $Na_2S{\cdot}9D_2O$ structure. Completely hydrated monoatomic anions have so far been encountered only for Cl^-, Br^- and I^-, *i.e.* for monovalent anions. The first two of them are known to form either distorted tetrahedral coordination, as in $HCl{\cdot}3H_2O$ [23] and $AlCl_3{\cdot}6H_2O$ [24], or distorted octahedral coordination, as in $HCl{\cdot}6H_2O$ [25] and $MgCl_2{\cdot}12H_2O$ [26]. Compared with the octahedral coordination of hexahydrated monovalent Cl^-, the transition to the divalent S^{2-} in the title compound is accompanied by a doubling of the number of coordinating water molecules from six to twelve. Hence the ratio between formal anion charge and

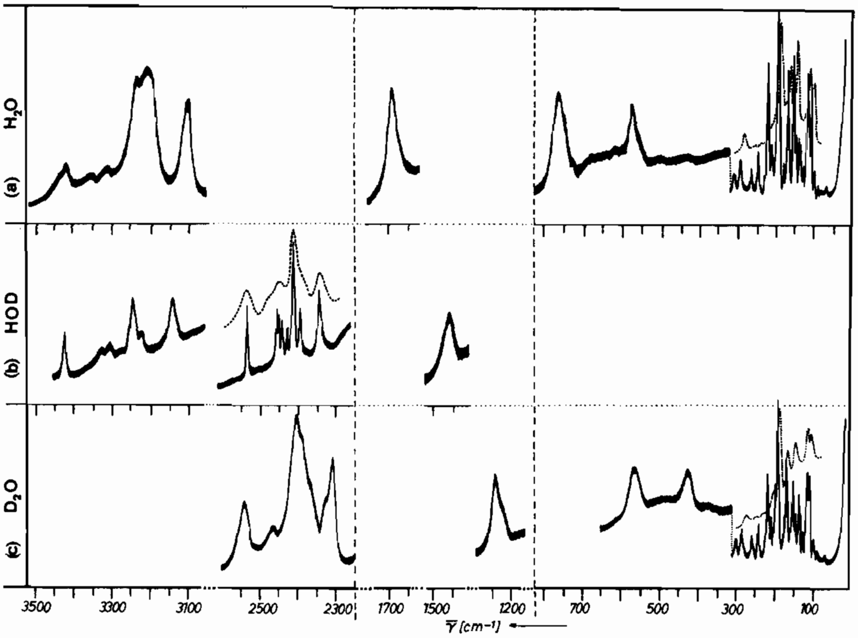

Fig. 4. Raman spectra of $Na_2S{\cdot}9(H,D)_2O$ at T = 75 K (full curves) and T = 295 K (dotted curves): (a) 100% H_2O, (b) 5% H_2O for $\tilde{\nu} > 3000$ cm^{-1} and 5% D_2O for $\tilde{\nu} < 3000$ cm^{-1}, and (c) >99% D_2O.

TABLE V. Site Group Analysis for $Na_2S \cdot 9D_2O$.

$422-D_4$		total	acoust.	transl.	rotat.	intern.
A_1	(R)	55		20	17	18
A_2	(IR)	59	1	23	18	17
B_1	(R)	56		21	18	17
B_2	(R)	58		23	17	18
E	(R,IR)	66	1	27	19	19

R = Raman active, IR = infra red active.

number of coordinating hydrogen atoms is the same in both cases. At this point it seems also worth noting that the $S(D_2O)_{12}$ icosahedron, as shown in Fig. 3, could be a model for the coordination behavior of the sulfide ion in aqueous solutions.

Raman Spectra

Single crystal Raman spectra of D_2O, H_2O and isotopically dilute (5% D_2O and 5% H_2O respectively) compounds were measured at temperatures of 295 and 75 K with a Jarrel-Ash 25–300 Raman spectrometer (slit width < 4 cm^{-1}). For low temperature measurements the samples were enclosed in a vacuum tight sample holder mounted on the cooling finger of an Oxford Instruments CF 100 cryogenic unit. The 647.1 nm line of a Kr-ion laser (Coherent Radiation CR 500 K) was used for excitation. Raman spectra of D_2O, H_2O and HOD compounds are shown in Fig. 4, frequencies are listed in Tables VI and VII. From the crystal structure described above 360 lattice vibrations result at k = 0, which are distributed among the irreducible representations of the factor group, $422-D_4$, as shown in Table V. Because of the large number of Raman-active lattice fundamentals, a detailed interpretation of the observed Raman lines seems to be almost impossible, nevertheless plausible assignments can be made in the range of

TABLE VI. Raman Frequencies – Rotational and Translational Modes (cm^{-1}).[a]

H_2O		$\tilde{\nu}(H_2O)/\tilde{\nu}(D_2O)$	D_2O	
295 K	75 K		295 K	75 K
(765)	775	1.36	555	570
(550)	580	1.35	410	425
	310			298
280	292	1.04	270	284
255	265	1.03	245	260
235	248	1.02	(230)	241
	222	1.03		216
	213	1.03		206
	(202)	1.03		196
191	196	1.04	183	188
	180	1.04		(173)
163	170	1.02	159	166
148	155	1.03	141	150
	148	1.03		144
	139	1.04		134
	134	1.02		(131)
	127	1.02	125	
114	116	1.04	108	112
103	106	1.01	100	105
	98	1.03		95
	88	1.02		86
	64	1.00		64

[a] Poorly resolved lines or shoulders are given in parentheses.

TABLE VII. Raman Frequencies at 75 K (cm^{-1}) – (a) Stretching and (b) Bending Vibrations of H_2O, D_2O and HOD.

	H_2O	H_2O/D_2O	D_2O	O–H[a]	O–H/O–D	O–D[a]	Assignments of uncoupled OD frequencies
(a)	3440[b]						
	3425	1.346	2541	3424	1.353	2532	O–D(22)···S
						2455	O–D(52)···S
	3355		2470	3325		2451	O–D(51)···O
	3310			3305		2442	O–D(32)···O
						2427	O–D(21)···O
	3235	1.345	2405	3243	1.345	2412	O–D(1)···S O–D(42)···S
	3200	1.342	2385[b] 2335[b]	3215	1.343	2394	O–D(31)···S
	3100	1.342	2310	3143	1.342	2344	O–D(41)···S
(b)	1695	1.367	1240	1465		1465	

[a] Isotopically dilute HOD. [b] Shoulder.

O–D(H) stretching frequencies. In particular the technique of isotopic dilution (5% D_2O or 5% H_2O), which largely excludes correlation field splitting effects as well as intramolecular vibrational coupling effects of the O–D(H) oscillators [27], proves to be a very powerful method for the investigation of hydrogen bonding in solid hydrates, even when dealing with the structure of $Na_2S{\cdot}9D_2O$, which is rather complicated from a spectroscopical point of view.

At decreasing temperatures the line frequencies slightly increase, $\tilde{\nu}(75K)/\tilde{\nu}(295K) \leqslant 1.05$, in agreement with the slightly decreasing lattice parameters (Table 1). Besides these very common frequency shifts and the usual line narrowing, there are no other differences between room and low temperature spectra, as can be seen from Fig. 4. Phase transitions and significant structural changes can, therefore, certainly be excluded. This is of some importance to the subsequent discussion and the proposed assignments, because well resolved spectra are only obtained at low temperatures, while the structural data are from room temperature diffraction measurements. Because of the almost perfect analogy between room and low temperature spectra, the latter may be interpreted without serious objections by referring to the room temperature structure data.

In the frequency range $\tilde{\nu} < 350$ cm^{-1} about 20 lines can be identified, which according to isotopic shifts of $\tilde{\nu}(OH)/\tilde{\nu}(OD) \sim 1.04$, must be due to translational modes. In the region of D_2O (H_2O) librations only two broad bands are observed (half widths about 30 cm^{-1}) which certainly are unresolved multiplets (Table VI). Very similar to this only one broad band (half width about 30 cm^{-1}) is observed in the region of D_2O (HOD, H_2O) bending vibrations (Table VII).

For studying hydrogen bonding effects the O–D(H) stretching frequencies, $\tilde{\nu} > 2000$ cm^{-1}, are of main interest, in particular the uncoupled frequencies of isotopically dilute O–D(H). Spectra of uncoupled O–D(H) should yield one distinct line for each kind of O–D(H) group [27], provided that the spectral resolution is sufficiently high. According to the number of different types of O–D···O,S groups in the title compound, nine different lines are expected. In the case of the very well resolved O–D spectrum at 75 K (half widths 5–10 cm^{-1}) eight different lines can be recognized, while in the O–H spectrum, due to the larger half widths (10–20 cm^{-1}), only six lines can be distinguished at 75 K. The uncoupled stretching frequencies of the three different O–D(H)···O type hydrogen bonds in the title compound may be estimated from suitable literature data, in particular from the structural and spectroscopic investigations of the different modifications of ice as summarized by [28]. Referring to these data, uncoupled O–D stretching frequencies $\tilde{\nu} \sim 2420$–2470 cm^{-1} are expected for the three different O–D···O groups (O···O = 2.73–2.77 Å) in the title compound. Assuming this estimate to be reasonable and assuming an approximately monotonous frequency–distance relationship to be valid for the straight O–D···S bonds, the lowest uncoupled O–D(H) stretching frequency at $\tilde{\nu}$ = 2344 (3143) cm^{-1} can be assigned to O(4)–D(H) (41)···S, which exhibits the shortest O···S distance, while the highest stretching frequency at $\tilde{\nu}$ = 2532 (3424) cm^{-1} must be due to O(2)–D(H) (22)···S, which has the largest O···S distance*. In a qualified sense the line at $\tilde{\nu}$ = 2394 (3215) cm^{-1} may be assigned to O(3)–D(H)(31)···S. The line at $\tilde{\nu}$ = 2412 (3243) cm^{-1} which, because of its high intensity, probably consists of more than one component, should be due to O(1)–D(H) (1)···S and O(4)–D(H) (42)···S, which have almost equal O···S distances. The remaining lines in the range of $\tilde{\nu}$ = 2427–2455 (3305–3325) cm^{-1} should then without further specification be due to the O(5)–D(H) (52)···S and the three above mentioned O–D (H)···O bonds. In Fig. 5 these assignments are visualized in a plot of $\tilde{\nu}$(OD) *versus* distance D···S. A correlation curve of the type $\tilde{\nu} = 2727 - A \times \exp[-B \times \text{distance (D···S)}]$ [29] has been fitted by least-squares method to the experimental points and is shown as solid line in Fig. 5. With the refined coefficients A = 6.30×10^4 and B = 2.24 the frequencies of the individual points deviate by less than ±20 cm^{-1} from the computed curve (r.m.s. deviation 5.7 cm^{-1}).

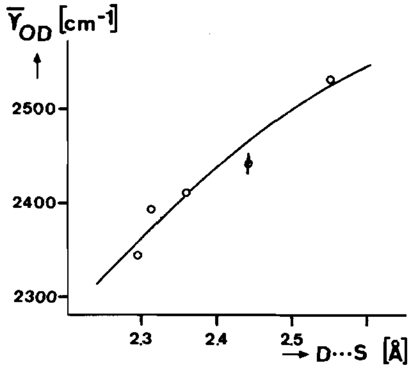

Fig. 5. Correlation between uncoupled O–D stretching frequencies and D···S bond distances in $Na_2S{\cdot}9(H,D)_2O$. The vertical bar shows the uncertainty of assignment (see text).

The O–D(H) stretching frequencies found for the title compound are at the lower limit of what is

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*Uncoupled O–H stretching frequencies are added in parentheses.

usually observed in the vibrational spectra of crystalline hydrates containing only monovalent cations like Na [27, 30]. The H-bond strengths may be roughly estimated from the O–D(H) stretching frequencies according to the well known Badger-Bauer rule [31], which, however, is not undisputed and may be even more questionable, when dealing with proton acceptors other than oxygen. Irrespective of these objections, hydrogen bond strengths in the range 17–36 kJ mol^{-1} are obtained from the frequencies given in Table VII, with a mean value of about 29 kJ mol^{-1} for the O–D(H)···S groups with mean bond distances of O···S $\sim$ 3.33 Å. These marked hydrogen bonding effects are certainly due to the high net charge of the sulfide anions acting as proton acceptors. It should be noted that the frequency shifts are significantly smaller in compounds with sulfur of lower net charge, like $\mathrm{P^{V}S_4}$, $\mathrm{As^{V}S_4}$ and $\mathrm{Sb^{V}S_4}$, as will be discussed in forthcoming papers [12, 32].

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